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The Open-Pit Mine of The Utah Copper Company, Bingham Canyon

METALLURGY *of* COPPER

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PREFACE

The aim of this book is to present a discussion of the various methods employed in winning copper from its ores and in refining the metal to commercial grade. Examples of modern practice are included to illustrate the application of these methods, but no attempt has been made to compile a complete and exhaustive treatise on the practice all over the world. Such a treatise might well require several volumes.

Confining the discussion largely to the extraction and refining of copper, it has been possible to touch only lightly on several related subjects because of space limitations. The chapter on ore dressing is merely a summary to indicate the methods used in dressing copper ores and the nature of the resulting concentrates. It was not possible to consider the subject of copper alloys in any great detail.

An attempt has been made to give credit at the proper place for all material used in the book. The authors extend their thanks to the various mining, smelting, refining, and manufacturing companies, and to the publishing companies for their kind and willing cooperation.

JOSEPH NEWTON
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CHAPTER I

FROM ORE TO CONCENTRATE

THE IMPORTANCE OF COPPER

From the beginning of recorded history until the end of the medieval period, copper was the world's most useful metal. Its use marked the transitory step in the progress of civilization from the Stone Age to the Metal Age. Although gold, owing to its sparkling yellow color, its high luster, its resistance to corrosion and tarnish, and its occurrence in the free or elemental state in nature, was unquestionably the first metal to attract the attention of man, and although in certain localities iron,[1] in the form of meteorites or even obtained by the reduction of the oxide with charcoal, may have been used before copper, nevertheless every ancient metal culture was actually introduced by the use of copper.[2] In the form of pure metal, fashioned first by the crude hammering of masses of native copper and later by melting, and in the form of bronze, obtained by smelting mixed tin and copper ores, it was employed originally for ornaments and statues and then as tools, domestic utensils, implements of war, and for every purpose in which its strength, hardness, and toughness proved its superiority to stone, wood, and other materials.

When the methods of producing iron evolved from the direct processes through the cast iron period to puddling, cementation, and the crucible process, iron and steel usurped copper's position of first importance; and with the advent of the Bessemer and open-hearth processes, ferrous materials attained such ease of large-scale production and such widespread use that they almost eclipsed copper The age of electricity, however, introduced new requirements for materials to be used in the generation and transmission of electrical energy; copper immediately entered its rejuvenation[3] and assumed first place in importance in the electrical field and second in general utility in our present-day civilization.

[1] Howe, H M , The Metallography of Steel and Cast Iron, p. 4, McGraw-Hill Book Co , New York, 1916.

[2] Rickard, T. A , The Early Use of Metals: Jour. Inst. Metals, Vol. 43, p. 297, 1930.

[3] Davis, Watson, The Story of Copper, p. 58, D. Appleton-Century, New York, 1924.

Next to iron, then, copper is the world's most important metal. It is important for three primary reasons: (1) because of its abundance, assuring a supply which will make possible its continued use in large quantities; (2) because of its high electrical conductivity, surpassed only by one other substance, silver, which is not abundant enough, cheap enough, nor strong enough to acquire a utilitarian role similar to that of copper in the electrical field; and (3) because of the important alloys which it forms. Chief among these are the brasses and bronzes. Brass is our most widely used non-ferrous alloy and therefore ranks second only to steel in all the alloys in use today.

COPPER ORE MINERALS

Copper is an important component of many minerals, a surprisingly large number of which are today ore minerals, that is, of industrial importance. These minerals are listed below in Table 1, together with their supposed chemical formulas and their theoretical compositions. By "theoretical" is meant that composition which corresponds to the supposed chemical formula, for although according to a common definition "a mineral is a naturally occurring substance of definite and uniform chemical composition with corresponding characteristic physical properties," nevertheless the chemical composition of many of the copper minerals does vary within limits For this reason differing chemical formulas have been assigned to them from time to time, derived almost always from the chemical analysis alone. Bornite, for example, is written Cu_3FeS_3 ($3Cu_2S{\cdot}Fe_2S_3$) and Cu_5FeS_4 ($5Cu_2S{\cdot}Fe_2S_3$), the former containing 55.6 per cent copper and the latter 63 3 per cent.

Minerals might be regarded in the same light as alloys, as being composed of mixtures or solid solutions of various components, which in the case of minerals are definite chemical compounds and elements. Chalcopyrite, to use a common example, is usually designated by the chemical formula $CuFeS_2$, which enlightens one merely with respect to the chemical composition but tells nothing about the structure or constitution. It can also be written $Cu_2S{\cdot}Fe_2S_3$, showing that it is an association of the two chemical compounds Cu_2S and Fe_2S_3. There is some doubt as to the existence of such a compound as Fe_2S_3; it might be the well-recognized chemical compound FeS with some sulfur in solid solution, as in the case of pyrrhotite. The laws of heterogeneous equilibrium will eventually establish the true constitution of minerals and definitely prove whether chalcopyrite, to use the same example again, is the cuprous salt of the hypothetical acid $HFeS_2$ or whether it is to be regarded as analogous to a pseudo-binary alloy and

therefore composed of a definite chemical compound $Cu_2S \cdot Fe_2S_3$, formed by the combination of the two components Cu_2S and Fe_2S_3, or finally whether it is to be regarded as a ternary system with the three components Cu_2S, FeS, and S. Investigations of such problems can be made only at great expense and with much patient effort, for although the study of chalcopyrite in the Cu_2S-FeS-S ternary system would be confined to only a portion of the entire Cu-Fe-S system, nevertheless, the variables would have to include not only composition and temperature but also pressure. Because the conditions under which minerals are formed are so difficult to duplicate, we cannot say with authority whether or not complex arrangements actually exist. In all probability they do not

The formulas given in the table are for the most part only approxima-

TABLE 1

COPPER ORE MINERALS

Mineral	Formula	Composition (per cent)				
		Cu	Fe	S	As	Sb
Native:						
Native Copper	Cu	99 9	. .		. ..	....
Sulfide:						
Chalcocite	Cu_2S	79 9	.	20 1	..	....
Covellite	CuS	66.5		33.5	.	....
Chalcopyrite	$CuFeS_2$ or $Cu_2S \cdot Fe_2S_3$	34.6	30 5	34 9	.	....
Bornite[a]	Cu_3FeS_3 or $3Cu_2S\ Fe_2S_3$	55 6	16 3	28 1		....
Enargite	Cu_3AsS_4 or $3Cu_2S\ As_2S_5$	48 4		32 6	19 0	....
Famatinite	Cu_3SbS_4 or $3Cu_2S\ Sb_2S_5$	43 3	.	29 1		27 6
Tetrahedrite[b]	Cu_3SbS_3 or $3Cu_2S\ Sb_2S_3$	46 7	. .	23 5	.	29.8
Tennantite[c]	Cu_3AsS_3 or $3Cu_2S\ As_2S_3$	52.7	. .	26 6	20 7	.. .
Oxidized.						
Cuprite	Cu_2O	88 8			.	....
Tenorite (melaconite)	CuO	79.9	....	....	...	....
Malachite	$CuCO_3 \cdot Cu(OH)_2$	57 5	....	....	..	. ..
Azurite	$2CuCO_3\ Cu(OH)_2$	55 3	....	....	...	. ..
Chrysocolla	$CuSiO_3\ 2H_2O$	36 2	.	....	. .	....
Chalcanthite	$CuSO_4\ 5H_2O$	25 5	....	....	.	....
Brochantite	$CuSO_4\ 3Cu(OH)_2$	56.2	. ..	....	....	...
Atacamite	$CuCl_2\ 3Cu(OH)_2$	59 5	..	.		.. .
Krohnkite	$CuSO_4\ Na_2SO_4\ 3Cu(OH)_2$	42 8		.	..	....

[a] Bornite also written Cu_5FeS_4 or $5Cu_2S\ Fe_2S_3$

[b] Tetrahedrite also written $Cu_8Sb_2S_7$ or $4Cu_2S \cdot Sb_2S_3$

[c] Tennantite also written $Cu_8As_2S_7$ or $4Cu_2S \cdot As_2S_3$.

tions; the percentage composition refers to the pure minerals and not to the ores. The copper in many minerals may be replaced by lead or some other metal, and the arsenic and antimony by each other.

As the source of the world's total production of copper, chalcocite represents approximately one-half, chalcopyrite one-quarter, enargite 3 per cent, other sulfides 1 per cent, native copper 6 or 7 per cent, and the oxidized copper minerals some 15 per cent.

Native copper occurs in most of the principal copper deposits of the world, but usually in small quantities. It has been found in 27 states of the United States, in Bolivia, Chile, Australia, and elsewhere. The deposits of the Lake Superior district are the only ones of economic importance, however. The metal is very pure, containing from 98 to 99 92 per cent copper, with small amounts of silver which are mechanically enclosed and not alloyed. From the standpoint of the genesis of ore deposits this fact is important, for had the metals been deposited from a molten magma they would exist as an alloy. Some iron, arsenic, nickel, bismuth, and mercury may also be present but strangely no gold.

Chalcocite is a steel-gray mineral with a metallic luster, often tarnishing to a dull blue or green. It crystallizes in the orthorhombic system, but distinct crystals are rare, the occurrence being commonly massive. Veins more than 20 feet across have been found in Butte and in Alaska. Its cleavage is indistinct and its fracture conchoidal.

Covellite, the cupric sulfide, is less stable chemically than chalcocite, the cuprous sulfide. It has a beautiful deep indigo blue color which upon being moistened turns to a characteristic, easily recognizable purple. It is a relatively rare ore mineral except at Butte, Montana, where it occurs massive in some of the mines.

Chalcopyrite is geographically the most widely distributed copper mineral, occurring in practically every copper field in the world. It is not the prevailing mineral of the greatest producing mines, however, and therefore ranks after chalcocite as a source of copper. It has a brass-yellow color, metallic luster, a greenish-black streak, and occurs usually in compact masses, although occasionally in crystals of the tetragonal system. It is considered the primary ore of copper along with bornite and cupriferous pyrite, and from these all other (secondary) copper minerals were generated. The theoretical composition is about 34.6 per cent copper, but the copper content may be as little as 2 per cent or less. Even such low-grade deposits can be smelted profitably under favorable conditions.

Bornite is another ore mineral in which the copper content varies, as has already been mentioned. It is fairly common but occurs

usually in subordinate amounts. The freshly broken surface exhibits a copper-red to bluish-brown color (" horseflesh ore "), which tarnishes to variegated blues and purples, from which it has likewise derived the name " peacock ore." Other complex sulfides, less important than bornite, are *chalmersite* $CuFe_2S_3$, and *cubanite* $CuFe_2S_4$.

Enargite, the sulfarsenate of copper, is a relatively rare mineral except in Butte, where it occurs in such large quantities that it has become the source of about 3 per cent of the world's copper production. It is a brittle, grayish-black mineral containing 19 per cent arsenic and as such is an important raw material for the byproduction of arsenic trioxide. When the arsenic is replaced by antimony, the sulfantimonate **famatinite** results. Where the Cu_2S is associated with antimony trisulfide Sb_2S_3, the sulfantimonite **tetrahedrite,** or gray copper ore, is found. The copper is often replaced by iron, zinc, mercury, or lead, as in *bournonite* $3(Pb,Cu_2)S{\cdot}Sb_2S_3$. Silver is usually present in tetrahedrite, making it an ore of silver as well as of copper. Tetrahedrite is the principal ore mineral at the Sunshine and other silver mines in the Coeur d'Alene mining district in Idaho. The sulfarsenite corresponding to tetrahedrite is called **tennantite.**

Cuprite, the cuprous oxide, Cu_2O, occurs in the upper zones of most oxidized copper ore deposits and, in early developments, was an important ore mineral. It is usually some shade of red or brown and in translucent crystals shows a ruby red, from which it has derived the name " ruby ore." The cupric oxide CuO is black and is known as **tenorite** or **melaconite.**

Malachite is the most abundant oxidized ore of copper, occurring usually in copper veins which lie in limestone. It has a beautiful green color, and when found in large solid masses, many of which are artistically marked, it is valuable not only as an ore of copper but also as a semi-precious stone, used for jewelry, table tops, vases, and other works of art. The pure mineral contains 57½ per cent copper, but because of its high coloring power and solubility it often stains and incrusts large areas of worthless rock, disguising it as valuable mineral.

Azurite, like malachite, is a basic copper carbonate but is less widely distributed. It possesses an intensely azure blue color from which it gets its name. When associated in alternating concentric rings with malachite, the contrast of colors is striking.

Chrysocolla is the only important silicate of copper. It likewise has a green to greenish-blue color but is non-crystalline and earthy in appearance. It occurs in commercial quantities in Arizona, Chile, and the Belgian Congo. Other silicates of copper, such as *dioptase, cornuite, plancheite, shattuckite* and *bisbeeite,* are rare.

Chalcanthite is an oxidation product of minerals containing copper sulfide. It is found dissolved in mine waters and crystallizes in the form of stalactites or incrustations.

Brochantite, the basic copper sulfate, is not of major importance in the United States but it occurs as the principal ore mineral in the oxidized zone at Chuquicamata, Chile. The basic chloride **atacamite** likewise occurs massive in Chile and Bolivia. **Krohnkite,** found in the upper zone at Chuquicamata, is the basic sulfate of sodium and copper.

COPPER ORES

Copper ores are widely distributed throughout the world, occurring in every continent and in almost every country. They are furthermore found in practically every type of ore deposit and are associated, in one place or another, with every metallic and rock-forming mineral. This distribution, though wide, is not uniform, so the present world production comes mainly from certain definite, limited localities.

> There are four major known sources of supply in the world at present. In the order of their importance as gaged by past production they are (1) the Rocky Mountain and Great Basin area of the United States; (2) the west slope of the Andes in Peru and Chile; (3) the central plateau of Africa in the Belgian Congo and Northern Rhodesia; (4) the pre-Cambrian shield area of central Canada and its extension into northern Michigan. These areas contain about 95 per cent of the total known reserves.[4]

Types of Copper Ores. In the metallurgical treatments required for the winning of metallic copper we may make the following rough classification of copper ores.

1. Sulfide Ores:
   - *a.* High-grade, direct-smelting ores.
   - *b.* Medium-grade ores which must be concentrated.
   - *c.* Low-grade ores which require concentration and must be mined and milled on a large-scale, low-cost basis.
   - *d.* Pyritic ores.
2. Oxidized Ores:
   - *a.* High-grade or medium-grade ores which can be smelted to "black copper" by reduction smelting, mixed with sulfide ore or concentrate for matte smelting, or leached.
   - *b.* Low-grade ores which are treated by leaching.
3. Native Copper Ore.

Under 1*c* and 2*b* appears the group of copper ore deposits which is the most economically important of all, the *porphyry coppers.* Twelve of these immense deposits are now being exploited — nine in south-

[4] Notman, Arthur, in Copper Resources of the World, Vol. 1, p. 31, Sixteenth Intern. Geol. Congr., 1935.

western United States and three on the west slope of the Andes in South America. These are "disseminated copper deposits," in which the copper minerals in the form of small grains are scattered uniformly through a large body of rock. The copper minerals in the upper portions are in general oxidized, and those lower down are sulfides. In the first four deposits to be developed the copper minerals were distributed in a porphyry — hence the name porphyry coppers. Although some of these deposits occur in schist or other host rocks the name porphyry coppers is generally applied to the entire group. Parsons[5] lists the following characteristics of the porphyry copper deposits.

1. The deposit is of such magnitude and shape that it can be mined advantageously by large-scale methods, either by underground caving or in open pits.

2 The distribution of the copper minerals is so general and uniform that "bulk" methods of mining are more profitable than selective methods whereby individual veins or thin beds would be stoped separately.

3. An intrusion of porphyry or closely related igneous rock has played a vital part in the genesis of the ore though the porphyry itself may not constitute the major part of the deposit The evidence is convincing that remarkably large, deep-seated, slow-cooling masses of rock were the source of the heat and energy and, directly or indirectly, of the metals in the deposits of the present day.

4. The process known as "secondary enrichment" has operated to concentrate the copper. At New Cornelia the zone of secondary enrichment is almost negligible but it exists

5. The extent of the ore body is usually determined by economic limits rather than by geologic structure This is because the copper content gradually diminishes as progress is made either downward or laterally from the core of an enriched mass At some point — which necessarily varies with the cost of production at the particular mine, with the price of copper, and with other economic conditions — a "cut-off" must be made between "ore" and "waste." This may be 0.5 per cent copper or it may be 1.5 per cent in different mines; and, considered literally, it would vary widely with respect to the *same* mine at different times.

6. The average copper content of the mass is comparatively low (with 3 per cent as the maximum) and grinding and mechanical concentration are necessary to produce a suitable smelter feed, if the ore is sulphide in character.

Some of the important facts about the porphyry copper deposits are summed up in Table 2. At the present time the production from the twelve porphyry copper deposits accounts for about one-third of the world production of copper.

[5] Parsons, A B., The Porphyry Coppers, Am. Inst. Min. and Met. Eng. (Rocky Mountain Fund), 1933.

TABLE 2

The Porphyry Coppers[a]

Property	Location	Date of First Production	Minerals in Oxidized Zone	Minerals in Sulfide Zone	Mining Method	Metallurgical Treatment	Production to Dec 31, 1931 (tons of copper)	Tons of Ore Reserve Dec. 31, 1931[b]	Grade of Ore Reserve[b] (% copper)	Tons of Copper in Reserve[b]
Utah	Bingham, Utah	1905		Chalcocite Chalcopyrite Covellite Bornite	Open cut	Concentration and Smelting	1,810,400	1,000,000,000	1 1	11,000,000
Morenci	Morenci, Arizona	1907		Chalcocite	Underground — block-caving Open cut[c]	Concentration and Smelting	611,100	450,000,000	1 1	4,950,000
Nevada	Ely, Nevada	1908		Chalcocite Chalcopyrite	Open cut, also underground— block caving	Concentration and Smelting	756,000	130,000,000	1 5	1,950,000
Braden	Sewell, Chile	1910		Chalcopyrite Chalcocite Bornite Tetrahedrite	Underground — block-caving	Concentration and Smelting	1,051,900	300,000,000	2 3	6,900,000
Miami	Miami, Arizona	1910		Chalcocite	Underground — block-caving	Concentration and Smelting	526,000	130,000,000	1 1	1,430,000
Ray	Ray, Arizona	1911		Chalcocite	Underground — block-caving	Concentration and Smelting	564,900	135,000,000	1 6	2,160,000
Chino	Santa Rita, New Mexico	1912	Native Copper Cuprite Malachite Azurite Chrysocolla	Chalcocite Malachite Azurite	Open cut	Concentration and Smelting	576,300	175,000,000	1 4	2,450,000

Property	Location	Date of First Production	Minerals in Oxidized Zone	Minerals in Sulfide Zone	Mining Method	Metallurgical Treatment	Production to Dec 31, 1931 (tons of copper)	Tons of Ore Reserve Dec 31, 1931[b]	Grade of Ore Reserve[b] (% copper)	Tons of Copper in Reserve[b]
Inspiration	Miami, Arizona	1915	Chrysocolla Chalcocite Malachite Azurite	Chalcocite	Underground — block-caving	Leaching, Concentration and Smelting	658,600	150,000,000	1 35	2,025,000
Chuquicamata	Chuquicamata, Chile	1915	Brochantite Atacamite Krohnkite Chalcanthite	Chalcocite Brochantite Enargite	Open cut	Leaching	1,306,800	1,000,000,000	2 5	25,000,000
New Cornelia	Ajo, Arizona	1917	Malachite Chrysocolla	Chalcopyrite Bornite	Open cut	Leaching,[d] Concentration and Smelting	374,900	200,000,000	1 1	2,200,000
Copper Queen	Bisbee, Arizona	1923		Chalcocite Covellite Chalcopyrite Bornite	Open cut, also underground — top-slicing	Concentration and Smelting, Heap Leaching	218,300	36,000,000	1 4	500,000
Andes	Potrerillos, Chile	1927	Malachite Azurite	Chalcocite Chalcopyrite	Underground — block-caving	Leaching, Concentration and Smelting	249,400	140,000,000	1 5	2,100,000

[a] Parsons, A B , op cit

[b] Estimated by Parsons, A B., op cit

[c] Stripping operations for a new open pit at Morenci were started in 1939.

[d] Discontinued, oxidized ore exhausted about 1930.

The ore deposits classified under 1*c* and 2*b* are for all practical purposes simply the porphyry copper ores. The other principal copper ore deposits of the world (except the native copper ores and some pyritic ores) do not fit so readily into a classification based on the metallurgical treatments used in winning the copper from the ore. Since, however, the metallurgy of copper is to be our chief concern, it will be best for our purposes to retain this simple tabulation rather than to attempt to set up an elaborate classification which would place each ore type in its proper geological category. We have already seen that in the porphyries we may have both oxidized and sulfide ores in a single deposit; the same thing is true in other deposits of copper ore. Also, we may find high-, medium-, or low-grade ores all in the same deposit. Without further preamble let us briefly consider some of the more important of the world's deposits of copper ore.

Second only to the porphyry deposits in importance are the African deposits in the Belgian Congo and Rhodesia. These ores are in a belt which extends through the province of Katanga in the Belgian Congo and into Northern Rhodesia. The ores usually contain the copper minerals uniformly disseminated throughout a mass of rock; in this respect they resemble the porphyry coppers, but they differ from the porphyries in two important respects: (1) the copper ore beds are usually sharply delimited by barren wall-rock, and gradational contacts or "economic cut-offs" are rare; and (2) the ore is of much higher grade — the grades of ore reserves are from 3 0 to 7.0 per cent copper in some of the mines as compared with 1 0 to 2.0 per cent for the porphyries (Table 2). The ores of the Katanga district (up to the present time) have been principally oxidized ores with malachite as the principal mineral and minor amounts of azurite, chrysocolla, cuprite, and native copper. Some of these ores are sufficiently high grade for direct reduction smelting; the lower-grade oxidized ores are treated by leaching. The ore minerals in the sulfide ores, which are typical of most of the Rhodesian ores, are chalcocite, chalcopyrite, and bornite, with very minor amounts of pyrite and covellite. These deposits differ from most other copper ores in that they are low in iron, and pyrite (FeS_2) is present only in very small amounts.

Butte, Montana, has produced more copper than any other district in the United States, although now its yearly production is exceeded by Bingham, Utah. The Butte ores occur in well-defined veins, and the principal copper ore minerals are chalcocite, bornite, and enargite, with minor amounts of chalcopyrite and tetrahedrite. Pyrite is abundant.

The Sudbury area in Ontario is one of the most productive regions

not only in Canada but in the world. There are two principal types of ores in this district — copper-nickel ores and zinc-copper-lead ores. This region supplies 90 per cent of the world's nickel and is one of Canada's largest producers of copper; it also supplies all the platinum produced in Canada. The copper-nickel ore bodies are either masses of pure sulfides or mineralized rock containing 10 to 60 per cent sulfides. The principal sulfide mineral is the iron sulfide pyrrhotite (Fe_7S_8); the copper mineral is chalcopyrite, and most of the nickel is in the form of *pentlandite* ((Fe,Ni)S). Platinum is present as *sperrylite* ($PtAs_2$). The copper-nickel ores are by far the most abundant in this district.

In northern Manitoba, Canada, there are large mineral deposits which contain both copper and zinc. The principal ore minerals are chalcopyrite and sphalerite (ZnS) with some gold and silver. Pyrite is abundant.

The ore of Kennecott, Alaska, consisted of both sulfides (chalcocite and covellite) and oxidized minerals (malachite and azurite) in a limestone-dolomite gangue; about half of the copper was in the form of sulfide and half in the oxidized state. This district has been a large producer of copper, but the ore bodies are now exhausted.

The ore deposits at Cananea, in the State of Sonora, Mexico, contain the ore minerals chalcocite, chalcopyrite, bornite, and pyrite; parts of the deposit are in a limestone gangue.

The deposits mentioned above will give some idea of the many types of ore from which copper is extracted, many of these deposits produce low- or medium-grade ore (" milling ore ") as well as a certain amount of high-grade (" direct-smelting ore "). While we have included some of the most productive districts in the world, it must not be assumed that this is an exhaustive list of all the important deposits of copper ore. The principal purpose of this information is to set before us some facts about various types of copper ore; this will serve to point up the discussions of metallurgical treatment methods which are to follow. Let us conclude this section with a brief glance at the two remaining types of copper ores — native copper and pyritic ores.

There is only one native copper ore deposit of economic importance in the world, and that is located on the Keweenaw Peninsula of northwestern Michigan. The ores are either amygdaloid or conglomerate, containing native copper grains. These copper particles range in size from a grain that is just visible to the eye to large nuggets; some masses have been found which weighed from 40 to 100 tons. In some parts of the deposits silver is found in the form of nuggets of native silver which is not alloyed with the copper; some of the copper also contains arsenic. This district is the second largest in the United

States in total amount of copper produced; in yearly production, however, it is now well below several of the other large producing districts.

The best known of the pyritic ores are the deposits of Rio Tinto in the Province of Huelva, Spain. The ores are massive pyrite containing chalcopyrite in the form of minute scattered grains, or threads and strings in crevices. Ore containing about 2 per cent copper is mined as copper ore, and the lower-grade or copper-free pyrite is mined and used in the manufacture of sulfuric acid. The mines at Rio Tinto have been exploited since Phoenician and Roman times. In the United States there is a deposit at Ducktown, Tennessee, where the ore contains chalcopyrite disseminated in massive pyrite and pyrrhotite. This deposit, like that at Rio Tinto, is exploited both as a copper mine and as a sulfur mine (for the manufacture of sulfuric acid).

Byproducts of Copper Ores. Very often copper is not the only commercial product obtained from copper ores; sometimes the byproducts are of minor importance, but occasionally their importance may equal or exceed that of the copper itself. The manner in which the copper is separated from its byproducts depends upon the nature of the association of the substance in the ore deposit, as we may see by a few random examples. The Butte district is a large producer of zinc as well as copper, but here it has been possible to mine the two ores separately, so that the problem is quite simple. At the Flin Flon mine in northern Manitoba, however, copper and zinc sulfides are so intimately associated that the ore must be ground and the two sulfides mechanically separated by ore-dressing processes. Many copper ores contain recoverable amounts of silver, and this metal will follow the metallic copper through all the stages of milling and smelting and is separated from it only by the final refining operation. Some of the important byproducts of copper ores are listed below.

Nickel. As mentioned above, about 90 per cent of the world's nickel is produced from the copper-nickel ores of the Sudbury, Ontario, district. The two metals are separated in either the smelting or refining operation as it is not possible to make a complete separation of the copper and nickel minerals by ore-dressing methods. Some of these ores are smelted to yield directly a natural alloy of nickel and copper — Monel metal. This alloy contains approximately 68 per cent nickel, 28 per cent copper, and 2 per cent iron.

Silver. Many copper ores contain silver, and the metal is usually found in the form of sulfides associated with the copper sulfides; occasionally native silver is found. Silver follows the copper through all the stages of its metallurgical treatment and remains alloyed with it through the fire-refining operation. Electrolytic refining methods

are used to separate the silver from copper. In 1936,[6] 17,388,289 ounces of silver was recovered from copper ores mined in the United States; this represented 28.46 per cent of the total domestic silver production.

Gold. Many copper ores contain gold as well as silver; it is practically always found as native gold associated with the sulfides; it behaves like silver in the smelting and refining operations and, like silver, is separated from the copper in the electrolytic refining operation. Most gold-bearing copper ores contain only small amounts of gold, but such large tonnages of ore are treated that the gold produced makes a respectable showing. In 1936[7] domestic copper ores yielded 379,159 ounces of gold, or 10 03 per cent of the United States production.

Platinum. Platinum and associated metals of the platinum group (palladium, osmium, iridium, ruthenium, and rhodium) are found in most copper ores which contain the other precious metals (gold and silver). Often they are present in minute amounts, as in the Butte ores, but they follow the gold and silver through the process and are eventually recovered when the gold and silver bullion is parted and refined. The copper-nickel deposits of the Sudbury district contain notable quantities of platinum and related metals; in 1937[8] the refineries treating the base metals from these ores produced 139,361 ounces of platinum and 119,867 ounces of palladium, rhodium, and other metals of the platinum group. This represented 44 per cent of the world's production of platinum. The copper ores of Katanga also yield platinum group metals, and in 1937[9] the copper refinery of the Union Minière du Haut Katanga reported the production of 12,860 ounces of palladium and 2570 ounces of platinum.

Molybdenum. Molybdenite, MoS_2, is found in small quantities in some copper ores, and recently it has become feasible to separate a high-grade molybdenite concentrate during the milling operations. Three large copper mines have already become important producers of molybdenum — Utah Copper, at Bingham, Utah; Chino, at Hurley, New Mexico; and Greene Cananea, at Cananea, Sonora, Mexico. In 1937[10] the United States produced 92 per cent of the world's output of molybdenum, 29,419,000 pounds out of a total of 32,000,000 pounds. Of this amount Utah Copper produced 4,912,569 pounds, and Mexico,

[6] The Mineral Industry During 1937, Vol 46, p. 250, McGraw-Hill Book Co., New York.

[7] Idem, p. 250.

[8] Idem, p. 487.

[9] Idem, p 486.

[10] Minerals Yearbook, 1938, p. 563, U. S. Bur. Mines.

the second largest producer of molybdenum in the world, produced about 1,200,000 pounds — entirely a byproduct of the Cananea copper ores.

Cobalt. Cobalt is associated with the copper ores of Katanga, Northern Rhodesia, and Sudbury, Ontario. The world's production of cobalt in 1937[11] was about 2800 metric tons, of which probably 60 to 70 per cent was obtained from cobaltiferous copper ores.

Lead and Zinc. Either lead or zinc or both may be associated with copper sulfide ores in the form of galena, PbS, and sphalerite, ZnS When these are associated with copper ores, and it is not possible to mine them separately, the minerals are mechanically concentrated by ore-dressing methods into copper, lead, and zinc concentrates, each of which is treated separately. Although a considerable tonnage of lead and zinc is produced from copper ores, it is small compared with the total production from lead, zinc, and lead-zinc ores

Arsenic. Practically all of the world's arsenic is obtained as a by product from either lead or copper smelters Arsenic-bearing minerals are associated with the sulfides, and when the ore or concentrate is roasted, the arsenic is carried off in the smoke in the form of volatile As_2O_3. This compound is recovered from the smoke, purified, and marketed as " white arsenic."

Sulfuric Acid. The source of much of the SO_2 which is used in making sulfuric acid is pyrite, FeS_2. The pyrite is oxidized (burned or roasted) to produce the SO_2, which is then further oxidized to SO_3 and dissolved in water to form H_2SO_4. In some of the large pyritic deposits containing only about 1 per cent copper, the ore is usually mined primarily for its sulfur content, and the copper is a byproduct. Many copper smelters maintain sulfuric-acid plants, using as raw material the SO_2 gas obtained by the roasting of all or part of their sulfide concentrates.

Tenor of Copper Ores. By " tenor " or " grade " of a copper ore is meant simply the copper content of the ore expressed in per cent. We have already said enough about copper ores to indicate that it is impossible to state what the lower limit should be in order that a given deposit might be classed as a commercial ore. An ore containing 2 per cent copper might conceivably be classed as high-grade in one mine and as waste in another. Modern methods of treatment in both mining and metallurgy have made it possible to treat deposits of lower grade. In the period 1851–1860, the average tenor of copper ore mined throughout the world was 20 per cent copper; in 1914–1930, the average grade

[11] Minerals Yearbook, 1938, p. 558, U. S Bur Mines.

of all the world's copper ore was 1.5 per cent.[12] This is a startling change to take place in only 70 years. It appears, however, that this downward trend may be checked or even reversed because of the development of the large and relatively high grade deposits in Africa.

Gangue Minerals in Copper Ores. In addition to the valuable minerals or "values" found in copper ores there are the worthless or "gangue" minerals which accompany them, and, of course, if the average copper ore contains only 1 or 2 per cent copper, the bulk of the ore as mined must consist of these gangue minerals. Quartz is the predominant gangue mineral in many vein deposits; pyrite is abundant in most deposits, although in some it is exploited for its sulfur content, in which case it is really not a gangue mineral. Limestone or dolomite is found as a gangue mineral in a few deposits, and in the porphyry deposits the gangue minerals are the various silicate minerals which make up the host rock The metallurgical treatment which a given ore is to receive is often determined by the nature of the gangue minerals; for example in treating the Kennecott ores, it was necessary to employ ammonia leaching rather than sulfuric-acid leaching because of the large amount of acid-soluble limestone in the gangue The principal gangue constituents of several typical copper ores are shown in Table 3. The examples listed in this table illustrate the fact that copper ores vary greatly in composition, and as we shall find later, each ore requires its own combination of metallurgical operations to win from it the copper and associated values at the maximum profit.

CONCENTRATION OF COPPER ORES

Most of the copper ore mined today is treated by *ore dressing* processes; low-grade oxidized ores are treated directly by leaching, and some sulfide and oxidized ores are sufficiently high grade for direct smelting, but the bulk of all copper ore is first *dressed* to put it into shape for more economical extraction of the copper and other valuable elements. The great advances in ore dressing have been made since 1900, and they have had a profound effect on the metallurgy of copper. Ore dressing methods have made possible the exploitation of the immense deposits of low-grade sulfide ore; but without the resources of modern milling, these would be masses of worthless rock and not copper ore. Not only has ore dressing had its effect on mining methods and copper ore reserves by making it possible to exploit lower-grade deposits, but it has had far-reaching effects on the pyro-

[12] Furness, J. W., Development of the Copper Industry, in Copper Resources of the World, p 2, Sixteenth Internat. Geol Congr., 1935.

TABLE 3

Composition of Some Typical Copper Ores

Location	Mine	Cu (%)	Other Metals (%)	Precious Metals (oz /ton)	Fe	S	Gangue (%)				Remarks
							SiO_2	Al_2O_3	CaO	Others	
Butte	(1)	4 1		Ag, 2 2 Au, 0 011	11 0	12 8	56 5	7 7	0 5		Typical mill feed at Anaconda concentrator, 1929, quartz gangue, pyrite predominating sulfide
Northern Rhodesia	Roan Antelope (2)	Total 3 24 Oxide 0 29			3 22	0 95	54 79	17 97	1 30	MgO, 4 78	Shale gangue, little pyrite, chalcocite principal copper mineral, milling ore
Katanga	(3)	9 31			3 21		64 17	7 42	1 29	MgO, 5 05	High-grade leaching ore, malachite principal copper mineral.
Northern Rhodesia	Nkana (4)	Total 4 34 Oxide 0 26	Co, 0 22		2 78	1 79	44 88				Mill feed, flotation section.
Sudbury, Ontario	Frood (5)	3 40	Ni, 3 00	Combined Au + Ag + Pt metals $4 00 per ton Total at 1930 prices	33 25	19 80	23 10				Flotation feed, total sulfide content of mill feed about 45%; pyrrhotite principal sulfide.
Manitoba	Flin Flon (6)	2 44	Zn, 4 25	Ag, 0 67 Au, 0 043							Mill feed during pilot mill run, 1927.

Location	Mine	Cu (%)	Other Metals (%)	Precious Metals (oz /ton)	Fe	S	Gangue (%)				Remarks
							SiO_2	Al_2O_3	CaO	Others	
McGill, Nevada	Nevada Consolidated (7)	Total 1 315 Oxide, 0 08		Ag, 0 060 Au, 0 019	4 4	2 7	70 3	10 5	0 9		Mill feed, principal sulfides are chalcopyrite and pyrite with some chalcocite, gangue is quartz and feldspar
Noranda, Quebec	Horne (8)	2 35		Ag, 0 35 Au, 0 15 (Au partly as Telluride)	44 6	33 9	18 3				Milling ore, contains 51 5% pyrrhotite, 22 1% pyrite, and 6 8% chalcopyrite
Chuquicamata, Chile	Chile Exploration Co (9)	Total, 2 1 Sulfide, 0 2 Oxide, 1 9	As, 0 002 Sb, 0 001 Mo, 0 010 Na, 1 10 K, 5 20		0 95		68 0	16 0		Cl, 0 012 NO_3, 0 015	Leaching ore, principal copper mineral brochantite.
Lake Superior, Michigan	Ahmeek (10)	1 45									Amygdaloid ore, containing native copper as the economic mineral

1 Morrow, B S, Both Copper and Zinc Ores Treated by Selective Flotation Eng and Min Jour, Vol 128, No 8, p 295, 1929
2 Littleford, J W, Concentrating Operations at Roan Antelope Copper Mines Am Inst Min and Met Eng Trans, Vol 112, p 937, 1934
3 Wheeler, A E, and Eagle, H Y, Leaching Operations of Union Minière du Haut Katanga Am Inst Min and Met Eng. Trans, Vol 106, p. 620, 1933.
4 Durham, L P, Nkana Mine Concentrator, Am Inst Min and Met Eng Trans, Vol 112, p 930, 1934
5 MacDonald, W T, Selective Flotation at Copper Cliff Eng and Min Jour, Vol 130, No 9, 1930
6 Gaudin, A M, Flotation, p 261, McGraw-Hill Book Co, New York, 1932
7 Weinig, A J, and Carpenter, C B, The Trend of Flotation Colorado School of Mines Quart, Vol 32, No 4, p 65, 1937
8 McLachlan, C G, Increasing Gold Recovery from Noranda's Milling Ore Am Inst Min and Met Eng Trans, Vol 112, p 570, 1934.
9 Campbell, T C, Reduction Plant of the Chile Exploration Company Am Inst Min and Met Eng Trans, Vol 106, p 577, 1933
10 Benedict, C H, Steam Stamps Hold Their Own at Ahmeek Mill Eng and Min Jour, Vol 139, No 12, p 53, 1938

metallurgy of copper as we shall have occasion to notice. The principal reason for the replacement of the blast furnace by the reverberatory furnace in copper smelting is the fact that the reverberatory furnace is more suitable for treating flotation concentrates. Roasting of copper ores and concentrates has as its primary function the lowering of the sulfur content. But in a few copper concentrates it has been possible to remove pyrite, the principal source of sulfur, by ore-dressing methods, thus lowering the sulfur content to such a degree that roasting was unnecessary.

Ore dressing is a series of processes by means of which the constituent minerals in ore are *mechanically separated* into two or more products. No chemical change takes place in any of the constituents of the ore — if copper is present as chalcopyrite in the ore it remains as chalcopyrite in the concentrate. The mineralogical analysis of an ore, and the size and association of the individual grains are the primary factors which govern the choice of ore dressing methods. The two fundamental processes in all ore dressing operations are: (1) *comminution,* or *crushing* and *grinding,* to liberate the individual mineral particles, and (2) *concentration* by means of which the comminuted ore is mechanically separated into two or more fractions. It is beyond the scope of this work to consider in any detail the subject of ore dressing; we shall be content to consider only two topics — the advantages and limitations of ore-dressing methods in the processing of copper ores, and the nature of its products, or concentrates, which must be smelted to recover the contained metals.

The simplest type of ore dressing operation is a two-product separation in which only one *concentrate* and one *tailing* result Suppose, for example, that we are treating a native copper ore containing 2 per cent copper and that the copper is the only valuable mineral; the rest of the ore is siliceous gangue. A perfect separation would yield a concentrate containing all the copper and only copper and a tailing containing all the siliceous matter and none of the copper. One ton of ore would yield 40 pounds of concentrate assaying 100 per cent copper and 1960 pounds of barren tailing to be discarded. Such a perfect separation is impossible of attainment, but these figures represent the limit which might be approached rather closely. To take another simple example, let us assume that we again have a 2 per cent copper ore with a siliceous gangue but that all the copper is in the form of chalcopyrite ($CuFeS_2$); again let us assume that we can make a perfect physical separation of the copper minerals from the gangue minerals. The 40 pounds of copper in one ton of ore is contained in 116 pounds of chalcopyrite which assays 34 5 per cent copper. Therefore, we should

have 116 pounds of concentrate assaying 34.5 per cent copper and 1884 pounds of barren tailing. This is also a theoretically perfect separation, but obviously the concentrate produced in the second case is less desirable than that in the first one; this is due to the ore minerals, and there is nothing that ore dressing methods can do about it.

Now let us consider what we might expect to attain practically in the dressing of these two simple ores The tabulations given below represent results which might reasonably be expected.

TABLE 4

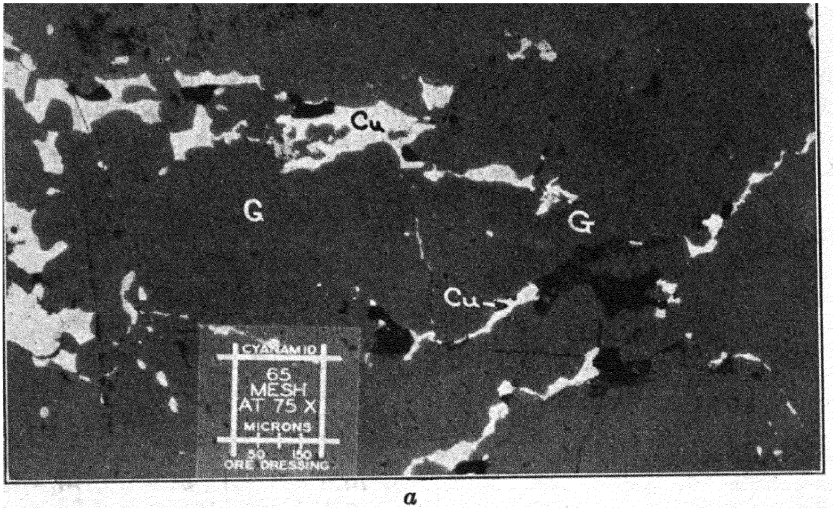
CASE 1. NATIVE COPPER ORE

	Weight (pounds)	Assay (per cent Cu)	Weight of Contained Copper (pounds)
Heads	2000	2 0	2000 × 0 02 = 40
Concentrates	54 3	70 0	54 3 × 0 70 = 38
Tailings	1946	0 103	1946 × 0 00103 = 2

CASE 2. CHALCOPYRITE ORE

Heads	2000	2 0	2000 × 0 02 = 40
Concentrates	131	29 0	131 × 0 29 = 38
Tailings	1869	0 107	1869 × 0.00107 = 2

Note that the practical results differ from the theoretical values in two respects. (1) The concentrate does not have its theoretical assay value but is always lower, hence there must be some of the gangue mineral in it, and (2) the tailing is not barren but contains some copper. In order to measure the effectiveness of a concentrating operation it is necessary to consider both of these. The effectiveness of the process *in recovering the valuable metal* is measured by the *recovery,* which is the per cent of the total amount of copper in the heads that is recovered in the concentrate. In both cases the recovery is the same, namely 38/40, or 95 per cent. The effectiveness of the process *as a concentrating operation* is measured by *the ratio of concentration,* which is the ratio of the weight of the heads to the weight of the concentrate. In case (1) the ratio of concentration is 2000/54.3 = 36.8, or 36 8 to 1, and in case (2) it is 2000/131 = 15.3, or 15.3 to 1. The grade of the concentrate, or its copper assay, will be directly proportional to the ratio of concentration for any given ore provided the recovery remains constant; of course, however, it would be possible to get very high values for both grade of concentrate and ratio of concentration by removing only the " cream " of the valuable fraction, in which case the recovery would be low.



a

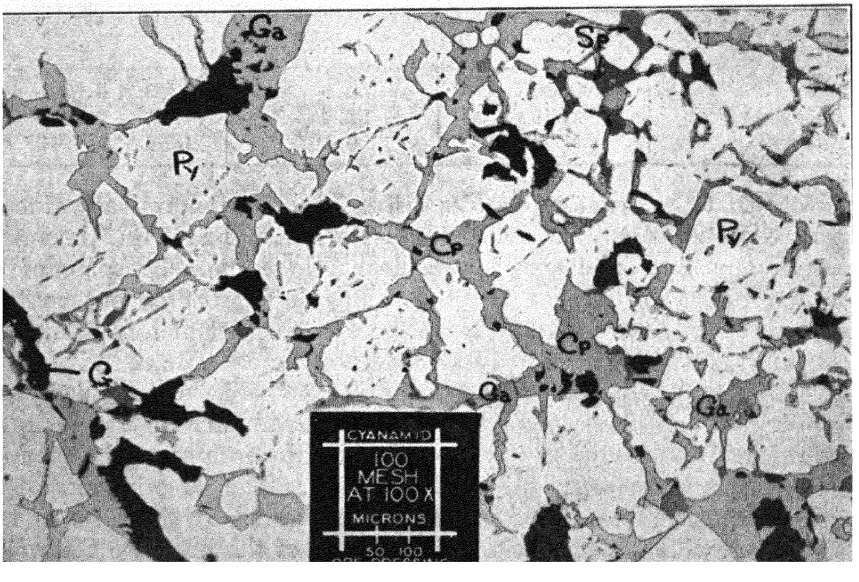
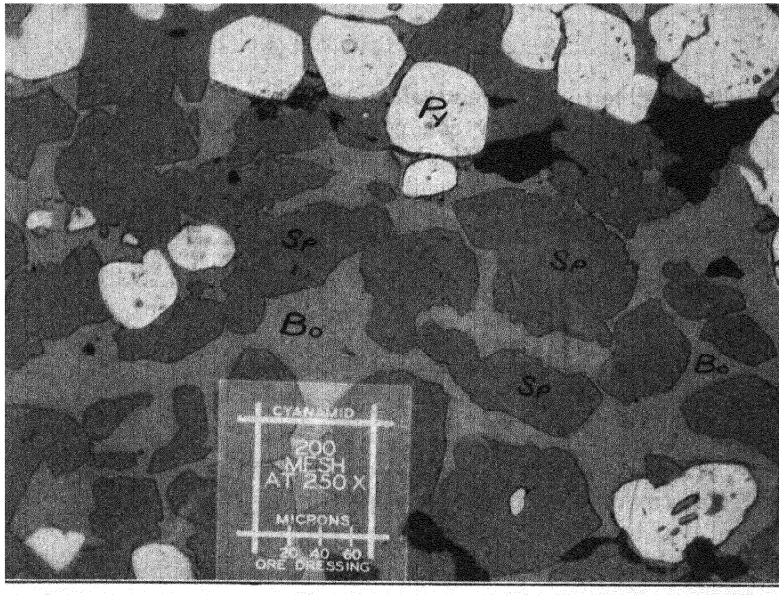
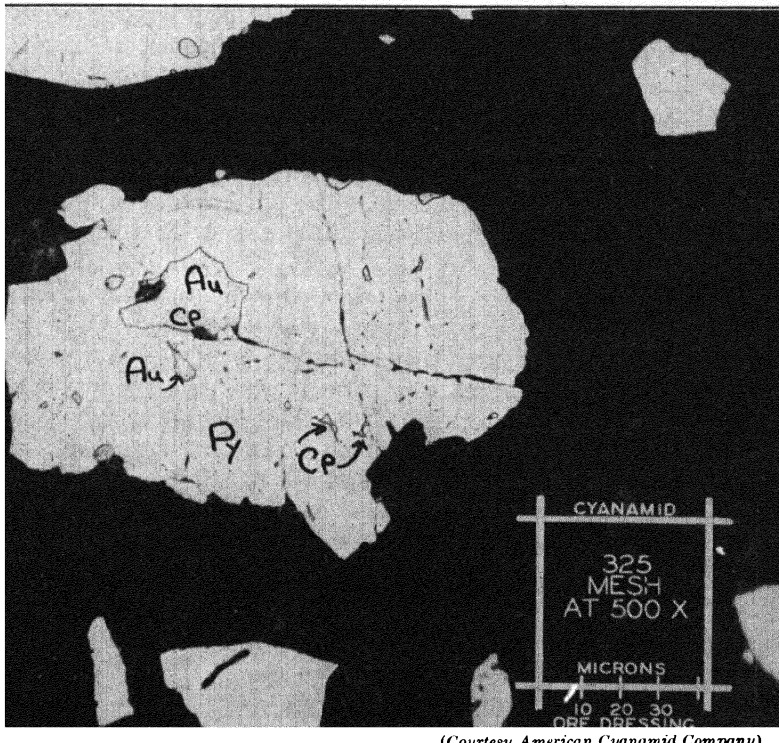


FIG. 1. Photomicrographs of Some Copper Ores.

a, Native copper and gangue.
b, Pyrite — chalcopyrite ore with small amounts of galena (PbS) and sphalerite (ZnS).
c, Bornite — sphalerite — pyrite ore.
d, Pyrite — chalcopyrite — gold ore.
G, Gangue; Ga, galena; Cu, native copper; Py, pyrite; Cp, chalcopyrite; Bo, bornite; Sp, sphalerite; Au, native gold.



c



(Courtesy American Cyanamid Company)

d

It is impossible to get a mineralogically pure concentrate or a perfectly barren tailing in any commercial ore dressing process. As a general rule, and regardless of what method of concentration is used, the recovery and grade of concentrate bear a sort of inverse relation to one another; if we strive to obtain a very high grade concentrate we ordinarily suffer greater losses in the tailing, and if we aim to get a high recovery and low tailing assays we must be content with a lower-grade concentrate. The operator should strive to balance grade of concentrate against the tailing loss so that the process gives the maximum profit on the ore being treated, all things considered.

The discussion thus far has been concerned with two very simple ores When the ore contains other valuable metals in addition to copper, when pyrite or pyrrhotite is present (which are difficult to separate from some copper sulfides), or when the particles of ore minerals are so small that it is difficult to liberate them from the gangue by grinding, the problem becomes more complex. A little later we shall consider some examples of the milling of copper ores to illustrate the various methods employed.

Comminution. Most copper concentrators employ large gyratory or jaw crushers for primary breaking, secondary crushers or crushing rolls for finer crushing, and rod mills or ball mills for fine grinding. The principal exception is that in the milling of native copper ores, steam stamps or other special crushers are used for crushing the ore because the presence of large pieces of the tough native copper make it difficult to use conventional types of crushers. The fine grinding may be done in ball mills after the ore has been stamped and the coarse copper removed.

Concentration. Flotation is the principal method employed for the concentration of copper ores, although some gravity devices such as jigs and tables are used; often they are used in conjunction with flotation. Until recently oxidized copper ores have been difficult to concentrate satisfactorily by any method, and these ores are usually leached directly without preliminary dressing. Flotation concentrate, as a rule, consists of very fine particles, and the roasting and smelting of flotation concentrate presents problems which are not involved in the smelting of ore or coarse gravity concentrates.

Examples of Copper Ore Dressing Practice. No two copper ores are alike, nor are any two given exactly the same ore-dressing treatment; the aim in each case is to divide the crude ore into several fractions such that the subsequent treatment or discarding of these fractions yields the maximum profit. Let us briefly consider a few examples of the milling methods used on some typical copper ores.

Anaconda. The concentrator at Anaconda, Montana, treats the ores from Butte; the copper concentrator has eight sections each of which can mill 1500 tons of ore in 24 hours. The ore is crushed successively in a primary gyratory crusher, Symons cone crushers, and rolls. The roll product is deslimed and sand and slime treated separately. Concentration is by flotation; the slime goes directly to a separate flotation circuit; the sand is ground in ball mills and treated by flotation in the main circuit. Metallurgical results of the existing flowsheet are shown in Table 5.[13]

TABLE 5

METALLURGICAL RESULTS AT THE ANACONDA CONCENTRATOR

Product	Weight (per cent)	Assays (per cent)				Copper Recovery (per cent)
		Cu	Fe	SiO_2	Al_2O_3	
Ore	100 00	5 50	.	.	.	100 00
Mill concentrate	13 98	30 60	24 1	4 1	1 4	77.77
Slime concentrate	5 08	20 00	25 4	10.3	2 6	18 47
Total concentrate	19 06	27 77	24 5	5 75	1 7	96 24
Mill tailing	69 52	0 24	.	...	...	3 03
Slime tailing	11 42	0 35		. .	.	0 73
Total tailing	80 94	0 256				3 76

The copper sulfides in the Butte ores are so intimately intergrown with pyrite that it would require extremely fine grinding for complete liberation — the low grade of the concentrate is due primarily to pyrite-copper sulfide middling grains. Morrow and Griswold[14] have demonstrated in the laboratory that by using a modified flowsheet involving the regrinding of a low-grade pyrite-copper middling it is possible to make a 40 per cent copper concentrate from the Butte ores with the same recovery as that obtained at present in the mill.

Ahmeek.[15] The Ahmeek mill treats the native copper ore from the Ahmeek mine of the Calumet and Hecla Consolidated Copper Company on the shores of Lake Superior in northern Michigan. The ore is an amygdaloid rock containing from 26 to 32 pounds of native

[13] Morrow, B. S., and Griswold, G. G., Production of High-Grade Concentrate from Butte Ores: Am. Inst. Min. & Met. Eng. Trans., Vol. 112, p. 413, 1934.

[14] Morrow, B. S., and Griswold, G. G., op. cit.

[15] Benedict, C. H., Steam Stamps Hold Their Own at Ahmeek Mill: Eng. and Min. Jour., Vol. 139, No. 12, 1938

copper per ton (1.3 to 1.6 per cent). The coarse ore flows over a picking table on the way to the steam stamps, and here the large masses of copper (" barrel work " or " mill mass ") are recovered by hand. The stamps crush the ore down to about $\frac{5}{8}$-inch diameter and the stamp discharge passes to trommels with $\frac{3}{16}$-inch openings. The trommel oversize is treated in bull jigs to remove copper; the jig tailings pass to crushing rolls in closed circuit with the trommels. Only material which passes the $\frac{3}{16}$-inch holes in the trommels escapes from this circuit except the copper concentrate from the bull jigs. The $\frac{3}{16}$-inch product is deslimed and the slimes go directly to flotation; the sands pass through another series of jigs. The tailings from this second set of jigs are ground in a ball mill and then treated in another set of flotation cells. Finally, the flotation tailing sands are passed over Wilfley tables to recover any copper that was too large to float. The copper concentrates from both sets of jigs are referred to as " high-grade " concentrate, that from the Wilfley tables and some jig products as " low-grade " concentrate. In addition to the tables used in scavenging operations on the flotation tailings, a Wilfley table is used in closed circuit with the ball mill ahead of the classifier, where it performs the same function as a " unit " flotation cell. Metallurgical performance is given in Table 6.

TABLE 6

METALLURGICAL RESULTS AT AHMEEK MILL[a]

Product	Copper Assay (per cent Cu)	Recovery (per cent)
Mill feed	1.3–1 6	....
Mill mass	95.0±	4.7
High-grade (jig) concentrate	90.0	50.4
Low-grade (jig and table) concentrate	80.0	26.3
Flotation concentrate	60.0	13.6
Final tailing	0 075	5 0

[a] Total recovery, 95 0 per cent, average grade of all concentrates, 78 0 per cent Cu, ratio of concentration, 60 to 1.

Roan Antelope.[16] The concentrator of the Roan Antelope Copper Mines in Northern Rhodesia treats from 8000 to 10,000 tons of ore per 24 hours; the average analysis of the ore is given in Table 3. Coarse crushing is done with two Superior McCully gyratory crushers

[16] Littleford, J. W., Concentrating Operations at Roan Antelope Copper Mines: Am. Inst. Min & Met. Eng. Trans., Vol. 112, p. 935, 1934.

and fine crushing with five Symons cone crushers. Fine grinding is performed by ten Marcy ball mills with one Fraser and Chalmers ball mill for regrinding. Concentration is entirely by flotation The average Roan Antelope concentrate will assay about as follows: Total Cu, 58.51 per cent, oxide Cu, 0.59; SiO_2, 11 52; Al_2O_3, 4.08; Fe, 5 27; S, 17.78; CaO, 0.15, MgO, 0 57; residue, 4.12 In general, with heads assaying from 3.15 to 3 25 per cent total copper and 0.15 to 0.25 per cent oxide copper, the Roan Antelope concentrator will produce a concentrate containing 58 per cent copper, representing 87 to 88 per cent total recovery and 90 to 91 per cent sulfide copper recovery. The ratio of concentration is about 20 to 1

Much of the oxide copper is lost in the tailings; more of this could be recovered by flotation if desired, but this would result in lowering the grade of the concentrate. The oxide copper does not present a very serious problem, however, because the amount of it in the ore is diminishing as mining proceeds downward from the oxidized zone. Smelting costs increase in proportion to the amount of alumina in the concentrate, hence it is desirable to keep the alumina in the concentrates as low as possible. By making a high-grade concentrate (56 to 60 per cent Cu) the alumina content of the concentrate can be kept down, but this means some sacrifice of recovery.

Katanga. The ores mined by the Union Minière du Haut Katanga in the Belgian Congo are largely oxidized ores. These ores are concentrated by various combinations of hand picking, gravity concentration, and flotation. Where the oxidized minerals can be freed in relatively large pieces, hand picking and gravity concentration are used; flotation is used on finer material Flotation gives good recovery on malachite, but very little of the chrysocolla can be recovered by flotation. The following data are taken from an article by Barthelemy.[17]

The largest mine working on oxide ores is the Kambove, and this ore is milled at the Panda concentrator. Ore is first crushed and sorted by hand on picking belts; the pickers remove high-grade, which is dropped directly into cars for shipment, and the ore remaining on the belt is fed to the gravity section The gravity section makes concentrates on both jigs and Wilfley tables, and the gravity tailings pass to the flotation section, which makes a flotation concentrate and a final tailing Metallurgical results are given in Table 7; note the exceptionally high grade of the mill feed and of the final tailing.

[17] Barthelemy, R. E., Katanga Ores Offer a Variety of Treatment Problems: Eng and Min Jour., Vol. 135, No 9, p. 401, 1934.

TABLE 7

MONTHLY METALLURGICAL RESULTS, PANDA CONCENTRATOR[a]

	Tonnage	Copper Assay (per cent Cu)	Recovery (per cent)
Mill feed	60,315	11 80	....
Picked concentrate	121	37 40	0 6
Gravity concentrate	7,799	35 10	38 5
Flotation feed	52,395	8 28	...
Flotation concentrate	10,498	35 33	52 2
Flotation tailing	41,897[b]	1 50	8 7

[a] Over-all recovery, 91 3 per cent, over-all ratio of concentration, 3 28 to 1, recovery of copper in flotation feed, 85 5 per cent.

[b] By difference.

The ore milled at the Panda concentrator contains oxidized copper minerals as the principal economic values. At other mines in the district, however, the ores are more complex. A copper-zinc ore from the Prince Leopold mine contains about 12 5 per cent total copper, 2.2 per cent oxide copper, 9.8 per cent zinc, and 9 8 ounces of silver. Ore from the Ruashi mine contains cobalt in the form of *carrollite*, a copper-cobalt sulfide containing 41.28 per cent cobalt and 15 53 per cent copper. In this district is also found the Chinkolobwe mine, the largest radium mine in the world.

Copper Cliff. Shortly after the completion of the 8000-ton concentrator of the International Nickel Company at Copper Cliff a description was published by W. T. MacDonald.[18] The ore treated in this mill contains copper as chalcopyrite, nickel as pentlandite, and large amounts of pyrrhotite; the mill feed will average about 45 per cent sulfides. This ore contains about 4.4 per cent copper, 2 2 per cent nickel, and about $4.00 per ton in precious metals (gold, silver, and platinum metals) Two important facts govern the milling of this ore: (1) in order to make a satisfactory recovery of the valuable metals it is necessary to recover all the sulfides, hence the over-all ratio of concentration can never be much greater than 2 to 1; and (2) a certain amount of selection is possible, but the mineral association is such that it is not possible to make clean copper and nickel concentrates. Since it is possible to depress pyrrhotite and pentlandite and float chalcopyrite, the first step is to make a copper concentrate containing about half of the copper in the ore; this concentrate contains about 25 per cent copper and 1.25 per cent nickel. After this concentrate is re-

[18] MacDonald, W. T., Selective Flotation Mill at Copper Cliff. Eng. and Min. Jour., Vol. 130, No. 9, p 465, 1930.

moved, all the remaining sulfides (pyrrhotite, pentlandite, and the remainder of the chalcopyrite) are removed as a bulk concentrate. The pentlandite is very intimately associated with pyrrhotite. This milling method cuts the bulk of the ore about in half by rejecting the non-sulfide gangue minerals and yields (1) a copper concentrate containing only a small part of the nickel, and (2) a bulk copper-nickel-iron concentrate. Concentration is entirely by flotation except that tables are used as scavengers on the tailing from the bulk flotation circuit.

Falconbridge.[19] At the mill of the Falconbridge Nickel Mines, Ltd., in Ontario, the mill feed is a copper-nickel ore somewhat resembling that treated by Copper Cliff. Concentration is by flotation and there is no selective action — all the sulfides are removed in a bulk concentrate. Flotation recovers 98 to 99 per cent of the copper and about 94 per cent of the nickel with a ratio of concentration of about 4 to 1. Metallurgical results are given in Table 8.

TABLE 8

COMPOSITE ANALYSES, IN PER CENT, OF FLOTATION PRODUCTS AT FALCONBRIDGE

	Cu	Ni	Fe	SiO_2	S
Mill heads	1 12	0 85	17 4	39 1	7 6
Concentrates	4 43	3 18	39 0	12 1	28 2
Tailings	0 03	0 065	10 1	48 8	0 3

Noranda.[20] The ore from the Horne mine in Quebec is a copper-gold ore (Table 3). Two types of ore are produced from the mine, a siliceous ore and a heavy sulfide ore containing more than 50 per cent pyrrhotite and 20 per cent pyrite. All the siliceous ore is sent directly to the smelter because its silica content is needed for fluxing. Whether or not the sulfide ore goes to the mill or directly to the smelter depends primarily on its gold content — if the gold content is high the ore is smelted directly, if it is low the ore goes to the mill. The "cut-off" which determines whether or not a given lot is milling or direct-smelting ore varies from time to time and depends on several factors. In general, direct smelting costs more but it gives almost perfect recovery of the gold and copper; milling followed by smelting is cheaper,

[19] Gronningsater, A., Gill, J. R., and Mott, R. C., Metallurgy at Falconbridge: Eng. and Min. Jour., Vol. 135, No. 5, p. 195, 1934.

[20] McLachlan, C. G., The Development of Concentrating Operations at Noranda: Canadian Min. Jour., Vol. 55, No. 4, 1934; Increasing Recovery from Noranda's Milling Ore: Am. Inst. Min. & Met. Eng. Trans., Vol. 112, p. 570, 1934.

but the losses of gold in the mill tailing are quite large. Of course it is *necessary that the feed to both smelter and mill be kept reasonably* constant so that the entire capacity of the equipment can be utilized, and Noranda has developed an elaborate milling process to produce the maximum yield from the milling ore We shall consider the Noranda process in rather more detail than the others, because it illustrates nicely many of the factors which must be taken into account in the milling of complex ore and it also shows the interdependence of milling and smelting operations.

The mineralogical analysis of the average ore milled at Noranda in 1933 is given in Table 9. The aim of the milling process is to produce from this heavy sulfide ore a single copper-gold concentrate containing as much of the valuable metals as possible and to discard a tailing containing the bulk of the silica and iron sulfides.

TABLE 9

AVERAGE MINERALOGICAL COMPOSITION OF NORANDA CONCENTRATING ORE TREATED DURING 1933

Mineral	Content[a]
Chalcopyrite	6 8
Pyrite	22.1
Pyrrhotite	51 5
Magnetite	0 5
Silica and silicates	18 3
Gold, native and as telluride	0 15
Silver, probably as argentite	0.35

[a] Au and Ag expressed in ounces per ton, all others in percentage.

Concentration is entirely by flotation, and it is possible by the use of suitable reagents (1) to float chalcopyrite, native gold, and gold telluride away from pyrite and pyrrhotite, and (2) to float pyrite away from pyrrhotite.

Flotation of chalcopyrite while depressing the iron sulfides recovers about 93 per cent of the copper but only about 66 per cent of the gold. The 34 per cent of the gold remaining in the copper-circuit tailings is largely associated with the pyrite and pyrrhotite; very little is found in the quartz. The gold in the pyrite is in the form of extremely small particles, many of which are not more than 1 or 2 microns in diameter (1 micron = 0 001 mm); gold and gold telluride found in the grains of pyrrhotite usually occur in the form of larger pieces.

The tailings from the copper circuit pass directly to another flotation circuit where the pyrite is floated off. The tailings, containing prin-

cipally pyrrhotite and silicates, pass to the pyrrhotite regrind circuit where they are given another grind and passed through a third series of flotation cells; here another copper-gold concentrate is removed and the tailings are discarded. The pyrite concentrate is sent to a fourth circuit — the pyrite regrind circuit — where it is subjected to intensive regrinding and then passed to flotation cells for the removal of another copper-gold concentrate. In other words, the first step is to remove most of the chalcopyrite and about 66 per cent of the gold; the tailing is then split into a pyrite and a pyrrhotite fraction by means of flotation, and each of these fractions is reground and refloated to give copper-gold concentrate. All three concentrates are combined and sent to the smelter. Recoveries made in each circuit are shown in Table 10.

TABLE 10

METAL RECOVERIES AND RATIO OF CONCENTRATION

Circuit	Recovery (per cent)		Ratio of Concentration
	Copper	Gold	
Main copper circuit	92 77	65 68	6.34 to 1
Pyrite regrind circuit	3 08	6 12	66 6 to 1
Pyrrhotite regrind circuit	1 05	7 33	56 3 to 1
Over-all	96 90	79 13	5 24 to 1

Note that the additional treatments of the main circuit tailing result in additional recoveries of 4 per cent of the copper and more than 13 per cent of the gold without too greatly affecting the ratio of concentration. Work is being continued in an effort to further decrease tailing losses, and it is also proposed to treat the pyrite tailing by cyanidation to extract more of the gold.

Magna and Arthur. Located near Bingham, Utah, the Magna and Arthur mills treat the ore from the porphyry mine in Bingham Canyon. They are similar in size and general flow sheet, and both are all-flotation plants. Table 11 gives typical metallurgical data for one month's operation at Magna. Note the low grade of the mill heads and the large daily tonnage. The Arthur and Magna plants represent the largest milling operation in the world. In addition to copper recovery as shown in the table, Utah Copper is now recovering substantial quantities of molybdenite[21] by selective flotation and is saving

[21] Minerals Yearbook, 1938, p. 563, U. S. Bur. Mines.

TABLE 11[a]

METALLURGICAL DATA AT MAGNA CONCENTRATOR FOR APRIL 1930

	Assays						
	Total Cu(%)	Non-Sulfide Cu(%)	Fe(%)	Insoluble(%)	S(%)	Au (oz/ton)	Ag (oz/ton)
Heads	0.9572	0.035	2.65	...	.....	0.0090	0 0884
Concentrates	31.4880	.. .	26 01	5 29	35 20	0 242	2 56
Tailings	0 1046	0 030	2 27		.	0 0025	0 0195

Average tonnage milled per day		28,127 tons
Average concentrate made per day		764 tons
Ratio of concentration		36.8 to 1
Recoveries, per cent:		
Total copper	89.37	
Sulfide copper	92 14	
Non-sulfide copper	16 61	
Gold	72 98	
Silver	78 54	

[a] Martin, H S , Milling Methods and Costs at the Arthur and Magna Concentrators of the Utah Copper Co U S Bureau of Mines Inf Circ 6479, July 1931

additional amounts of gold by passing the flotation tailings through burlap-lined launders.[22]

SUMMARY

All the *primary* or " new " copper produced in the world comes from one of the deposits of copper ore The copper ore deposits differ from one another in many respects, among the most important of which are the following:

1. Size of the deposit.
2. Grade of the copper ore.
3. Mineralogical nature of the ore minerals.
4. Mineralogical nature of the gangue minerals.
5. Presence of other valuable substances or byproducts in the ore.
6. Geographical location of the deposit.

With the exception of the native copper ores from Lake Superior, all these ores contain their copper in the form of chemical compounds, and before metallic copper can be produced from these raw materials one or more chemical processes must be utilized to break up the chemical union between copper and other atoms and to purify the crude copper. We shall be concerned with these chemical processes in

[22] Engelmann, E. W., Recovering Gold from Copper Mill Tailing: Mining and Metallurgy, Vol. 16, p. 331, August 1935.

later chapters. Where " wet " or leaching processes are employed for extracting copper the crude ore itself is the raw material, but when copper is extracted by " dry " or pyrometallurgical methods (" smelting ") the raw material or feed may be either crude ore or concentrate or both. In modern practice only a relatively small amount of the feed to pyrometallurgical copper plants is crude ore; most of the copper-bearing material entering the plant is concentrate made by treating the crude ore by ore dressing methods.

Ore dressing, or the mechanical separation of crude copper ore into (1) a tailing to be discarded and (2) one or more valuable concentrates for further treatment, is an important step in the treatment of most copper ores. Some of the important facts about the milling of copper ores are listed below.

1. Concentration is usually the cheapest way of getting rid of the bulk of valueless minerals in the ores. It would be economically impossible to employ pyrometallurgical methods on such ores as the porphyry coppers, but it is both feasible and profitable to make a high-grade concentrate from these ores and to subsequently smelt this concentrate.

2. In many cases ore dressing methods give a partial or complete separation of copper minerals from other valuable substances, thus greatly facilitating subsequent treatment.

3. Where the mine is some distance from the smelter, the erection of a concentrating plant near the mine lowers transportation costs, since only the relatively small bulk of high-grade concentrate need be shipped. This fact is not always of great importance in milling copper ores, because often the mill and smelter are located on the same site (e g., Anaconda, Noranda).

4. Flotation is by far the most effective concentration method used in the treatment of copper ores; it has long been used with notable success with sulfide ores, and recently it has been employed with good results in the treatment of oxidized copper minerals. The physical nature of flotation concentrate (principally the fine subdivision of the mineral particles) has required certain changes in pyrometallurgical processes which were originally used on crude ore Flotation has also made it possible to separate copper sulfides from pyrite and pyrrhotite in some cases, and this, too, has had its effect on pyrometallurgical treatment.

5. The various processes classed under the general heading of ore dressing are flexible and easily adapted to a wide variety of ores, as shown by the examples cited. Very often it happens that a mill can be easily adapted to meet changing conditions, whether these are changes in the ore itself or changes caused by economic forces.

CHAPTER II

THE EXTRACTION OF COPPER FROM ITS ORES

Copper is extracted from its ores by various modifications of pyrometallurgical and hydrometallurgical processes, the former being used mainly with sulfide, native copper, and some high-grade oxidized ores, and the latter almost entirely with low-grade oxidized ores. Electrolysis is commonly used in conjunction with both types of extraction; the impure copper bullion produced by smelting methods is usually refined electrolytically, whereas the solution obtained in leaching practice may be depleted of its copper by electrolysis, although precipitation upon scrap iron is quite common where scrap iron is available. Fire refining is likewise standard practice with all methods of extraction. It is generally used to bring copper to a higher degree of purity before refining electrolytically, and for electrolytically refined copper which, although chemically in a highly purified form, is nevertheless weak and brittle, fire refining is used to impart the necessary physical properties, such as ductility, malleability, and strength, which are required in the final fabrication.

Figure 1 gives in flow-sheet form a general outline of the methods of extracting copper from its ores. Detailed steps are not included; neither is the disposition of various byproducts, such as gas, fume, flue dust, anode mud, spent electrolyte, and the like. The precipitation of metallic copper from solution by sulfur dioxide gas and several other practices are purposely omitted as not being general.

Pyrometallurgical Processes. Approximately 85 to 90 per cent of the world's total output of copper is extracted from its ores by pyrometallurgical processes. There are three distinct, although by no means equally important, modifications in use today, based upon the character of the copper minerals.

1. *Native copper ores,* and the product obtained by concentrating such ores, are smelted by simple fusion. The gangue material is removed by adding a suitable flux, which forms with the gangue minerals a molten slag. The slag and the copper are readily separated in the liquid state, due to the great difference in their respective specific gravities.

2. *Sulfide copper ores* are smelted almost entirely by what is known as " matte smelting." This type of smelting is so widely practiced in

the metallurgy of copper and so peculiar to that metal that a separate section of this chapter is devoted to its theoretical aspects.

3. *Oxidized copper ores,* when of a fairly high grade, that is, containing from 6 to 20 per cent copper, may be reduced by coke and carbon monoxide in a manner analogous to the reduction of iron ores. The product is metallic copper, usually high in iron and other impurities. From the black color of the reduced metal this type of smelting has

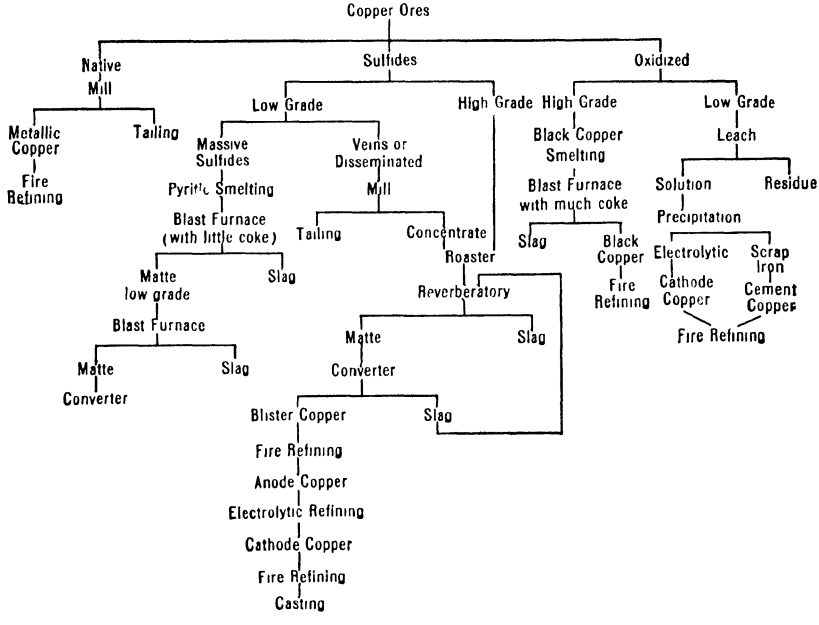


FIG. 1. General Treatment of Copper Ores.

been called "black copper smelting." It is being supplanted by leaching, or, where sulfide ores are available for mixing, by matte smelting.

Hydrometallurgical Processes. Although by far the greater portion of the total copper of the world is produced today by smelting, and only from 10 to 15 per cent by leaching, nevertheless the hydrometallurgical processes are improving rapidly in attractiveness, ease of operation, and efficiency of extraction. With the ever increasing practicability of roasting flotation concentrate, leaching the roasted material, and then precipitating the copper from solution either electrolytically or chemically, it is not at all impossible that leaching processes might some day displace entirely the smelting methods used at present. The results of laboratory tests, however, are not so readily attainable on a commercial scale.

The outstanding advantage of hydrometallurgical processes lies in the fact that the solvent acts only upon the copper minerals, and leaves the larger mass of gangue material unattacked. In smelting methods this gangue must be fluxed and melted, involving the expense of a fluxing material, fuel, and a costly furnace. With low-grade ores this expense is prohibitive, and as flotation methods for low-grade oxidized ores have not yet been brought to an economic status, such ores can be treated profitably only by leaching.

A variety of hydrometallurgical methods are in use today, but in general the steps have been standardized as follows: The ore is first prepared for leaching, either mechanically by crushing or chemically by roasting, or both. The roasting may be oxidizing, sulfatizing, or chloridizing The solvent is next brought in contact with the prepared ore, either by percolation, which is cheaper, or by agitation, which is more rapid and more efficient. The separation of the solution and the residue is effected by gravity or pressure filtration; continuous counter-current decantation has been found most convenient. The copper is precipitated from solution chemically or electrolytically, and the precipitate is melted, refined, and cast.

THEORY OF MATTE SMELTING

The ultimate objective of any method of extracting copper from its ores is to obtain, as economically and as completely as possible, the copper in a highly purified form and to reject the accompanying materials in such a form that valuable byproducts, if present, may be recovered. In smelting sulfide copper ores, the aim is to separate the copper from the iron, sulfur, and gangue materials. The precious metals, such as gold, silver, platinum, and palladium remain with the copper until the final step of electrolytic refining. The separation is accomplished in three distinct operations, as follows:

1. *Roasting* removes a portion of the sulfur, as well as some of the volatile components like arsenic, antimony, and bismuth, and oxidizes some of the iron to FeO. In pyritic smelting, the roasting may be accomplished simultaneously with smelting, and in the same furnace. As will be shown later, the degree of roasting determines the amount of sulfur left in the roasted ore, and this in turn determines the grade of the matte, that is, the per cent of copper in the matte, which is a measure of the ratio of concentration.

2. *Smelting,* either in the blast furnace, with or without extraneous fuel, or in the reverberatory furnace, performs as its main function the removal of the gangue minerals to the slag and the smelting of the copper, iron, and sulfur, plus the precious metals, down to a matte.

The iron oxide formed during roasting and some sulfur are likewise removed.

3 *Converting* separates the copper of the matte from iron and sulfur by oxidizing the sulfur to the gaseous product SO_2, which is emitted through the mouth of the converter; the iron is oxidized to FeO and fluxed immediately by free silica, forming a ferrous silicate slag. The liquid slag is separated from the liquid copper in the same manner that oil is separated from water, and is poured off. The crude copper remaining contains the gold, silver, and other precious metals, as well as some arsenic, antimony, selenium, tellurium, iron, nickel, lead, zinc, bismuth, and other impurities. These are removed later by fire refining and electrolysis.

Fundamentals of Matte Smelting. The smelting of sulfide copper ores (or mixtures of sulfide and oxide ores) to a copper matte is based upon the strong affinity of copper and sulfur for each other, as compared with that of other metals and sulfur, and the relatively weak affinity of copper and oxygen for each other. In a reducing or neutral atmosphere and at smelting temperatures, copper and sulfur form the stable cuprous sulfide, Cu_2S, either by direct combination or by the decomposition of higher valence copper sulfides. There is usually more sulfur present than required by the copper to form this compound. The excess sulfur, under reducing conditions, then unites with iron to form a correspondingly stable ferrous sulfide, FeS. The iron present in excess of the amount required by the sulfur is usually in the form of ferrous oxide, FeO, and combines with silica to go into the slag as ferrous silicate. Cuprous sulfide and ferrous sulfide are miscible in all proportions in the liquid state In the solid state they form a eutectic. The mixture, whether liquid or solid, is known as **copper matte.**

Copper Matte.[1] A matte is any sulfide which has been prepared artificially by fusion. Under the ordinary conditions of preparation, a copper matte consists of a mixture of cuprous sulfide, Cu_2S, and ferrous sulfide, FeS. In practice these are usually accompanied by the sulfides of such other metals as PbS, NiS, Ag_2S, as well as gold, arsenic, antimony, selenium, and tellurium. For the present purpose it is convenient and not at all impractical to consider copper matte as a mixture of Cu_2S and FeS in any proportions of the two substances. It is likewise convenient and sufficiently accurate here to use the atomic weight of copper as 64, iron 56, and sulfur 32.

Cuprous sulfide, Cu_2S, consists then of 2×64 parts by weight of copper and 32 of sulfur, or 4 parts of copper and 1 of sulfur, or 80 per cent copper and 20 per cent sulfur. Ferrous sulfide, FeS, consists of

[1] See also Chapter IV.

56 parts by weight of iron and 32 of sulfur, or 63.6 per cent iron and 36.4 per cent sulfur. Inasmuch as the copper and iron are both present combined with definite proportions of sulfur, it is necessary to know the per cent of only one component of the matte in order to calculate the other two. A matte containing, for example, 40 per cent copper obviously contains $\frac{5}{4} \times 40$, or 50 per cent Cu_2S, and 50 per cent FeS. Therefore, $0.636 \times 50 = 31.8$ per cent iron present; and $100 - (40 + 31.8) = 28.2$ per cent sulfur. The percentage composition of the matte can also be calculated if either the per cent iron or the per cent sulfur is known. The calculations may be summarized as follows:

Let x represent the per cent of copper in the matte. Then

$$\begin{aligned} \text{Cu} &= x \\ \text{Cu}_2\text{S} &= \tfrac{5}{4}x \\ \text{FeS} &= 100 - \tfrac{5}{4}x \\ \text{Fe} &= \tfrac{7}{11}(100 - \tfrac{5}{4}x) \\ \text{S} &= \tfrac{1}{4}x + \tfrac{4}{11}(100 - \tfrac{5}{4}x) \end{aligned}$$

As the sum of the three components is equal to 100 per cent of the matte,

$$\text{Cu} + \text{Fe} + \text{S} = 100$$

or

$$x + \tfrac{7}{11}(100 - \tfrac{5}{4}x) + \tfrac{1}{4}x + \tfrac{4}{11}(100 - \tfrac{5}{4}x) \equiv 100$$

Let y represent the per cent of iron in the matte. Then

$$\begin{aligned} \text{Fe} &= y \\ \text{FeS} &= \tfrac{11}{7}y \\ \text{Cu}_2\text{S} &= 100 - \tfrac{11}{7}y \\ \text{Cu} &= \tfrac{4}{5}(100 - \tfrac{11}{7}y) \\ \text{S} &= \tfrac{4}{7}y + \tfrac{1}{5}(100 - \tfrac{11}{7}y) \end{aligned}$$

Again, as the sum of the three components is equal to 100 per cent of the matte,

$$\text{Cu} + \text{Fe} + \text{S} = 100$$

or

$$\tfrac{4}{5}(100 - \tfrac{11}{7}y) + y + \tfrac{4}{7}y + \tfrac{1}{5}(100 - \tfrac{11}{7}y) \equiv 100$$

The sulfur is distributed between the copper and the iron; simultaneous equations are therefore necessary. We know that

$$\text{Cu} + \text{Fe} + \text{S} = 100$$

and

$$\tfrac{1}{4}\text{Cu} + \tfrac{4}{7}\text{Fe} - \text{S} = 0$$

From these two simultaneous equations it follows that, letting z represent the per cent of sulfur in the matte,

$$\begin{aligned} \text{S} &= z \\ \text{Cu} &= 177.8 - 4.89z \\ \text{Cu}_2\text{S} &= \tfrac{5}{4}(177.8 - 4.89z) \\ \text{Fe} &= 3.89z - 77.8 \\ \text{FeS} &= \tfrac{11}{7}(3.89z - 77.8) \end{aligned}$$

To check that

$$\text{Cu} + \text{Fe} + \text{S} = 100$$
$$177.8 - 4.89z + 3.89z - 77.8 + z \equiv 100$$

Where constant reference is made to the theoretical composition of copper mattes, a table such as recommended by Richards[2] may be drawn up, giving the per cent of each component and constituent for

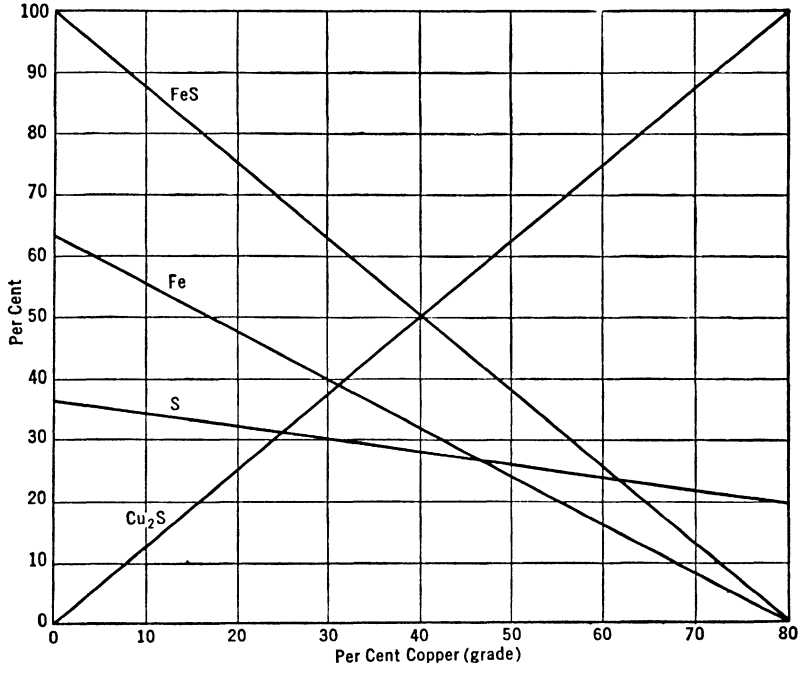


FIG. 2. The Composition of Copper Mattes.

varying percentages of copper Such a compilation is shown in Table 1. Figure 2 represents the composition of copper mattes in graphical form.

Ratio of Concentration. The smelting of copper ores to a matte is just one step, although a very important one, in bringing the copper content of the ore or concentrate to a higher degree of purity by removing a certain portion of the accompanying impurities. In other words, the metal is concentrated into a product of smaller bulk containing a higher percentage of copper. The ratio of the weight of ore or concentrate smelted to that of matte produced is known as the

[2] Richards, J. W., Metallurgical Calculations, p. 471, McGraw-Hill Book Co, New York, 1918.

TABLE 1

THEORETICAL COMPOSITION OF COPPER MATTES, IN PER CENT

Cu	Fe	S	Cu_2S	FeS	Cu	Fe	S	Cu_2S	FeS
0	63.64	36 36	0 00	100 00	41	31.02	27 98	51 25	48 75
1	62 84	36 16	1 25	98 75	42	30 23	27.77	52 50	47.50
2	62 05	35 95	2 50	97.50	43	29 43	27 57	53 75	46.25
3	61 25	35 75	3 75	96 25	44	28 64	27 36	55 00	45.00
4	60.45	35.55	5 00	95 00	45	27 84	27 16	56 25	43 75
5	59 66	35 34	6 25	93 75	46	27.05	26 95	57 50	42 50
6	58.86	35 14	7 50	92.50	47	26 25	26 75	58 75	41 25
7	58 07	34 93	8 75	91.25	48	25 45	26 55	60 00	40 00
8	57 27	34 73	10 00	90 00	49	24.66	26 34	61 25	38 75
9	56 48	34.52	11 25	88.75	50	23.86	26 14	62 50	37 50
10	55 68	34 32	12 50	87 50	51	23.07	25 93	63 75	36 25
11	54 89	34 11	13 75	86 25	52	22 27	25 73	65 00	35 00
12	54 09	33 91	15 00	85 00	53	21 48	25 52	66 25	33 75
13	53 30	33 70	16 25	83 75	54	20 68	25 32	67 50	32 50
14	52 50	33 50	17 50	82 50	55	19 89	25 11	68 75	31 25
15	51 70	33.30	18 75	81 25	56	19 09	24 91	70 00	30 00
16	50 91	33 09	20 00	80 00	57	18 30	24 70	71 25	28 75
17	50 11	32 89	21 25	78 75	58	17 50	24 50	72 50	27 50
18	49 32	32 68	22 50	77.50	59	16 70	24 30	73 75	26 25
19	48 52	32 48	23 75	76.25	60	15 91	24 09	75 00	25 00
20	47.73	32.27	25 00	75.00	61	15 11	23 89	76 25	23 75
21	46.93	32 07	26 25	73.75	62	14 32	23 68	77 50	22 50
22	46 14	31 86	27 50	72 50	63	13 52	23 48	78 75	21 25
23	45 34	31 66	28 75	71.25	64	12 73	23 27	80 00	20 00
24	44.55	31 45	30 00	70.00	65	11 93	23 07	81 25	18 75
25	43 75	31 25	31 25	68.75	66	11 14	22 86	82 50	17.50
26	42 95	31 05	32 50	67 50	67	10.34	22 66	83 75	16 25
27	42 16	30 84	33 75	66 25	68	9 55	22 45	85 00	15 00
28	41 36	30 64	35 00	65.00	69	8.75	22 25	86 25	13 75
29	40 57	30 43	36 25	63.75	70	7.95	22 05	87 50	12 50
30	39 77	30 23	37 50	62 50	71	7 16	21 84	88 75	11 25
31	38 98	30 02	38 75	61 25	72	6 36	21 64	90 00	10 00
32	38 18	29 82	40 00	60 00	73	5 57	21 43	91 25	8.75
33	37 39	29 61	41 25	58.75	74	4.77	21 23	92 50	7.50
34	36 59	29 41	42 50	57.50	75	3.98	21 02	93 75	6.25
35	35 80	29 20	43 75	56 25	76	3 18	20 82	95 00	5 00
36	35 00	29 00	45 00	55 00	77	2.39	20 61	96 25	3 75
37	34 20	28 80	46 25	53 75	78	1 59	20.41	97 50	2.50
38	33.41	28.59	47.50	52.50	79	0.80	20 20	98.75	1.25
39	32.61	28 39	48.75	51.25	80	0.00	20.00	100.00	0 00
40	31.82	28.18	50.00	50.00					

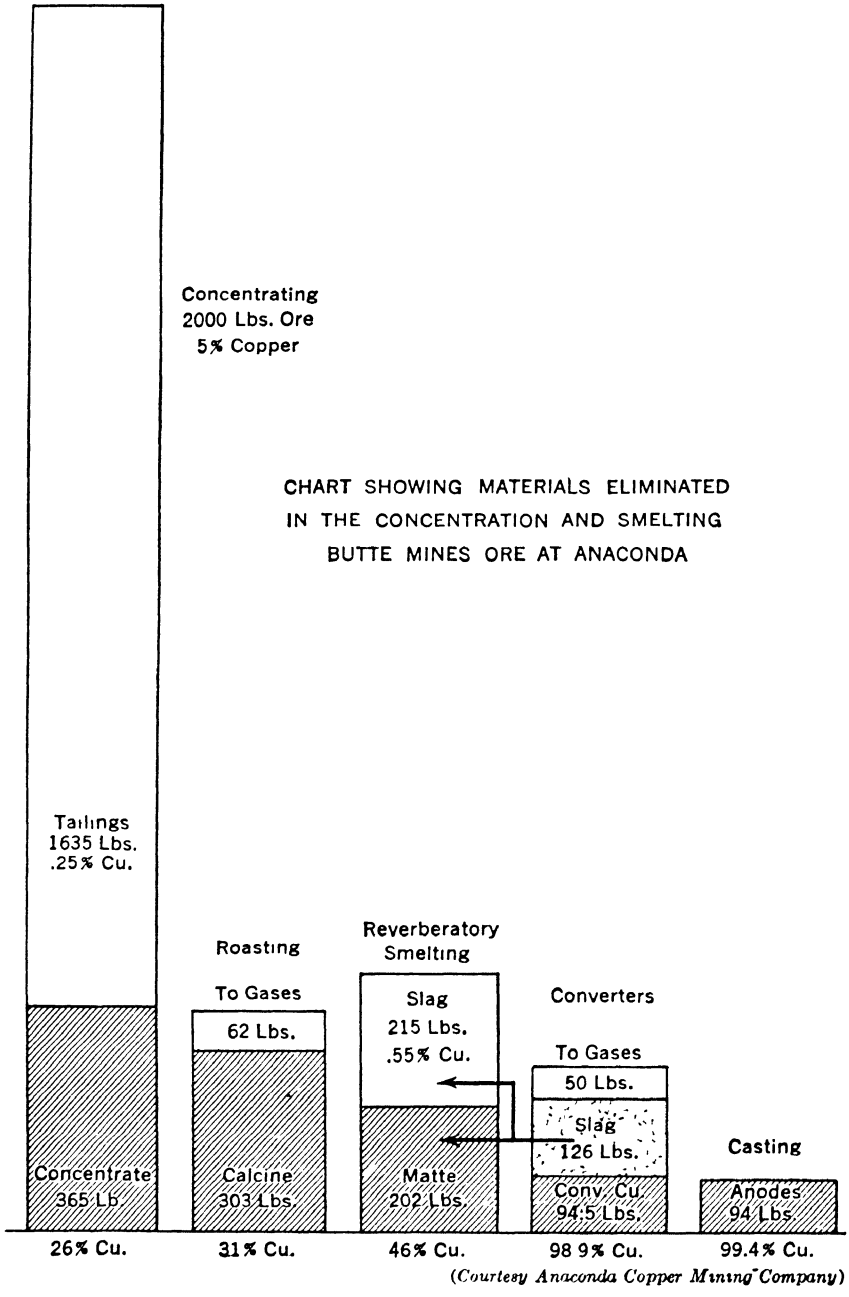
ratio of concentration. Thus if 10 tons of ore containing 4 per cent copper are smelted to 1 ton of matte containing 40 per cent copper, the ratio of concentration is 10 to 1. This can likewise be expressed as the ratio of the copper contents of the matte and the raw material.

As classified by Peters,[3] an ore consists of two portions, a metallic portion and an earthy portion. In the former are included the copper, gold, and silver minerals, as well as sulfides, arsenides, and antimonides; in the latter quartz, limestone, and oxides of iron and manganese The valuable materials for which the ore is being exploited are usually found in the metallic portion of the ore, whereas the earthy portion is generally worthless. Some of the constituents of the metallic portion, as for example barren pyrite, may likewise be worthless, but the above classification has been made on the basis that most of the metallic portion, on smelting, goes into the matte and the earthy portion goes into the slag In most deposits of copper ore the earthy part is present in a much larger proportion than the metallic part An obvious desideratum is to remove the usually larger, valueless earthy portion from the smaller metallic portion which contains the valuable materials.

The art of ore dressing has made such a step quite feasible by mechanical means, and selective flotation has gone farther and made it possible to separate the valuable metallic minerals from the barren ones. A flotation concentrate of high copper content can now readily be obtained, in some cases attaining almost any desired percentage of copper up to that contained in the pure ore minerals Until methods of treating the practically pure copper minerals or even the highest-grade flotation concentrate directly in the converter have been perfected, it usually will be found advantageous to leave a certain amount of pyrite with the concentrated ore, in order to furnish fuel for the converter in the form of ferrous sulfide in the matte.

Within certain limits, which will be discussed in a later paragraph, the greater the ratio of concentration attained in smelting the more economical will be the subsequent operation of converting, based upon the cost per ton of charge smelted. Thus, assuming that the cost of converting copper matte is $4 00 per ton of matte and that this matte has been obtained from a smelting operation working on a ratio of concentration of 8 to 1, the cost of converting ore or roasted concentrate is 50 cents per ton. That is, 8 tons of ore have been smelted to 1 ton of matte, which costs $4 00 to convert, or 50 cents per ton of ore. If, on the other hand, the ratio of concentration has been only 4 to 1, then 4 tons of ore have been smelted to 1 ton of matte, which, we will again

[3] Peters, E. D , Principles of Copper Smelting, p 5, McGraw-Hill Book Co., New York, 1907.



(Courtesy Anaconda Copper Mining Company)

FIG. 3.

assume, costs $4.00 to convert, which results in a converting cost of $1 00 per ton of ore.

The cost of converting a low-grade matte is usually higher than that of converting a high-grade matte, so the low-grade matte, obtained from a low ratio of concentration in smelting, would result in a still higher cost per ton of charge smelted than in the preceding illustration. As an example, assume that the cost of converting 1 ton of a 30 per cent copper matte is $6 00, while 1 ton of matte con aining 45 per cent copper can be converted for $4.00 If the concentrate to be smelted contains 15 per cent copper, the ratio of concentration in smelting to a 30 per cent matte is 2 to 1, and the cost of converting per ton of concentrate is $6 00 − 2, or $3 00 By producing a 45 per cent copper matte from this same raw material, the ratio of concentration becomes 3 to 1, and the cost of converting this matte is $4 00 − 3, or $1 34 per ton of concentrate.

The desired ratio of concentration can be obtained, as already mentioned, by regulating the amount of sulfur in the roasted ore or concentrate. In blast-furnace smelting, the amount of air entering (the blast) affects the amount of sulfur which is removed by oxidation. In any event, *the amount of sulfur available for the matte determines the ratio of concentration and therefore the grade of the matte.* Just how this is accomplished is shown by a study of the action of heat upon various sulfide minerals

Smelting in a Reducing Atmosphere. When the sulfides of copper are heated in a reducing or neutral atmosphere, in which no oxidation takes place, all the sulfur in combination with the copper in excess of that required by the compound Cu_2S will be expelled by volatilization. The resulting cuprous sulfide is rather stable and will fuse without decomposing Thus covellite, or cupric sulfide, CuS, on being heated to a high temperature in the absence of air, will decompose according to the equation

$$2CuS \rightarrow Cu_2S + S$$

yielding molten cuprous sulfide and volatilized sulfur In practice this sulfur is carried away with other gaseous products of combustion until it comes in contact with air, when it is oxidized to SO_2.

In a similar manner, when the sulfides of iron (or solid solutions) are heated in an atmosphere which is not oxidizing, all the sulfur present in excess of that required by the compound FeS will be expelled by volatilization, and the resulting stable ferrous sulfide will fuse without decomposing. Thus pyrite, on being heated to a high temperature in the absence of air, loses one-half of its sulfur according

to the equation

$$FeS_2 \rightarrow FeS + S$$

The more complex associations of copper, iron, and sulfur break down in the same way, resulting in a molten mixture of cuprous and ferrous sulfides, and eliminating superfluous sulfur. As chalcopyrite is an important ore mineral of copper, it may be used as an example. Employing approximate atomic weights, chalcopyrite, $CuFeS_2$, is composed of 35 per cent copper, 35 per cent sulfur, and 30 per cent iron. On heating it decomposes into a mixture of Cu_2S and FeS and loses thereby one-fourth of its sulfur according to the equation

$$2CuFeS_2 \rightarrow \underbrace{Cu_2S + 2FeS}_{\text{matte}} + \underbrace{S}_{\text{volatilizes}}$$

The resulting matte contains about 38 per cent copper, so that in case the pure mineral were smelted under reducing conditions, some concentration would have been effected, although very little

The sulfur volatilized from FeS_2 and other sulfides which contain more sulfur than the stable sulfides is sometimes called "free-atom" sulfur. In reverberatory smelting the removal of this free-atom sulfur often accounts for the bulk of the sulfur volatilized from the charge.

When an ore contains chalcopyrite and a gangue which can be fluxed, a greater ratio of concentration will naturally be obtained, although the grade of the matte will not be greater than 38 per cent copper.

EXAMPLE 1

An ore contains 40 per cent chalcopyrite. On smelting in a reducing atmosphere, what would be

(*a*) The weight of matte produced from 100 pounds of ore?
(*b*) The grade of the matte?
(*c*) The ratio of concentration?

Take 100 pounds of ore

= 40 pounds of chalcopyrite
= 0.35×40 = 14 pounds of copper.

$$\underset{2 \times 184}{2CuFeS_2} = \underset{160}{Cu_2S} + \underset{2 \times 88}{2FeS} + S$$

(*a*) $\frac{336}{368} \times 40 = 36.5$ pounds of matte produced, containing 14 pounds of copper

(*b*) $\dfrac{14 \times 100}{36.5} = 38.3$ per cent copper in the matte.

(*c*) $\dfrac{100 \text{ pounds of ore}}{36.5 \text{ pounds of matte}}$ or $\dfrac{38.3\% \text{ Cu in the matte}}{14\% \text{ Cu in the ore}} = \dfrac{2.74}{1}$

= the ratio of concentration.

When free pyrite is present in an ore, the ferrous sulfide resulting from the decomposition of the pyrite melts with the matte, diluting it and lowering its grade.

EXAMPLE 2

An ore contains 25 per cent chalcopyrite and 25 per cent pyrite. On smelting in a reducing atmosphere, what would be

(*a*) The weight of matte produced?
(*b*) The grade of the matte?
(*c*) The ratio of concentration?

Take 100 pounds of ore

= 25 pounds of chalcopyrite and 25 pounds of pyrite
= 0.35 × 25 = 8.75 pounds of copper

$$\underset{2 \times 184}{2CuFeS_2} = \underset{160}{Cu_2S} + \underset{2 \times 88}{2FeS} + S$$

$\frac{336}{368} \times 25 = 22.8$ pounds of matte from the chalcopyrite.

$$\underset{120}{FeS_2} = \underset{88}{FeS} + S$$

$\frac{88}{120} \times 25 = 18.3$ pounds of FeS to the matte from the pyrite.

(*a*) 22.8 + 18.3 = **41.1** pounds of matte produced, containing 8.75 pounds of copper

(*b*) $\frac{8.75}{41.1} \times 100 =$ **21.3** per cent copper in the matte

(*c*) $\frac{\text{100 pounds of ore}}{\text{41.1 pounds of matte}}$ or $\frac{\text{21.3\% Cu in the matte}}{\text{8.75\% Cu in the ore}} = \frac{\mathbf{2.43}}{\mathbf{1}}$
= ratio of concentration

Ordinarily the analyses of ores are reported in percentages of copper, iron, and sulfur rather than in percentages of the minerals present. In such cases the calculations are made on the basis of the copper uniting with as much sulfur as is required to form the compound Cu_2S; the remaining sulfur then unites with iron to form ferrous sulfide, FeS, and the two sulfides melt together to form the matte. Usually an excess of iron is present, and this, if not already in that form, is converted into the basic oxide FeO which is fluxed by the acid flux SiO_2, forming a ferrous silicate slag. Where a raw sulfide is smelted, some of the sulfur of the pyrite or chalcopyrite will volatilize and will not therefore be available for matte formation. The furnace conditions with respect to the amount of sulfur volatilized must then be known before the grade of the matte can be calculated. Such examples will be cited later on.

EXAMPLE 3

An ore contains 25 per cent copper, 30 per cent sulfur, and sufficient iron for both the matte and the slag Assuming that all the copper and sulfur go into the matte, what would be

(*a*) The weight of matte produced?
(*b*) The grade of the matte?
(*c*) The ratio of concentration?

Calculate the same for this ore when roasted to 16 per cent sulfur and 25 per cent copper

Take 100 pounds of ore

		Raw	Roasted
	Copper in the ore	25	25
	Sulfur in the ore	30	16
	Sulfur to Cu_2S	$\frac{1}{4} \times 25 = 6\frac{1}{4}$	$\frac{1}{4} \times 25 = 6\frac{1}{4}$
	Sulfur to FeS	$30 - 6\frac{1}{4} = 23\frac{3}{4}$	$16 - 6\frac{1}{4} = 9\frac{3}{4}$
	FeS formed	$\frac{88}{32} \times 23\frac{3}{4} = 65\ 31$	$\frac{88}{32} \times 9\frac{3}{4} = 26\ 81$
(*a*)	Weight of matte	$25 + 6\frac{1}{4} + 65\ 31 = \mathbf{96.56}$ pounds	$25 + 6\frac{1}{4} + 26\ 81 = \mathbf{58.06}$ pounds
(*b*)	Grade of matte	$\frac{25}{96\ 56} = \mathbf{25.9}\%$ Cu	$\frac{25}{58\ 06} = \mathbf{43\ 1}\%$ Cu
(*c*)	Ratio of concentration	$\frac{100}{96\ 56}$ or $\frac{25\ 9}{25} = \frac{\mathbf{1.04}}{\mathbf{1}}$	$\frac{100}{58\ 06}$ or $\frac{43\ 1}{25} = \frac{\mathbf{1.72}}{\mathbf{1}}$

The preceding example illustrates nicely how the grade of the matte is regulated by the preliminary roasting operation. It is, of course, not altogether practical to assume that all the sulfur in the raw sulfide ore goes to the matte. Where an oxidized copper ore is mixed with a sulfide ore, some of the volatilized sulfur may serve as a scavenger to recover the copper from the oxidized ore or from the slag.

Effect of Copper Oxides upon the Grade of Matte. Mixing an oxidized copper ore with a sulfide ore produces a higher-grade matte and is the practical equivalent of roasting the sulfide ore.

EXAMPLE 4

A sulfide ore contains 40 per cent chalcopyrite Assuming that one-fourth of the sulfur in the chalcopyrite is driven off and is not available for making matte, how much malachite ore containing 15 per cent copper must be mixed with the sulfide ore in order to produce a 50 per cent copper matte under strongly reducing conditions, such as those prevailing in a blast furnace using a large amount of coke? (Under these conditions the oxygen combined with the copper in the oxidized ore is removed by means of the carbon in the coke A later example will show what takes place when the smelting operation is performed in a neutral atmosphere, such as prevails in the reverberatory furnace.)

Take 100 pounds of ore

= 40 pounds of chalcopyrite,

= $0.35 \times 40 = 14$ pounds of copper, and 14 pounds of sulfur

$14 - \frac{14}{4} = 10.5$ pounds of sulfur available for making matte

A 50 per cent copper matte (from Table 1 or Fig 2) contains 26 14 per cent sulfur

$\frac{10.5}{0.2614} = 40.1$ pounds of a 50 per cent copper matte formed from 10 5 pounds of sulfur

$0.50 \times 40.1 = 20.05$ pounds of copper in the 50 per cent copper matte

$20.05 - 14 = 6.05$ pounds of copper to be supplied by the malachite ore

$\frac{6.05}{0.15} = 40.3$ pounds of the malachite ore to be added to 100 pounds of the sulfide ore in order to produce a 50 per cent copper matte

EXAMPLE 5

An oxidized ore contains 25 per cent copper How much pyrite must be added to produce a 40 per cent copper matte if smelted under reducing conditions? Assume that one-half of the sulfur in the pyrite is volatilized

Take 100 pounds of the oxidized ore

= 25 pounds of copper, which will produce

$\frac{25}{0.40} = 62.5$ pounds of a 40 per cent matte

A 40 per cent copper matte (Table 1) contains 28 18 per cent sulfur

$62.5 \times 0.2818 = 17.6$ pounds of sulfur required

Pyrite, FeS_2, contains 53 33 per cent total sulfur, or under the stated conditions of smelting, 26 67 per cent sulfur available for the matte

$\frac{17.6}{0.2667} = 66$ pounds of pyrite to be added to 100 pounds of the oxidized ore in order to produce a 40 per cent copper matte

Smelting in a Neutral Atmosphere. When an oxidized copper ore is mixed with a sulfide ore, or when copper oxides have been formed by roasting a sulfide ore, the grade of matte produced will vary according to whether the material is smelted under reducing or under neutral conditions In a strongly reducing atmosphere, as in coke blast-furnace smelting, the oxygen with the oxidized copper compounds combines with the carbon of the coke to form carbon monoxide, or with the carbon monoxide to form carbon dioxide. In the reverberatory furnace the atmosphere is generally a neutral one, and under these conditions the oxygen with the copper in the oxidized ore combines with some of the sulfur present, eliminating that element as gaseous sulfur dioxide, according to the chemical reactions

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

and

$$Cu_2S + 2CuO \rightarrow 4Cu + SO_2$$

Eliminating the sulfur in this fashion is again the practical equivalent of roasting, for less sulfur remains to form matte, less matte is therefore produced with the same amount of copper, and as a consequence the matte is higher in copper. In actual practice the copper formed by the above chemical reactions may remain as metallic copper and can be seen as small particles disseminated throughout the matte. Or it may, because of its affinity for sulfur, take that element from the iron sulfide present, and the iron remaining will be oxidized by some other material in the bath and go into the slag. A matte obtained from a given roasted ore, or mixture of sulfide and oxidized ores, may therefore be expected to be higher in copper if smelted in the reverberatory furnace than if smelted under the strongly reducing conditions of the coke blast furnace.

EXAMPLE 6

A roasted copper ore contains 24 per cent copper and 16 per cent sulfur. Of the copper in this roasted ore,

10 per cent exists as $CuSO_4$
5 per cent exists as CuO
10 per cent exists as Cu_2O and
75 per cent exists as Cu_2S

Determine the grade of matte produced from this ore if smelted

(*a*) In the blast furnace
(*b*) In the reverberatory furnace.

(*a*) The determination of the grade of the matte obtained on smelting in the blast furnace, that is, under reducing conditions, is the same as in Example 3.

Take 100 pounds of the roasted ore

Copper in the ore	24	pounds
Sulfur in the ore	16	"
Sulfur to Cu_2S	$\frac{1}{4} \times 24 = 6$	"
Sulfur to FeS	$16 - 6 = 10$	"
FeS formed	$\frac{88}{32} \times 10 = 27.5$	"
Matte formed	$24 + 6 + 27.5 = 57.5$	"
Grade of the matte	$\frac{24}{57.5} = 41.7$ per cent copper, when smelted in the blast furnace.	

(*b*) In the reverberatory furnace, the oxygen with the oxidized copper compounds oxidizes some of the sulfur in the cuprous sulfide The reaction between the copper sulfate and the cuprous sulfide is as follows.

$$\underset{64}{CuSO_4} + Cu_2S \rightarrow 3Cu + \underset{2 \times 32}{2SO_2}$$

from which it can be seen that every 64 parts of copper as $CuSO_4$ eliminate 64 parts of sulfur as SO_2, or one part of copper as sulfate eliminates one part of sulfur as gas.

In the reaction with CuO,

$$\underset{2 \times 64}{2CuO} + Cu_2S \rightarrow 4Cu + \underset{32}{SO_2}$$

or one part of copper as CuO eliminates $\frac{1}{4}$ part of sulfur as SO_2.

In the reaction with Cu_2O,

$$\underset{4 \times 64}{2Cu_2O} + Cu_2S \rightarrow 6Cu + \underset{32}{SO_2}$$

or one part of copper as Cu_2O eliminates $\frac{1}{8}$ part of sulfur as SO_2.

Take 100 pounds of the roasted ore

= 24 pounds of copper,

= 0.10 × 24 = 2.4 pounds of copper as $CuSO_4$, eliminating 2.4 pounds of sulfur;

= 0.05 × 24 = 1.2 pounds of copper as CuO, eliminating 0.3 pound of sulfur;

= 0.10 × 24 = 2.4 pounds of copper as Cu_2O, eliminating 0.3 pound of sulfur.

Of the 16 pounds of the sulfur in the 100 pounds of roasted ore, (2.4 + 0.3 + 0.3) = 3.0 pounds of sulfur is eliminated as SO_2. The determination of the grade of the matte produced is then made as before.

Copper in the ore		24	pounds
Sulfur in the ore		16	"
Sulfur eliminated		3.0	"
Sulfur to matte	16 − 3.0 =	13.0	"
Sulfur to Cu_2S	$\frac{1}{4} \times 24$ =	6	"
Sulfur to FeS	13.0 − 6 =	7.0	"
FeS formed	$\frac{88}{32} \times 7.0$ =	19.25	"
Matte formed	24 + 6 + 19.25 =	49.25	"
Grade of the matte	$\frac{24}{49.25}$ =	48.75	per cent copper, when smelted in the reverberatory furnace.

Objections to Maximum Grade of Matte. In the paragraph on "The Ratio of Concentration," it was shown that the higher the ratio of concentration in smelting, the more economical would be the results with respect to the cost of converting the matte per ton of ore or roasted concentrate smelted. As the ratio of concentration can be regulated by the amount of sulfur left in the ore, and this in turn can be regulated by roasting or by mixing with an oxidized ore, the question naturally arises, why not make the maximum ratio of concentration in smelting and obtain thereby the most economical results? In other words, why not make the highest grade matte possible, even to producing the pure cuprous sulfide containing about 80 per cent copper?

There are four important reasons why the highest grade matte is not desirable.

1. *In order to obtain a relatively high grade matte on smelting a sulfide copper ore, an excessively complete preliminary roast would be necessary.*

EXAMPLE 7

To what sulfur content must an ore containing 8 per cent copper be roasted in order to obtain on smelting a 70 per cent copper matte?

Take 100 pounds of ore

= 8 pounds of copper.

$\frac{8}{0\,70}$ = 11.4 pounds of 70 per cent copper matte.

A 70 per cent copper matte contains about 22 per cent sulfur.

$$0.22 \times 11.4 = 2\,5 \text{ pounds of sulfur}$$

The ore must therefore be roasted to approximately $2\frac{1}{2}$ per cent sulfur. An efficient type of roaster will roast 125 tons of a concentrated copper sulfide ore from 30 per cent sulfur down to 7 per cent sulfur for about 35 cents a ton It would probably cost four times as much to carry the roasting operation from 7 per cent down to $2\frac{1}{2}$ per cent sulfur.

In order to produce a high grade matte, the cost of the necessary roasting operation becomes prohibitive.

2 *In smelting a sulfide copper ore to obtain an unusually high grade matte, the accompanying slag is likewise unusually high in copper.* As has already been shown, in order to produce a high-grade matte, it is necessary to roast the ore to a low sulfur content Copper has a strong affinity for sulfur and a relatively weak affinity for oxygen, so the presence of sulfur prevents the oxidation of the copper. In the oxide form, copper is decidedly basic and is therefore acted upon by the silica present to form a copper silicate. Sulfur is furthermore a scavenger for copper, and will remove that metal from the slag as cuprous sulfide. It is evident that if the ore has been roasted to a low sulfur content in order to produce the required higher-grade matte, there will be less sulfur available to protect the copper from oxidation and to remove the copper from the slag.

Furthermore, as a higher ratio of concentration is necessary in order to produce a higher-grade matte, more tons of raw material will be required to produce 1 ton of matte, and consequently more tons of slag will be made. As this slag will have a greater copper content than one produced simultaneously with a lower-grade matte, the actual loss of copper during the smelting operation will be considerably larger.

EXAMPLE 8

Assume that a slag produced in smelting an ore to a 40 per cent matte contains 0 4 per cent copper, whereas one with a 70 per cent matte contains 0.6 per cent copper. If the original ore contains 10 per cent copper, the production of a 40 per cent matte requires a ratio of concentration of 4 to 1; 4 tons of ore are smelted to 1 ton of matte, producing at the same time about 3 tons of slag containing

0.4 per cent copper, or a total of 24 pounds of copper lost in the slag. For every 4 tons of ore smelted, 24 pounds of copper are lost, representing a loss of 6 pounds per ton of ore. As the ore contained 10 per cent copper, the percentage loss is 3 per cent.

Smelting this same ore to a 70 per cent copper matte requires a ratio of concentration of 7 to 1; 7 tons of ore are smelted to 1 ton of matte, producing at the same time about 6 tons of slag containing 0.6 per cent copper, or a total of 72 pounds of copper lost in the slag. This represents a loss of about 10 pounds of copper per ton of ore (compare with 6 pounds of copper per ton of ore on smelting to a 40 per cent matte), or a percentage loss of about 5 per cent.

3. *Smelting to a high-grade matte means producing a relatively small amount of matte.* In copper smelting, matte is the collector of the gold, silver, and other precious metals, just as lead is the collector in lead smelting and in fire assaying. A small amount of matte may mean an insufficient matte rain to collect all the precious metals. A loss of these may more than offset any advantage gained by smelting to a higher-grade matte.

4. *A high-grade matte is difficult to treat in the converter.* From Table 1 and Figure 2, it is to be seen that a matte high in copper is high in cuprous sulfide and correspondingly low in ferrous sulfide. As will be discussed in greater detail later on, the converting process consists in blowing air through molten matte, oxidizing the ferrous sulfide to SO_2 and FeO, this FeO is fixed immediately by free silica, forming a ferrous silicate slag. The slag is poured off, and the next stage consists in oxidizing the cuprous sulfide to SO_2 and metallic copper. During the converting process the ferrous sulfide acts as a fuel, and if the matte is too low in that constituent, as it is in very high grade mattes, there will not be sufficient fuel present to keep the temperature high enough to carry on the reactions.

The matte produced in copper smelting operations usually ranges between 40 and 50 per cent; a 45 per cent copper matte seems to give most desirable results.

CHAPTER III

ROASTING

The ultimate objective of roasting sulfide copper ores is, as has been indicated in the preceding chapter, to regulate the amount of sulfur in the ore or concentrate in order to obtain, on smelting, a matte which can be treated in the converter efficiently and economically. Roasting, when used, is obviously a preliminary step to smelting, but as a separate and distinct operation may be eliminated altogether under certain conditions.

1. In blast-furnace smelting, for example, it is possible to regulate the amount of sulfur oxidized by proportioning correctly the coke and the blast; from 10 to 90 per cent of the total sulfur may thereby be eliminated. In this process the roasting is actually performed in the blast furnace, simultaneously with the smelting operation.

2. Mixing an oxidized copper ore with the sulfide likewise obviates the necessity of roasting, as has been shown in the preceding chapter.

3. The preparation of the ore by selective flotation concentration may yield a product which, upon simply melting in the reverberatory furnace and eliminating some sulfur by the decomposition of certain sulfides, may result in a matte having the required copper, iron, and sulfur contents.

As the modern trend in copper smelting practice is toward the preliminary preparation of ores and concentrates followed by smelting in the reverberatory furnace, roasting is a generally favored operation.

Definition. Roasting is a pyrometallurgical process and consists simply in heating an ore or concentrate in a certain atmosphere to a high temperature (but below the melting points of the mineral constituents) in order to effect a definite chemical change and usually to eliminate one or more components by volatilization. As distinguished from calcining, which is usually considered to mean the expelling by volatilization of some constituent through *decomposition*, roasting is essentially a process of *combination*. Depending upon whether the combination is with oxygen, sulfur trioxide, or chlorine, the various types of roasting are classified as *oxidizing*, *sulfatizing*, and *chloridizing* roasting. Sulfatizing and chloridizing roasting are important preliminary steps only in hydrometallurgical processes, and will not be

considered here. Although, as we have noted, roasting is fundamentally different from calcining, the roasted product is usually called *calcine* or *calcines*.

Object. The objects of applying an oxidizing roast to sulfide copper ores are

1. To eliminate a portion of the sulfur as SO_2.
2. To eliminate by oxidation and sublimation certain components, such as arsenic, antimony, and bismuth, which may prove detrimental to the subsequent extracting and refining operations.
3. To convert a portion of the iron into the oxide form, in which form it will combine with the silica in the smelting operation and be removed as a constituent of the slag.

In order to attain these objects in a reasonable length of time it is necessary to consider the conditions which favor a rapid and efficient roast.

Theoretical Considerations. In order to obtain a rapid and efficient roasting of sulfide copper ores, four conditions are theoretically essential. These are (1) sufficient surface of the solid material; (2) sufficient oxygen in the roaster atmosphere; (3) sufficient stirring of the charge; (4) proper temperature.

1. *Sufficient Surface* The sulfide particles should be small in diameter in order that the oxygen of the air may come in contact with them. The smaller the size of a particle the greater is its surface in proportion to its volume, and therefore also to its weight; consequently the finer the material is divided the greater will be the surface with which the oxygen may come in contact. A one-pound lump of coal, for example, has a surface area of about ¼ square foot. When this lump has been ground fine enough to pass through a 100-mesh screen, the total surface area of all the particles is considerably over 2000 square feet. The comparative rapidity and efficiency of oxidation of the smaller-sized particles is obvious. Experimentally, the relative roasting efficiencies of large and small particles may be tested by making a screen analysis of the roasted product and then determining the sulfur content of the sized fractions. More sulfur is invariably found in the larger pieces, indicating less efficient oxidation and less complete roasting.

If the finer the sulfide ore particles the more rapid and thorough is the oxidation, the question may arise, why not pulverize the entire charge to the finest degree possible? The objections to such procedure are, among others, the expense of such pulverizing, the production (during roasting and subsequent smelting) of a large amount of flue dust, and the tendency of fine sulfide particles to melt together. If the

material is too fine, it will pack down to a mass which is impervious to air. The fine concentrate produced by the flotation process, passing easily through a 200-mesh screen and containing particles which are even smaller than the hypothetical 800-mesh, may be roasted without difficulty.

The required fineness of the particles depends largely upon the nature of the ore. Some pyrite, for example, decrepitates, and the largest particles may have a diameter of $\frac{3}{16}$ to $\frac{1}{4}$ inch and still roast satisfactorily. Some ores seem to roast more readily than others and may therefore be more coarsely ground and still result in a rapid and efficient roast.

2. *Sufficient Oxygen.* As the roasting of sulfide copper ores preliminary to matte smelting is essentially an oxidizing process, sufficient oxygen must be present to supply the sulfur, iron, and other chemical elements with the required amount. Not only must the required amount be present, but concentration of the oxygen must be high enough to insure rapid roasting. A candle will burn in air containing 20 per cent oxygen; decrease the concentration to 18 per cent oxygen and the candle will go out. A human being cannot continue to exist in an atmosphere containing less than 16 per cent oxygen. The same reasoning applies to the oxidation of sulfide particles; for if the SO_2 in the atmosphere surrounding the ore is more than 4 per cent by volume, the subsequent sulfur elimination becomes markedly slight.

A sufficient amount of oxygen at an adequate concentration is obtained by allowing a current of air to pass over the roasting ore. This current of air not only brings the oxygen in direct contact with the ore particles, but it likewise removes the gases resulting from the oxidation.

Theoretically it is of interest to consider the possibility of having too strong an air current. In the first place, there is a limit to the amount of sulfide exposed per unit of time to the action of the oxygen, and therefore to the amount of heat liberated per unit of time. A large excess of air may absorb so much of this heat that the remainder is not sufficient to keep the roasting ore above the ignition point, and the oxidation of the sulfide minerals, taking place only above a definite temperature, will cease as soon as this temperature is no longer maintained. On the other hand, supposing that the ore particles could be stirred efficiently enough so that contact with the oxygen of the air was possible to any degree of rapidity, then the heat would be generated at such a rate that only a relatively small proportion could be removed by convection and radiation. The temperature of the roasting ore could then rise until the melting point was reached, and the resulting coalescence of the molten sulfide particles would eliminate immediately

that first essential condition to a rapid and efficient roast, namely, sufficient surface.

3. *Sufficient Stirring.* As roasting is largely a surface effect, it is necessary, even when the ore has been crushed to a fine enough degree to provide sufficient surface, to bring new unaltered surfaces in contact with the oxygen of the air. When sulfide minerals are heated without access to air, they either decompose, as in the case of pyrite and chalcopyrite, or simply fuse, if the temperature is high enough. By presenting new hot surfaces to the oxidizing influence of the air, oxidation takes place before the sulfide can melt. The more efficient the stirring operation, the greater will be the capacity of the roasting process.

4. *Proper Temperature.* Before combustion will take place, the ore particles must be heated to a temperature known as the ignition temperature. This temperature varies with the character and size of the sulfide mineral particles, ranging from 325° C for 1 mm pyrite grains to 800° C and more for 2 mm sphalerite grains. Most of the copper sulfide minerals require a dull red heat for ignition. The proper temperature for roasting is not the same throughout the entire operation At the beginning of roasting, when there is a large proportion of easily fusible sulfides present, the temperature must not be so high as to melt the particles, else that first requirement for a rapid and efficient roast, namely, sufficient surface, will no longer be fulfilled If this initial relatively low temperature were maintained throughout the entire roasting period, sulfates of the metals would be formed. This is in agreement with a rule of thermochemistry, which states that " of two or more possible chemical reactions, that one is the more likely to occur which evolves the greater amount of heat." The heat of formation of sulfates is higher than that of the corresponding oxides, so if the temperature is low enough, sulfates will be formed, with the obvious decreased elimination of sulfur. Towards the end of the roasting period it is therefore necessary to maintain a higher temperature than at the beginning, in order to decompose the sulfates which have a tendency to form. Such a decomposition or " desulfatization " temperature is not difficult to attain, being in the neighborhood of 550° C to 600° C, at which temperature the sulfates begin to break up. As the roasting operation is usually carried on in a moving stream of air, the resulting SO_3 is removed rapidly, preventing the building up of an increased partial pressure, under which condition the desulfatization temperature likewise decreases. As most of the easily fusible sulfides have been decomposed and oxidized during the earlier stages of roasting, it is not necessary to hold the temperature to such a low value towards the end of the roasting period.

Self-Roasting Ores. Some ores, when roasting has once been started by bringing them to the ignition temperature, will continue to roast without the aid of any extraneous fuel, simply because the heat produced by their oxidation is sufficient to maintain the reacting ore particles and the air, as well as the various products of combustion, at or above the ignition temperature. Such ores are known as "free-burning" or "self-roasting" ores and are obviously more desirable and more economical than those which require additional fuel.

In order to assist self-roasting in an ore, it is necessary to conserve as efficiently as possible the heat liberated by the oxidation of the sulfide minerals. This heat is removed eventually from the furnace in which the roasting operation is taking place in three major ways. (1) It is removed *through the furnace walls.* The loss of heat, however, is minimized by making the walls thick and by making the exposed area of the walls small as compared to the area of the hearth upon which the ore particles are spread for roasting (2) The losses *in the outgoing gases* are curtailed by a countercurrent system. Cold ore or concentrate is fed into the furnace through the current of hot outgoing gases, absorbing from these hot gases a certain amount of heat. (3) In the same manner losses *in the hot discharged roasted ore* are decreased by bringing the ore in contact with the cold incoming current of air, where it gives up a certain amount of its heat to the air going back into the furnace.

Through efficient design and operation of roasting furnaces, some self-roasting ores may be "dead roasted," that is, roasted down to such a low sulfur content that rabbling reveals a black or "dead" ore surface, instead of the bright red surface of oxidizing sulfides. For matte smelting, however, dead roasting is not desirable, as a definite amount of sulfur is necessary to form the matte.

ROASTING METHODS

Before turning our attention to the types of furnaces used in roasting copper ores and concentrates, let us briefly recapitulate some of the items which are necessary for satisfactory roasting; all these must be considered in the design of a roasting furnace.

1. Roasting is essentially an oxidation of the copper and iron sulfides; the oxidizing agent is oxygen from the air, and provision must be made for an adequate supply of air.

2. No part of the roaster charge ever becomes liquid; both the feed and the calcine are in the form of solid particles. As the reaction can only proceed when the particle surfaces are exposed to the oxidizing

gases, the roasting material must be continually stirred or *rabbled* in order to expose fresh surfaces to the oxygen.

3. The principal gaseous product of roasting is sulfur dioxide, SO_2. Provision must be made to remove this from the roaster atmosphere before its concentration becomes great enough to slow up or reverse the oxidation reactions.

4. The temperature must be maintained high enough to kindle or ignite the sulfides and to keep them above the ignition temperature. However, the temperature must never become high enough to cause fusion of any of the sulfides. Some sulfide ores and concentrates liberate enough heat when roasted to maintain the proper temperature without the use of extraneous fuel. When such *self-roasting* ores are roasted, the process is known as *autogenous roasting*.

5. In roasting solid particles, a current of air sweeps over the material, and there is always a certain amount of dust loss as the finer particles are carried away by the stream of gas. An effort should be made to minimize dust losses in the furnace itself, and provision should be made to recover the dust which escapes from the roasting furnace.

Heap Roasting. The earliest method used for the roasting of copper ores was "heap roasting," in which the ore to be roasted was heaped up on a suitably built pile of cordwood, the pile kindled, and the ore allowed to burn or roast slowly. This was an extremely crude method, and we shall briefly consider some of its outstanding disadvantages; heap roasting in many respects is the antithesis of good roasting practice as we have outlined it in this chapter, and it will be instructive to keep these faults in mind to appreciate how many of them have been overcome in the design of modern roasting furnaces.

1. Although heap roasting could employ cheap and unskilled labor for the handling of material, the construction of the heap required considerable skill and knowledge of the ore, and the roasting heap had to be watched carefully all during the roasting operation to prevent overheating and fusion of the sulfides or to prevent the fire from going out altogether. Large heaps often required 3 or 4 months to roast completely, necessitating large roast yards and careful planning of the firing of the heaps in order to yield a continuous supply of roasted ore for the smelting furnaces.

2. Even under the best conditions, the product from heap roasting was never uniformly roasted, nor did the final product have a uniform sulfur content. Parts of the heap would be dead roasted, other parts would melt down to matte, and still other parts of the heap would contain "green" or unroasted ore. It was not possible to roast an

entire charge to a definite sulfur content, and this is the principal objective in roasting copper ores and concentrates.

3. Building the heaps and tearing them down again after roasting resulted in high labor costs because of the amount of handling required.

4. Because of the high sulfur content and low roasting temperature, heap roasting often resulted in the formation of large amounts of water-soluble copper sulfate. In rainy weather this meant heavy losses of copper as well as the damaging of any of the iron parts of handling equipment exposed to the corrosive copper sulfate solution.

5. In heap roasting (and, later, in stall and kiln roasting) natural draft was used, and there was no way to confine or control the sulfurous gases formed by the burning sulfides. Where heap roasting was practiced on a large scale, these gases would kill all the vegetation within a wide area surrounding the roast yards. This reason alone would be sufficient to prevent the return to heap roasting practice in most localities, even if there were no other objections to it.

6. In roasting a heap of ore it was necessary that the ore contain enough coarse material to permit free circulation of air and gases throughout the mass. The roasting of finely divided flotation concentrate, for example, would be practically impossible with such technique.

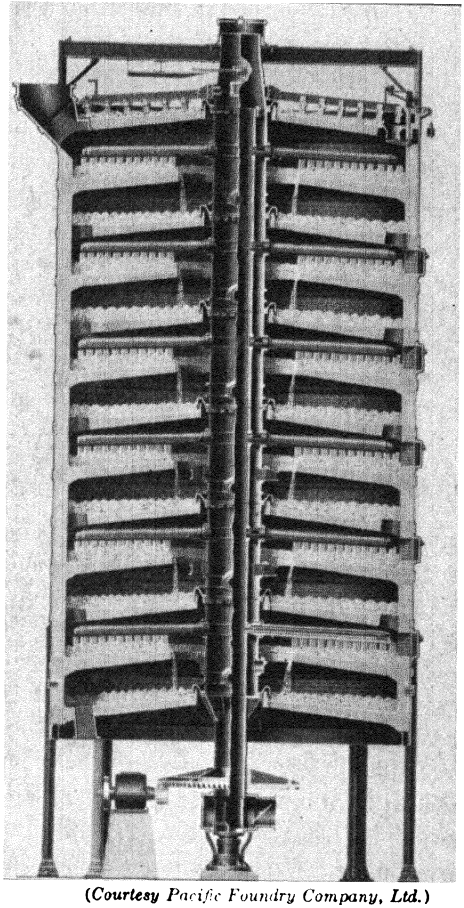
The many disadvantages of heap roasting were recognized from the beginning, and efforts were made to develop better methods of roasting. Stalls and kilns employing natural draft were used first, and although these made the handling problem a little simpler and resulted in a better control of the sulfurous gases, they were still unsatisfactory. What was needed was a continuously operating roasting furnace that would operate as efficiently as possible and permit close control of the sulfur content of the roasted products.

Roasting furnaces eventually developed along two main lines. (1) In furnaces for *hearth roasting* the roasting ore was spread over a hearth in a shallow layer and exposed to the oxidizing gases; the ore on the hearth had to be continually stirred or rabbled to expose fresh surfaces. (2) In furnaces for *blast roasting* the ore was not rabbled, but a blast of air was forced through the mass of roasting ore. A still more recent development is *flash* or *suspension* roasting, which is in some respects an outgrowth of hearth roasting. Flash roasting has not yet been applied commercially to the roasting of copper ores and concentrates, and the use of blast roasting in copper metallurgy is largely confined to the preparation of charges for the copper blast furnace. Hearth roasting in the multiple-hearth furnace is by far the most prevalent method for roasting copper ores and concentrates.

furnace. The furnace shown in this diagram has seven roasting hearths and a drier hearth. The hearths are constructed of refractory brick and are arched slightly. The external portion of the furnace is a brick-lined steel shell fitted with hinged doors and smaller inspection doors on each hearth. The rabble arms are attached to the hollow central shaft, and as the shaft is turned by the driving mechanism at the bottom, the rabble blades set in these arms plow through the material on the hearth, turning it over to expose fresh surfaces to the oxidizing gases. These rabble blades are set at an angle, and in addition to stirring the ore they move it either toward the center of the hearth or towards the periphery. The feed enters the roaster proper through an annular opening in the center of the drier hearth; it passes over the next hearth to discharge through holes on the periphery; it is discharged near the center of the third hearth, and continues alternately in this fashion until it is discharged as finished calcine through holes on the circumference of the bottom hearth. The moist concentrate is fed onto the drier hearth near the outside, and the rabble arms move it across the hearth toward the center; the discharge to the second hearth is luted so that the material forms its own seal and prevents the escape of gas from the interior of the roaster. Roaster gases are drawn off through gas outlets (usually two) located just below the drier hearth. Air circulates through the central shaft, and cold air is circulated through the hollow rabble arms to keep them cool. The air required for roasting is admitted through the central shaft, and by means of valves the air supply to each hearth can be regulated; also the entering air may be either cold or preheated. The central shaft is insulated against heat and gases by a 4-inch wall of special radial tile and a layer of insulating material between the steel shell and the fire wall. This insulation together with the natural current of air through the hollow shaft keeps the temperature low enough so that workmen can enter the shaft without shutting down and cooling the roaster. Rabble arms are fastened to the central shaft by means of special holders and can be locked or released simply by tightening or loosening a single nut inside the shaft.

The design permits constant and accurate control of the material in process at all points. Thermocouples can be installed in the rabble arms to permit the operator to read the temperature on each hearth. Burners (for fuel oil, gas, or pulverized coal) are usually set in the side walls of the furnace to be used when the ore or concentrate does not contain enough sulfur to be self-roasting. The operator can regulate rate of feed, air supply, and temperature in such a way as to obtain the maximum roasting efficiency for the material being treated.

The Nichols Herreshoff Furnace. Figure 2 is a cross-section of the Nichols Herreshoff multiple-hearth roasting furnace. These furnaces are made in various sizes; the diameters range from 6 to 21 feet, and they may contain from 4 to 12 hearths. The rabble arms are fastened to the rotating central shaft which is supported on a step bearing and driven by gears, as shown on the diagram. The central shaft is a vertical cast-iron column constructed in sections. It consists of an inner, cylindrical part or the "cold air tube" and an outer annular part or the "hot air compartment." Cold air is forced in through the cold air tube and passes from here into the hollow rabble arms, thus serving to keep them cool. The heated air coming from the rabble arms enters the hot air compartment, and from here it may be discharged to waste at either the top or bottom of the shaft, or admitted to the hearths as preheated combustion air. All rabble arms are in parallel, and each arm receives its own supply of cooling air directly from the cold air tube.



(*Courtesy Pacific Foundry Company, Ltd.*)

FIG. 2. The Nichols Herreshoff Roasting Furnace.

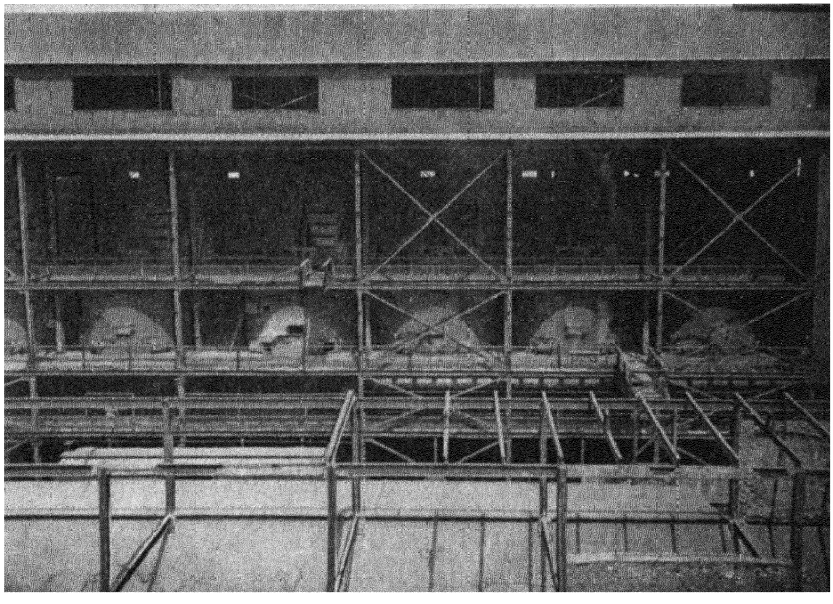
BLAST ROASTING AND SINTERING

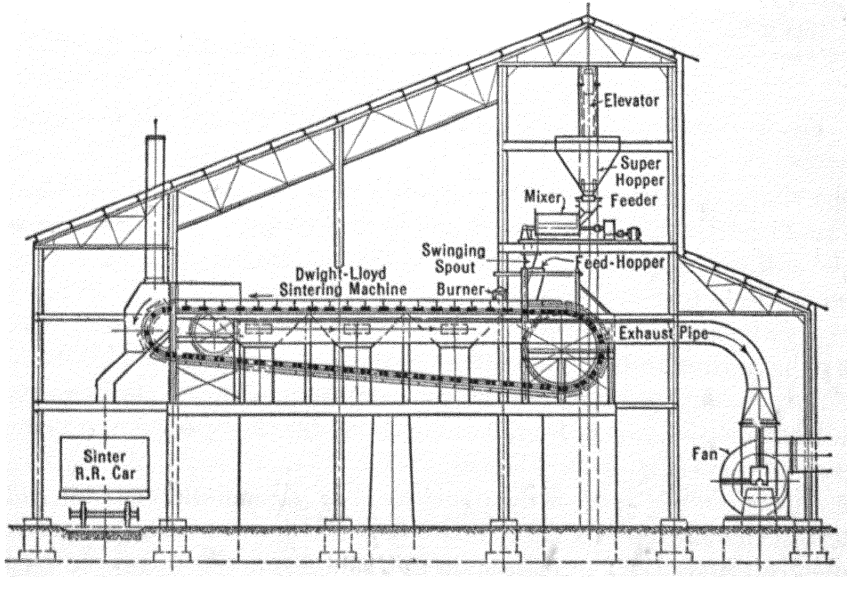
The *Dwight-Lloyd sintering process* is today the most widely used method for blast roasting and sintering. As we have noted, blast roasting is a roasting method in which the charge is held stationary and the air for roasting the particles is forced or drawn through the interstices of the bed of ore or concentrate. The principle of the Dwight-

Lloyd process consists in subjecting a thin bed of fine materials to heat developed by combustion of fuel within the bed while the individual particles are held in a quiescent state. Of course, in roasting sulfide concentrates the sulfides themselves serve as the fuel; if the material to be sintered contains no combustibles, a small amount of coke breeze or other fuel is mixed with the charge *Sintering* refers to a physical change in the material undergoing treatment, in which the finely divided particles are converted to a cellular porous sinter cake; in sintering sulfide concentrates, the process may also give a complete or partial roast depending upon how much of the sulfur is oxidized and removed. Material such as finely divided oxide iron ores may be mixed with coke breeze and sintered, and such an operation would be simply sintering and would not be considered roasting in the sense that the word is used in non-ferrous practice. There is, then, a definite distinction between **sintering** and **roasting;** the first term refers to the physical process of agglomerating fine particles into coarse pieces, and the second term refers to a chemical change brought about by oxidation of the charge (usually meaning the elimination of sulfur by the burning of sulfides).

The Dwight-Lloyd sintering machine (Fig 4) is a structural steel framework supporting a closed track around which travels a series of small grate-bottom cars or pallets for carrying the charge, driving mechanism, suction boxes beneath the upper pallet track section connected to an exhaust fan for drawing air through the bed, a feed hopper, and an igniter for starting combustion of the fuel in the charge. The charge is fed to the mixer, where it is moistened, mixed, and worked up to a fluffy, air-permeable condition; then it passes to the distributing device which delivers it evenly across the full width of the pallets behind the feed hopper. The hopper carries no storage but is a three-sided open-backed leveling plate for maintaining a uniform depth of bed in the pallets and for laying the charge on the grates with the coarser particles on the bottom and the finer ones on top. As the pallet moves from under the feed hopper the charge passes under the igniter at the front end of the suction box. The igniter may be fired with gas, oil, coal, powdered coal, or even wood; its purpose is to project an intense flame on a small area of the upper surface of the bed and kindle the fuel in the charge. After passing the igniter the charge moves across the suction boxes, where sintering takes place, and is finally discharged as finished sinter cake.

Combustion, in the sintering process, proceeds downward through the bed in a relatively thin zone, only a small layer of the charge being at the maximum (sintering) temperature at any given time, as shown

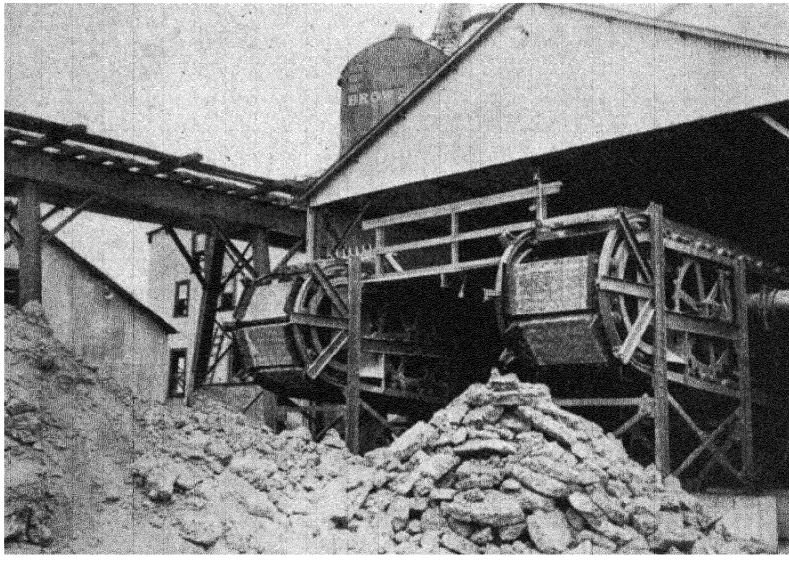




(Courtesy Dwight and Lloyd Sintering Company, Inc.)

Fig. 4. Sectional View of a Dwight-Lloyd Machine.

in Figure 6, a time-temperature curve taken at a point halfway down in the bed of charge. Thus, when the charge on any given pallet is half finished, the sintering zone will be found halfway down in the bed with everything above it finished sinter. In this narrow sintering zone



(Courtesy Dwight and Lloyd Sintering Company, Inc.)

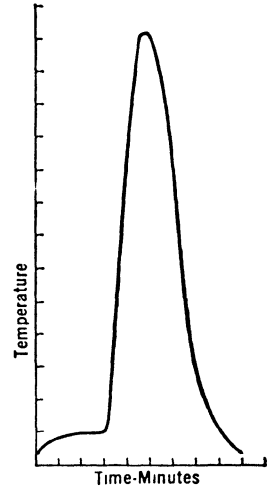
FIG. 5. Discharge End of Dwight-Lloyd Machines Showing Finished Sinter.

the charge particles are semi-fluid as a result of the rapid combustion caused by the air blast, which has been preheated in passing through the still warm sintered zone above. The hot combustion products pass on down, in turn preheating the charge in the zone beneath. While the charge is brought to fusion for an instant in the sintering zone it does not have time to become molten, as the action passes quickly beyond any individual particle and the cold air blast following chills it before it has time to flow together, leaving the sinter in the form of a cellular porous cake (Fig. 5).

The speed of travel of the pallet train is so regulated that the pallet leaves the suction box zone at the moment the charge has been completely sintered. The pallets do not completely fill the space on the tracks, and when a pallet passes around the discharge curve track section it separates from the rest of the line, bumps against the pallet ahead, and jars loose the charge, now transformed into sinter, to discharge the cake into a bin or directly onto a railroad car. The empty

pallet travels back along the lower track section towards the drive sprocket to complete the cycle.

The Dwight-Lloyd process produces a sinter which makes ideal feed for the blast furnace; it is free from fines and dust, strong enough to support the weight of the charge, porous, and hence readily permeable by the gases; and the material is prefused so that it smelts more easily. Blast roasting and sintering are not used in the metallurgy of copper nearly as much as is the multiple-hearth roasting process. Most copper smelting is done in reverberatory furnaces, and the feed for these furnaces is usually either calcine from multiple-hearth roasting furnaces or raw concentrate. When finely divided material is to be smelted in a copper blast furnace, however, the Dwight-Lloyd process is used; in this case the principal purpose of the treatment is the sintering of the charge, and the roasting is merely incidental.



(Courtesy Dwight and Lloyd Sintering Company, Inc.)

FIG. 6. Time-Temperature Curve at a Point near the Center of the Bed on a Dwight-Lloyd Machine.

At the copper-nickel smelter[1] of Falconbridge Nickel Mines, Ltd, near Sudbury, Ontario, the ore and concentrate are smelted to a copper-nickel matte in a blast furnace. Fine ore and flotation concentrate are sintered on two standard 42 by 264 inch Dwight-Lloyd machines. The ore contains considerable quantities of iron sulfides in addition to the copper and nickel sulfides, and the coarse ore suitable for direct smelting contains about 55 per cent sulfides. The feed to the Dwight-Lloyd machines consists of "fines" or ore less than ⅝ inch in diameter containing about 40 per cent sulfides, bulk flotation concentrate obtained by milling the leaner ore, and flue dust. The charge consists of 66 per cent fines, 27 per cent flotation concentrate, and 7 per cent flue dust. The Dwight-Lloyd charge carries about 19.5 per cent sulfur, and this is reduced to 10.5 per cent in the sinter. Each machine requires about 14,000 cubic feet of air per minute, uses 0.4 gallon of oil per ton of sinter in the igniter, and produces on an average 4.35 tons of sinter per hour. Since sulfur forms part of the fuel in the blast furnace, the sulfur loss on sintering is considered a drawback rather than an advantage; this sacrifice must be made, however, to provide the fuel necessary for the sintering action.

[1] Gronningsater, A., Gill, J. R., and Mott, R. C., Metallurgy at Falconbridge: Eng and Min Jour Vol. 135, No. 5, May 1931.

Another example of the use of Dwight-Lloyd machines is the practice employed at the Coniston smelter of the International Nickel Company.[2] Here the process is also used to sinter fine ore previous to blast furnace smelting; resulting sinter plus the coarse ore make up the blast furnace charge. There are six 42 by 396 inch Dwight-Lloyd machines in this installation, and the capacity of each machine is about 250 tons per day. Fuel oil is used to ignite the charge, and the sulfur content is reduced from about 15 per cent to 10 per cent.

FLASH ROASTING

The process of *flash* or *suspension* roasting has not had any commercial application to the roasting of copper concentrates as yet. However, it is possible that it may be used in the future, and as we shall have occasion to refer to flash roasting in the discussion of certain aspects of copper smelting in the next chapter, we shall present here a brief discussion of the principles involved. The description and diagram used for an illustrative example refer to the suspension roasting of zinc sulfide concentrate as practiced at the zinc plant of the Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B. C.[3]

In the ordinary hearth roaster, a large part of the roasting takes place while the particles are dropping from one hearth to the next; each particle is completely surrounded by the oxidizing gases in the furnace atmosphere, and combustion is much more rapid than if the particles were lying on the hearth and exposed to the furnace gases only when turned up by the action of the rabble blades. In the process of suspension roasting, all the roasting is done while the sulfide particles are falling through a stream of oxidizing gas; obviously the method can be used only for roasting finely divided material.

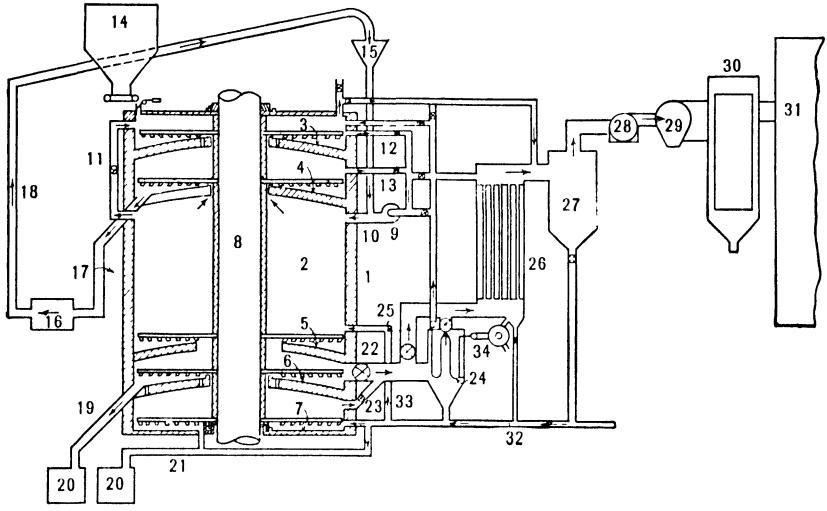
The flash-roasting equipment used at Trail consists essentially of a standard 25-foot diameter Wedge roaster with the central hearths removed to form the combustion chamber; a diagram of the equipment is shown in Figure 7.

The wet concentrate feed enters through the hopper (14) and passes over the drying hearths (3 and 4). The dry material passes through a chute and feeder (17) into a ball mill (16) which is used primarily to break up agglomerations formed in drying. An elevator (18) conveys the dried and disintegrated concentrate to the hopper and feeding device (15). By means of a combustion air fan (9) and burner (10)

[2] Canadian Min Jour., Vol 58, No. 11, p 683, 1937.

[3] Stimmel, B A , Hannay, W. H., and McBean, K. D., The Electrolytic Zinc Plant of the Consolidated Mining and Smelting Company of Canada, Ltd.: Am. Inst. Min & Met. Eng. Trans , Vol. 121, p 540. 1936.

the powdered concentrate is sprayed into the combustion chamber (2) where the burning takes place; the combustion maintains the chamber at a temperature of 1650° to 1750° F. The calcine settles out on the collecting hearths (5 and 6), and after being rabbled across these is



(*Stimmel, et al., Am Inst Min & Met Eng Trans., Vol. 121, p. 542, 1936*)

FIG. 7. Arrangement of Apparatus in Trail Suspension Roasting Process.

discharged as finished calcine (19). If desired the calcine can be diverted to the chamber (7) below hearth (6), and by rabbling in an atmosphere containing large amounts of SO_2 a certain amount of the zinc oxide can be sulfated. The air used for combustion may be preheated if necessary. Eight of these suspension roasters at Trail have replaced 25 standard Wedge furnaces, indicating a three-fold increase in capacity.

CHEMISTRY OF ROASTING

The roasting operation is primarily one of oxidation of solid material by means of oxidizing gases, and some typical chemical reactions are presented below. Pyrite and chalcopyrite tend to decompose on simple heating to yield elemental sulfur and the stable sulfides Cu_2S and FeS.

$$FeS_2 \rightarrow FeS + S \quad (1)$$

$$2CuFeS_2 \rightarrow Cu_2S + 2FeS + S \quad (2)$$

Of course any liberated sulfur would be immediately oxidized to SO_2. However, this decomposition breaks up the solid particles and allows

the oxidizing gases to penetrate the interior. For this reason pyrite, for example, usually roasts more readily than pyrrhotite (Fe_7S_8) which does not decrepitate with the expulsion of elemental sulfur, and hence oxidizes only on the surface. The oxidation of these iron sulfides is of importance because a certain amount of pyrite or pyrrhotite is present in all copper concentrates which are to be roasted. In general it is the burning of the iron sulfides which accounts for most of the sulfur elimination — the copper sulfides tend to remain as such in the calcine. The reactions for the complete oxidation of pyrite and chalcopyrite are:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 \quad (3)$$

$$4CuFeS_2 + 13O_2 \rightarrow 4CuO + 2Fe_2O_3 + 8SO_2 \quad (4)$$

The hot Fe_2O_3 and SiO_2 found in roaster products act as catalyzers to promote the further oxidation of sulfur dioxide:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad (5)$$

and the resultant SO_3 gas reacts with metallic oxides to form sulfates or basic sulfates according to reactions such as these:

$$CuO + SO_3 \rightleftharpoons CuSO_4 \quad (6)$$

$$FeO + SO_3 \rightleftharpoons FeSO_4 \quad (7)$$

$$Fe_2O_3 + 3SO_3 \rightleftharpoons Fe_2(SO_4)_3 \quad (8)$$

$$2CuO + SO_3 \rightleftharpoons CuO{\cdot}CuSO_4 \quad (9)$$

Sulfur must be in the form of SO_2 or SO_3 in order to be eliminated; sulfur contained in sulfates or basic sulfates will remain in the calcine. All reactions in which SO_2 is formed will slow down as the SO_2 content of the atmosphere increases, and if the roaster atmosphere contains more than about 9 per cent SO_2 by volume the roasting practically stops. The equilibrium shown in Equation 5 indicates that the SO_3 content of the gases will increase as the SO_2 content increases; higher SO_3 concentrations mean the formation of larger amounts of sulfates (Equations 6 to 9). Higher temperatures, however, drive the reactions in Equations 6 to 9 to the left and decompose the sulfates.

According to recent research on the reactions and mechanics of roasting, it appears that sulfides do not oxidize directly to oxides and SO_2, but that the primary reactions result in the formation of sulfates; oxides and SO_2 are products of secondary reactions. The following summary is taken from an abstract of a paper presented by Mr. Ash-

croft[4] before the Sixty-Third Meeting of the American Electrochemical Society.

(*a*) Reactions in roasting proceed primarily and definitely to the formation of sulphates, not oxides, the latter as well as the sulphur dioxide evolved, being secondary products, formed by decomposition of the sulphates. Iron oxide acts as an efficient catalyst in the formation of these sulphates.

(*b*) Iron is probably the only element, or at least the only principal element, which, by reason of the great heat of formation of the higher oxide, Fe_2O_3, is completely converted to oxide in a sufficiently oxidizing atmosphere, yielding the undecomposed acid radical to a basic material such as copper oxide or the basic constituents of the gangue.

(*c*) As a corollary to the preceding statement, iron sulphate is not, as generally assumed, *per se* decomposed normally at a temperature so far below the decomposition temperature of copper sulphate that a mere roasting at a carefully regulated temperature may be employed to assure complete conversion into soluble copper and insoluble iron.

(*d*) Formation of cupric ferrite, $CuO{\cdot}Fe_2O_3$, takes place at any temperature above 550° C, when the oxides of copper and iron are brought in juxtaposition; at 700° C, such formation is prohibitively rapid.

(*e*) The ordinary rabbled furnace is inimical to complete conversion into copper sulphate, on account of the following reaction:

$$CuSO_4 + CuS + O_2 \rightarrow 2CuO + 2SO_2 \qquad (10)$$

In well-rabbled charges the reaction begins at a temperature almost as low as that at which the oxidation of sulphur to sulphates starts. It certainly proceeds rapidly at 400° C.

It appears from Mr. Ashcroft's conclusions that the reactions in roasting involve the primary formation of sulfates followed by the decomposition of these sulfates to yield oxides and gaseous oxides of sulfur either because of interaction between sulfates and sulfides as indicated by Equation 10 or by the simple decomposition of these sulfates on heating (Equations 6 to 9). The rabbling of the charge promotes Reaction 10 by bringing sulfide and sulfate particles in contact. The decomposition or formation of sulfates depends upon the *dissociation tension* of the sulfate in question; this is a *pressure* (given in mm of mercury) which measures the tendency of the compound to dissociate; it increases with the temperature. To illustrate the meaning of this let us consider an example. The dissociation tension of $Fe_2(SO_4)_3$ at 553° C, is 23 mm; this means that at 553° C the reaction

$$Fe_2(SO_4)_3 \rightleftharpoons Fe_2O_3 + 3SO_3 \qquad (11)$$

[4] Sulphatizing Roasting: Eng. and Min. Jour., Vol. 134, No. 10, p. 420, 1933.

is at equilibrium if the partial pressure of SO_3 in the atmosphere is 23 mm; if the partial pressure of SO_3 is less than 23 mm the reaction will go to the right and more of the sulfate will decompose; if the partial pressure is greater than 23 mm, the reaction will go to the left and more of the oxide will be sulfated. Table 1 lists the dissociation tensions of copper and ferric sulfates at various temperatures.

The temperature and partial pressure of SO_3 will determine whether or not a given sulfate will decompose, provided that no undecomposed sulfides are left in the roaster charge, if sulfides are present, and the charge is being rabbled, reactions such as 10 will take place and the sulfates will be decomposed even though the temperature may be too low for normal decomposition of the sulfate In this connection, Ashcroft's work[5] shows that if a sulfatizing roast is desired, no movement (rabbling) of the charge must take place as long as unoxidized sulfides are present.

TABLE 1[a]

DISSOCIATION TENSIONS FOR SULFATES

$Fe_2(SO_4)_3 \rightleftharpoons Fe_2O_3 + 3SO_2$		$2CuSO_4 \rightleftharpoons 2CuO\,SO_3 + SO_3$		$2CuO\,SO_3 \rightleftharpoons 2CuO + SO_3$	
Temp °C	mm	Temp °C	mm	Temp °C	mm
553	23	546	43	600	62
570	33	588	55	653	98
592	45	615	70	686	123
614	70	642	98	705	139
634	113	665	130	728	173
650	149	700	233	745	209
660	182	714	324	775	298
680	286	725	460	805	542
690	401	731	647	...	...
699	560		.	...	...
707	715			.	.

[a] Liddell, D M , Handbook of Non-Ferrous Metallurgy, Vol 1, p 341, McGraw-Hill Book Co , New York, 1926.

Roasting of copper concentrates in the multiple-hearth furnace may be characterized by the following items:

1. Although sulfates appear to be the primary products formed, the high temperatures in the furnace and the interaction of sulfates and sulfides cause a decomposition which results in the formation of oxides of the metals and gaseous oxides of sulfur.

[5] Sulphatizing Roasting, op cit , p. 420.

2. The bulk of the sulfur elimination is due to the oxidation of iron sulfides; the copper tends to remain in the sulfide form.

Practically all the concentrate treated in multiple-hearth roasters is subsequently smelted to matte in reverberatory furnaces, and, as we have seen from the examples in Chapter II, the principal factor is the ratio of copper to sulfur, as it is this that determines both the amount and grade of the matte. All the charge is melted down in the smelting furnace, and the compounds of copper, sulfur, and iron react one with another to form the Cu_2S and FeS which make up the matte. If copper sulfate is present (Example 6, Chapter II), the interaction of sulfates and sulfides cause the elimination of some sulfur as SO_2, but with this exception, the actual distribution of sulfur, copper, and iron in the compounds which make up the calcine is not of great importance as far as the smelting operation is concerned. We have also noted that the amount of sulfate present in the ordinary calcine is quite small.

In recent years, however, there has been considerable interest in the problem of developing a technique for roasting and then leaching copper concentrates in a process similar to that used for producing zinc from zinc concentrates. Although the process has not yet been commercially adopted, it will warrant our consideration for a brief space.

The principal problem in the preparation of copper concentrate for leaching is to find a preliminary treatment which will put the copper in a soluble form but still leave the bulk of the iron in such condition that it is insoluble in the solvent used, here the actual distribution of copper, iron, and sulfur in the compounds which make up the calcine is of paramount importance. The methods which have been investigated aim to do this by (1) sulfating as much of the copper as possible to form the water-soluble $CuSO_4$ and (2) oxidizing as much of the iron as possible to Fe_2O_3, which is insoluble in water and in dilute sulfuric acid; if some copper remains as an oxide it can be leached with dilute acid. Ashcroft's[6] investigation was essentially for the purpose of determining if the requisite conditions could be attained by a controlled roast. We have already noted some of the facts which he has listed, and it appears that two of the conditions necessary for such a roast are:

1. Preliminary roasting without rabbling to completely oxidize all free sulfides and form sulfates.

2. A finishing roast in a rabbled apparatus at the proper temperature to decompose the sulfates of iron, but leave the copper sulfate unchanged.

[6] Sulphatizing Roasting, op. cit., p. 420.

In addition to these items, there are a number of other factors of importance which we shall not discuss in detail; for example the formation of copper ferrites must be avoided. These are insoluble in dilute acid, and would result in copper losses on leaching. The presence of ferrites in a calcine which is to be smelted, however, is not of great importance because these compounds decompose readily in the smelting furnace.

Another method for the differential sulfating of copper which has been investigated is the process of baking a previously roasted concentrate with sulfuric acid. The preroasted calcine is mixed with the proper amount of sulfuric acid and then baked at the proper temperature to cause the maximum formation of copper sulfate.[7]

The two principal objects which would be attained by a successful technique for preparing concentrates and then leaching them, are: (1) the purified leach solution (copper sulfate solution) could be electrolyzed and the process would produce highly purified electrolytic copper directly and (2) such a treatment might well be less expensive than smelting followed by converting, fire refining, and electrolytic refining. On the other hand, in addition to the difficulties inherent in the process itself, the recovery of precious metals found in copper concentrates must be considered. The matte formed in smelting is an excellent collector for precious metals, and these remain with the copper until separated by electrolytic refining. A sulfuric acid leach, however, would not remove the precious metals, and if leaching methods are ever to compete with smelting for the treatment of copper concentrate, there will have to be a parallel development of a suitable process for recovering the precious metals in the leach residue.

In addition to the removal of sulfur from the roaster charge, arsenic and antimony are removed to some extent. Arsenides and antimonides found in the roaster feed are oxidized. The lower oxides As_2O_3 and Sb_2O_3 are quite volatile and pass off with the roaster gases. In an oxidizing atmosphere, however, much of the arsenic and antimony will oxidize to the higher oxides As_2O_5 and Sb_2O_5, which are less volatile and form stable, non-volatile arsenates and antimonates with other metallic oxides. Usually it is necessary to alternate oxidation and reduction several times to completely remove arsenic and antimony, and in ordinary roasting operations only a part of these elements will be

[7] Floe C. F., and Hayward, C. R., Differential Production of Soluble Sulfates from Mixtures of Metallic Oxides: Am. Inst. Min & Met. Eng Tech. Pub. 735, 1936; Floe, C. F., Extraction of Copper from Roasted Concentrates by Sulphuric Acid Baking Idem, Tech Pub. 768, 1937.

volatilized, the exact amount depending upon the nature of the atmosphere within the roaster.

SOME EXAMPLES OF ROASTING PRACTICE

Copper Cliff.[8] At the Copper Cliff smelter of the International Nickel Company, the feed to the roasters is a nickel-copper concentrate containing considerable amounts of iron sulfides. The plant contains 30 Nichols Herreshoff roasters, which are located in two rows over the burner end of the reverberatory furnaces, with six roasters for each reverberatory furnace.

Each roaster has a top drier hearth and 10 interior hearths; the height of the roasters is 31 feet 8 inches, and the outside diameter is 21 feet 6 inches. The roaster shell is ½-inch plate lined with 9-inch firebrick and strengthened at each hearth with 8- by ⅝-inch steel bands. The hearths are constructed of high-alumina firebrick. There are two rabble arms for each roasting hearth, and these are attached to the central shaft by a single pin; the arms can be easily removed through the furnace doors. All rabble arms on the ten interior hearths and the central shaft are air cooled; this cooling air may be allowed to escape into the furnace to provide air for combustion, or it may be conducted to the outside air from the top of the shaft. The rabble blades on the interior hearths are of white cast iron, and the blades for the drier hearth are of mild steel. The shaft rests on a step bearing and is operated by a 25-horsepower motor. The shaft is usually operated at a speed of 2 rpm, but a two-speed step pulley permits operation at 0.5 rpm when this is desired.

The maximum charge to each furnace is 275 tons per day, and the sulfur content is reduced from 28 per cent to 16 per cent. Oil heating is used only at times when the operation of the roasters has been interrupted; when operating normally the combustion of the sulfides supplies all the necessary heat.

Noranda.[9] At the Noranda smelter, eight seven-hearth Wedge roasters are used to serve two reverberatory smelting furnaces. These roasters were originally designed to handle 100 tons of charge per day each, but by stepping up the speed of rotation from 0.75 rpm to 1.09 rpm the capacity of each furnace was increased to a maximum of 325 tons per day; at this speed the sulfur content is reduced from 25 per cent in the feed to about 11 or 12 per cent in the calcine.

The material roasted averages about 65 per cent smelting ore, 19

[8] Canadian Min Jour., Vol 58, No 11, p. 673, 1937.

[9] Boggs, W. B , and Anderson, J N., The Noranda Smelter: Am. Inst. Min. & Met. Eng Trans., Vol. 106, p 183, 1933.

per cent fluxing ore, and only about 16 per cent concentrates; the copper content of the roaster feed is comparatively low, ranging from 3.5 to 5 per cent copper. This charge is not self-roasting, so 5 to 10 pounds of pulverized coal must be burned for each ton of calcine produced. The smelting ore, which makes up most of the roaster charge, is massive sulfide ore containing chalcopyrite, pyrite, and pyrrhotite; it is simply crushed and is not ground fine as is the concentrate. The fluxing ore is an acid flow rock mineralized with sulfides, and the concentrate consists almost entirely of chalcopyrite and pyrite. The relatively coarse size of the particles of crushed ore and the fact that a large quantity of pyrrhotite (which does not decrepitate as does pyrite) is present tend to make the charge rather difficult to roast. The high sulfur and low copper content of the calcines means that the smelting of this calcine yields a low-grade matte (18 to 24 per cent copper), as the amount of sulfur eliminated in the reverberatory furnace by the interaction of sulfides and oxides (see Example 6, Chapter II) is not great. It is of interest to briefly consider some of the factors that are responsible for this particular roasting practice.

1. The temperature of the calcine formed in a "dead" roast is always lower than the temperature of a "green" (incompletely) roasted calcine. This means that the dead roasted calcine would carry less sensible heat into the reverberatory, and more fuel would be needed for smelting.

2. Roasting of high-iron ores and concentrates produces quantities of Fe_3O_4 and Fe_2O_3 in the calcines; these oxides must be reduced to FeO in the smelting furnace before they can unite with the silica to form a slag. The most important reactions for the reduction of these oxides are:

$$3Fe_2O_3 + FeS \rightarrow 7FeO + SO_2$$

$$3Fe_3O_4 + FeS \rightarrow 10FeO + SO_2$$

If, therefore, the calcine is roasted to a low sulfur content, there is not sufficient sulfur left (as FeS) to reduce the higher oxides of iron, and as a result a low-sulfur calcine is more refractory toward smelting than a calcine containing more sulfur. Note that these reactions cause the elimination of a certain amount of sulfur from the reverberatory charge.

3. At this plant the production of a low-grade matte means that more of the fluxing ore is needed in the converters, and the practice is controlled so as to keep the converters operating at full capacity. Thus the total smelting capacity of the plant is actually increased

because of the additional amount of the fluxing ore which is consumed by the converters.

Anaconda.[10] There are 14 seven-hearth roasting furnaces of the Anaconda McDougal-Wedge type, 25 feet in diameter, in the smelter at Anaconda, Montana. These each treat about 200 tons per day of a concentrate containing about 25 per cent copper and 32 per cent sulfur, bringing the sulfur content of the calcine down to about 18 per cent. Small quantities of oil are used when necessary, but as a rule these concentrates are self-roasting

It is interesting to compare these figures with those previous to 1927. Up to this time the roasters had a feed containing about 12 per cent copper and 36 per cent sulfur, and it was necessary to roast to about 8 per cent sulfur in the calcine to produce the desired grade of matte. In 1927 the practice in the mill was changed so that the concentrate delivered to the roasters assayed about twice as much copper. This meant (1) that the tonnage of roaster feed was cut in half, (2) that the sulfur content of the feed was lower, and (3) that because of the higher copper content it was not necessary to roast to as low a sulfur content to get the same grade of matte. Previous to 1927, a single roaster would handle about 40 tons of charge per day, as compared with 200 tons after roasting was started on the new concentrate.

Andes.[11] The Andes plant includes a copper smelter for the treatment of sulfide concentrates and a leaching plant for low-grade oxidized ore. The sulfuric acid for the leaching plant is supplied from an acid plant which makes acid from the sulfurous gases obtained by roasting the sulfide concentrates There are two separate roasting plants — the sulfide roaster plant and the acid-plant roasters. The concentrate to be roasted for acid-making must be high in sulfur and low in arsenic; consequently the mill produces two grades of concentrate — one low in arsenic and high in sulfur and another which contains the remainder of the copper and arsenic. This second concentrate is high enough in copper to be smelted directly after drying.

The sulfide roasting plant contains seven Wedge roasters, each 22 feet in diameter with seven roasting hearths and a drier hearth. Oil burners are used on the third, fifth, and seventh hearths; the oil is burned in firebrick muffles or combustion chambers set into one of the inspection doors on each of these hearths. These muffles are 2 feet long and have an opening 8 inches square. The roaster shaft makes

[10] Bender, L. V., Development of Copper Smelting at Anaconda Eng and Min. Jour , Vol. 128, No. 8, p 301, 1929.

[11] Callaway, L A and Koepel, F N , Metallurgical Plant of Andes Copper Mining Co.: Am. Inst. Min. & Met Eng Trans., Vol. 106, p 683, 1933.

0.75 rpm and the tonnage per roaster day ranges from 90 to 160 tons, depending upon the moisture content of the feed and product.

While these roasters may be used for actual roasting they are usually used only as driers for both types of concentrate. The high-copper concentrate and flux is dried to about 3 5 per cent moisture and then goes directly to the reverberatory; the high-sulfur concentrate is dried to below 1 per cent moisture, and it then goes to the acid-plant roasters. Fuel used for this drying ranges from 0.04 to 0.08 barrel of oil per ton of charge.

There are seven Wedge roasters in the acid plant similar to those used in the sulfide roasting plant. The feed to these roasters is the dried concentrate from the sulfide roasters. The calcine goes to the reverberatory furnaces, and the gases are cleaned and conveyed to the Glover towers of the acid plant.

Flin Flon.[12] Three Nichols Herreshoff roasting furnaces are employed at the Flin Flon smelter of the Hudson Bay Mining and Smelting Company, Ltd., Flin Flon, Manitoba. Each roaster is 21 feet 6 inches in diameter and 30 feet 3 inches high, outside dimensions, and contains 10 interior hearths and 1 drier hearth. The central column and rabble arms are air cooled, and the column turns at 2 rpm. Each roaster has a pulverized coal burner on the eighth hearth and an auxiliary burner on the fourth hearth; the auxiliary burner is used when the moisture content of the charge is higher than average. Additional heat is provided by electrically heating the combustion air which enters the bottom hearth of each furnace. This method is economically possible because of an adequate supply of cheap power. Each furnace has its own preheater which contains 18 ribbon heating elements over which the air is blown by a fan; the heated air passes into the roaster at 180° to 200° C. These preheaters operate at 600 volts and have a rating of about 660 kw.

The feed to the roasters consists principally of moist flotation concentrate (15 per cent moisture on an average) plus smaller amounts of direct smelting ore and flux. The copper content of the roaster feed is about 7.35 per cent, iron 28.9 per cent, and sulfur 28.7 per cent. Sulfur is reduced to about 13 per cent in the calcine. The roasters can handle a maximum of 360 tons of charge per roaster day and consume 7 4 pounds of coal per ton of charge roasted — less than half the amount of coal used before the air preheaters were installed.

[12]Ambrose, J. H., Flin Flon Copper Smelter: Canadian Min. Met. Bull. 281, September 1935.

SUMMARY

The most important type of roasting in the metallurgy of copper is the roasting of sulfide concentrates in multiple-hearth roasters, the calcine from which goes directly to reverberatory smelting furnaces. The primary purpose of roasting is to reduce the sulfur content to give the proper grade of matte when the calcine is smelted. The sensible heat in the calcine is utilized in the reverberatory furnace, and this reduces the amount of fuel required for smelting.

As may be noted from the examples we have cited, the details of roasting practice vary considerably with the nature of the material to be roasted. Smelters treating high-grade copper concentrate may use the roasters simply for drying, or may dispense altogether with the roasting operation and send the cold, wet concentrate directly to the smelting furnace.

Blast roasting and sintering are used to prepare sulfide ores and concentrates for blast furnace smelting; this method is not nearly as important as hearth roasting, however, because only a relatively small amount of copper-bearing material is smelted in blast furnaces. Some experimental work has been done on the flash roasting of copper concentrates, but no commercial application has been made as yet. Studies have also been made of methods of using controlled roasts to render copper concentrates amenable to water or acid leaching.

We have not considered in this chapter the gases produced in the roasting operation, the dust losses, nor the methods used in recovering the dust and treating the gases. After we have discussed smelting, converting, and refining we shall devote a separate chapter to a consideration of the gases and smokes produced in the pyrometallurgy of copper.

CHAPTER IV

SMELTING

INTRODUCTION

Copper smelting is a pyrometallurgical process in which solid material is melted and subjected to certain chemical changes. Products of a smelting furnace are liquids (slag, matte, metal, etc.), gases, and solid material carried out in the gas stream (dust and fume) The copper-bearing material to be smelted may be (1) ore, (2) calcines, (3) sinter, or (4) raw (unroasted) concentrates. Suitable *fluxes* are charged with the copper-bearing material to form a slag; the nature of the fluxes will be determined by the impurities in the charge. They may be either barren fluxes or revenue-bearing materials (copper ores, gold ores). Fuel used in blast furnaces is coke, and this coke is mixed with the rest of the charge; reverberatory smelting furnaces are fired with such fuels as oil, fuel gas, or pulverized coal.

The copper may be tapped from the smelting furnace either as matte or as crude metallic copper; the smelting furnace may be either a reverberatory furnace or a blast furnace In modern practice, by far the most important type of copper smelting is the smelting of either calcines or raw concentrates to copper matte in reverberatory furnaces, but there are other types of copper smelting which we shall consider also, viz.:

1. Matte smelting in the blast furnace.
2. Electric smelting for matte.
3. Smelting of native copper concentrates in the reverberatory to produce metallic copper.
4. Smelting of high-grade oxidized material to produce a crude metallic copper (" black copper ").

REVERBERATORY MATTE SMELTING

A reverberatory furnace is a long shallow furnace consisting of a *hearth* or *laboratory*, side and end walls, and a roof. The furnace is heated by means of burners placed in one end wall, and the products of combustion escape at the other end. A long-flame fuel is used — gas, fuel oil, or pulverized coal — and the flame extends over a large

part of the hearth. The material on the hearth is heated by radiation from the flame. The reverberatory is essentially a melting furnace, and there is ordinarily no extensive reaction between the gases in the furnace atmosphere and the charge on the hearth; it is possible to get some oxidation of the charge by using a large excess of air for the combustion, but this is wasteful of heat and is seldom practiced. As a rule the principal chemical reactions that take place in the charge of a reverberatory furnace are reactions between various constituents of the charge itself; we have already noted some of these in Chapter II.

Before presenting a description of the modern copper reverberatory it will be profitable to give brief consideration to the history and development of the reverberatory copper smelting furnace in the United States. Much of the material given here is taken from an article by Frederick Laist[1] dealing with the development of the reverberatory furnace at Butte and Anaconda.

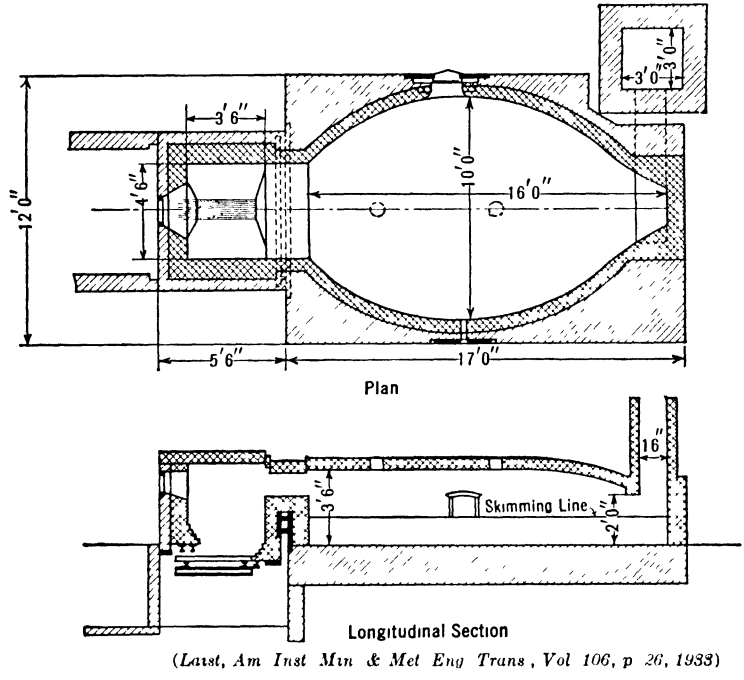
Development of Reverberatory Smelting. In the early days of copper smelting in the United States, reverberatory smelting was practiced at Butte and Anaconda, Montana, almost from the beginning of the exploitation of the copper deposits of the district. Reverberatory furnaces were used in other parts of the country as well, in fact were used in Colorado some 30 years before the first furnace was constructed in Montana. It was in the Montana district, however, that the most intensive study of reverberatory smelting was made, and many of the improvements discovered there were instrumental in establishing the superiority of the reverberatory furnace over the blast furnace in the smelting of copper sulfide ores and concentrates.

The first reverberatory furnace in the State of Montana was built at Butte in 1879 at the plant of the Colorado Smelting and Mining Company. This furnace had a hearth 14 feet long by 9 feet wide and used wood as fuel. It smelted about 10 tons of ore per 24 hours and produced a matte assaying 60 per cent copper and from 700 to 800 ounces of silver per ton. This matte was then hauled 200 miles to a railroad and shipped abroad This furnace and others built in the period 1879–1890 were similar to those used in Wales, which was up to then the world's foremost center of copper smelting and refining; similar furnaces had been operated in Wales for at least 100 years previous to this time.

Figure 1 is a plan and section of a wood-burning matte furnace of the early 80's. These furnaces were fired by means of a firebox; the flame was drawn over the bridge wall between the firebox and the hearth,

[1] Laist, Frederick, History of Reverberatory Smelting in Montana, 1879 to 1933: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 23, 1933.

and the products of combustion passed out the stack at the opposite end of the furnace. Roasting the copper ores was done in wood-fired hand-rabbled reverberatory roasters, and the calcine was cooled by quenching it in water; the calcine going to the reverberatories usually



(*Last, Am Inst Min & Met Eng Trans, Vol 106, p 26, 1933*)

FIG. 1. Wood-Burning Matte Furnace of the Early Eighties.

contained about 10 per cent moisture About 3 tons of the wet calcine would be shoveled by hand into the furnace through the side doors, and after this had been melted down the slag would be skimmed, cast into slabs in sand beds, and then wheeled to the dump on barrows. After every third charge the matte was tapped into sand molds, cooled, sacked, and shipped abroad. The inside of the empty furnace was then examined, and wet crushed quartz was shoveled onto corroded portions of the hearth; the furnace was then ready for another cycle. The fuel used (wood or coal) was also loaded or shoveled into the fireboxes by hand.

The external shape of these early furnaces was rectangular, but the hearth itself was oval. Side walls were constructed of firebrick, and these walls supported the arched roof; the walls were lined with another layer of firebrick which could be replaced without disturbing the roof. The furnace was strongly braced by means of external steel I-beam

buckstaves and tierods. The bridge wall between the firebox and hearth was built around a hollow steel "conkerplate" through which air was circulated; this served the double purpose of strengthening the bridge wall and cooling it. The roof arch was made of silica brick, and it sloped rather steeply toward the front of the furnace; at this end the roof was usually only 12 to 14 inches above the level of the skimming plate.

The hearth was constructed of quartz or sand containing about 97 per cent silica; sometimes 3 or 4 per cent of crushed slag would be mixed with it to help sinter it into shape. After a new bottom had been placed in a furnace, the doors were closed and the furnace fired slowly until the maximum temperature was reached and then maintained thus for several hours. The furnace was then allowed to cool, crushed slag was spread over the surface, fused, and absorbed by the porous sand bottom. A second similar fusion completed the saturation of the lower hearth, and then more sand was thrown in to form the second hearth; this was saturated with slag and smelted in in much the same way as the bottom hearth It was essential that the hearth be prepared very carefully to give a solid monolithic mass; improperly prepared hearths would break up, and pieces would float to the top of the bath of matte during the regular smelting After the hearth was completed, the furnace was *fettled*, and was then ready for its regular work. Sand or crushed quartz was heaped up along the side walls of the furnace to protect the bricks in the side wall from corrosion by the slag, and this process was known as *fettling;* the term *fettling* is also applied to the material used for this purpose.

As far as principles are concerned, there is little or no difference between the methods used for smelting matte today, and those which were practiced in 1880 and 1890. The furnaces, however, have changed radically in the course of half a century; the capacity of the furnaces has increased fiftyfold, the heat required to smelt a ton of charge has decreased to about one-third of what it was originally, and the amount of necessary labor has been enormously reduced. Before turning our attention to the improvements which led to the modern furnaces, let us briefly summarize a few of the characteristics of these early furnaces.

1. The early furnaces were built over an open space, through which air was circulated to keep the hearth cool. It was believed that this was necessary to the satisfactory operation of the furnace. On this point Laist[2] states

[2] Laist, Frederick, op. cit , p. 34.

It is difficult to understand why that part of a reverberatory which is hardest to keep hot should have been deliberately cooled, but such had been the custom for generations and ideas firmly rooted in the past die hard. It is to the credit of the Montana metallurgists that they recognized the anomaly and had sufficient enterprise to break away from it. Gradually the modern practice of constructing the furnaces on a solid foundation became universal.

2. Charging was done by hand; matte and slag were tapped, cast, and transported by hand labor; and the firebox was fired by hand. These operations definitely limited the size of the furnace and contributed heavily to operating costs.

3. The hearths of the furnace were oval in shape, and the roof sloped sharply downward near the front (flue end or " verb ") of the furnace. It was believed that this shape was essential to proper operation of the furnace, but it was later shown that this was not an important factor.

4. Calcines were usually quenched in water and charged into the furnace wet. This not only dissipated the sensible heat in the hot calcines but made it necessary for the reverberatory to evaporate considerable water.

5 The smelting process was essentially a batch operation; charges were added and smelted down, and after a sufficient amount of matte had collected (say after three charges), the slag was skimmed and all the matte was tapped out. It was believed that matte was harmful to the hearth and that the matte must all be tapped out at frequent intervals, the hearth patched up, and the furnace fettled.

6. The charge was ordinarily high in copper and readily fusible; the *matte fall* was heavy, being 25 to 30 per cent of the total weight of the charges. The matte ordinarily contained from 50 to 65 per cent copper and considerable silver. These items permitted the use of technique which would be prohibitively expensive in smelting leaner and more refractory material.

7. It was at first believed essential that each reverberatory furnace have its own stack; later this was found unnecessary, and it became common practice to connect several furnaces to a common stack by means of a system of flues.

One of the first changes to be made in reverberatory smelting furnaces was to increase their size. It was evident that it would be more economical to operate a single large furnace than several small ones if the same amount of material could be smelted, and for a long period of time the size of the furnaces steadily increased. The length increased more rapidly than the width, because the width was limited

by the fact that the arched roof would not support itself over too wide a span. As the size of the furnaces increased, charging, tapping, and handling of material became more difficult, so that other innovations in furnace design and practice became necessary.

Another factor that was of great importance was the ratio of the area of the grate in the firebox (which determined the rate at which fuel could be burned) to the area of the hearth. The firebox was lined with firebrick, and the grate was usually ordinary iron rods about an inch square; a pit was provided below the grate for the removal of ashes. In the small furnaces which were in use in 1880, the hearths measured about 10 by 15 feet and the fireboxes 4 by 5 feet, giving a ratio of approximately 1 to 5 for the areas. At first, the tendency was to increase the hearth area more rapidly than the grate area on the theory that a better utilization of heat would be obtained and that less coal would be used per ton smelted. Accordingly, the 35- by 14-foot furnaces of a later date had 5- by 8-foot fireboxes giving a ratio of 1 to 9, and the longer furnaces which followed had a ratio of 1 to 18. In these latter furnaces, however, most of the smelting was done in about one-third of the hearth.

In this connection it will be well to consider briefly what is meant by the *capacity* or *smelting power* of a furnace; obviously this quantity is measured by the tonnage of charge smelted per day, but there are several factors which determine this. The reverberatory copper matting furnace has two simple functions: (1) to melt down the charge and form liquid matte and slag at a temperature high enough to insure free-running slag, and (2) to provide sufficient space for these liquids to collect so that they have time and opportunity to separate cleanly into two layers and be tapped out of the furnace separately. The furnace should accomplish these two tasks with the consumption of the minimum amount of fuel.

Size alone does not determine the smelting capacity of a furnace, nor does the amount of fuel burned. If the size is increased more material can be charged into the furnace, but unless the amount of fuel burned is increased, there will be little or no increase in smelting power. Consequently as furnaces become larger they must be equipped to burn larger amounts of fuel per unit of time; if the fuel consumption is insufficient, part of the interior volume of the large furnace is simply wasted space. The flame temperature is also of importance, because the heat for smelting must come from the gaseous products of combustion, and these can transmit their heat to the furnace charge only if they are hotter than the charge. Suppose, for example, that the furnace slag had to be discharged at 1000° C; if the flame temperature

were only 100° above this figure, only a small portion of the total heat of combustion would be available for smelting, and a large excess of fuel would be consumed. The maximum temperature attainable with a given fuel requires that exactly the theoretical amount of air be used for combustion; if too little air is used, part of the fuel is unoxidized and its heating value is lost; if too much air is used, the excess dilutes the products of combustion and lowers the flame temperature.

In 1890, a number of reverberatories 27 feet long were installed at Anaconda, and, for the first time, were fed with hot calcine direct from the roaster bins by means of feed hoppers set in the roof of the furnace. This was more efficient than the feeding of wet calcine, which had been the previous practice.

Another important improvement in operating technique was the maintenance of a large pool of matte in the furnace at all times The old idea that the furnace must be emptied, repaired, and fettled at frequent intervals went into the discard when it was found that the matte was not injurious to the hearth, as had been thought, but actually served to protect it. Therefore it became the practice to tap only part of the matte and slag at a time and to leave a pool of matte in the furnace at all times. This matte layer was from 12 to 24 inches deep and covered the entire hearth from one end to the other. This new technique had many very important effects on furnace operation.

1. By skimming only part of the slag, tapping only part of the matte, and feeding the calcine in small amounts, the temperature of the furnace could be maintained more nearly constant at all times, and smelting became a *continuous* rather than a *batch* process.

2. When high-grade matte was being made for shipping, it was not essential that the matte be tapped at any particular time. However, when the smelters began to install converters to treat their own matte, it was necessary that a supply of hot liquid matte be available at all times to supply the converters. The pool of matte in the reverberatory served as a storage reservoir from which matte could be drawn as needed by the converters.

3 The molten, semi-metallic bath of matte was a good conductor of heat, and aided in conducting heat to the hearth; this made it easier to keep the hearth hot than when it was covered with a thick layer of a poorly conducting solid charge.

4. Hot calcines from which SO_2 gas is still evolving will flow like water. When these calcines were charged onto the heavy liquid layer of matte, they would flow over the top of the liquid, and the charge would level itself off. The old practice of leveling the charge by means of hand-operated rabbles and spades thrust through the side doors of

the furnace was abandoned, and the time and heat losses caused by hand leveling were no longer important. The furnaces could now be built with fewer doors and openings, and the air leakage and heat losses diminished; also the size of the furnaces could be further increased because they no longer depended upon the limitations of man power as a controlling factor.

5 Fettling was done at longer intervals — sometimes only once a month.

6. The deep bath was particularly important when grate firing was still used. It was necessary to grate the fires at 4-hour intervals, and during this period most of the evolution of heat stopped and the laboratory of the furnace cooled off considerably. The heat stored in the bath helped to maintain its temperature even though the space over the hearth became much cooler for a short time.

7. The principal disadvantage to the "deep-bath" smelting technique was the danger of a break-out in the furnace, the matte pool in a large furnace would weigh some 150 tons, and this could cause considerable damage.

The "deep-bath" smelting method prevailed for a long time and is still used in many plants In other plants it has been superseded by the "dry-hearth" technique, which we will take up shortly. Before we proceed to take up the modern furnaces and methods, let us consider the furnace shown in plan and section in Figure 2 This was a 112-foot furnace. Note the great increase in size as compared with Figure 1, also the difference in the shape of the hearth This was still a grate-fired furnace but coal was fed to the firebox by means of a four-chute coal hopper, and an ash sluice was provided beneath the grates. Calcine was fed through the center of the roof by means of three calcine hoppers located near the back of the furnace. Two waste-heat boilers were employed to abstract part of the sensible heat in the flue gases leaving the furnaces. Waste-heat boilers are now standard equipment on almost all reverberatory matting furnaces.

In the process of development of the reverberatory, many other modifications were used, but most of these have not survived. For instance, tilting furnaces were built, and also regenerative furnaces in which the combustion air was preheated. Let us now consider some of the changes which followed the type of furnace illustrated in Figure 2, and this will lead us up to the present-day furnace.

One of the most important developments was the change from grate firing to firing by means of fuel oil, pulverized coal, or gas The burners used for the combustion of these fuels were set in the back wall of the furnace, and the grates and bridge wall disappeared — the

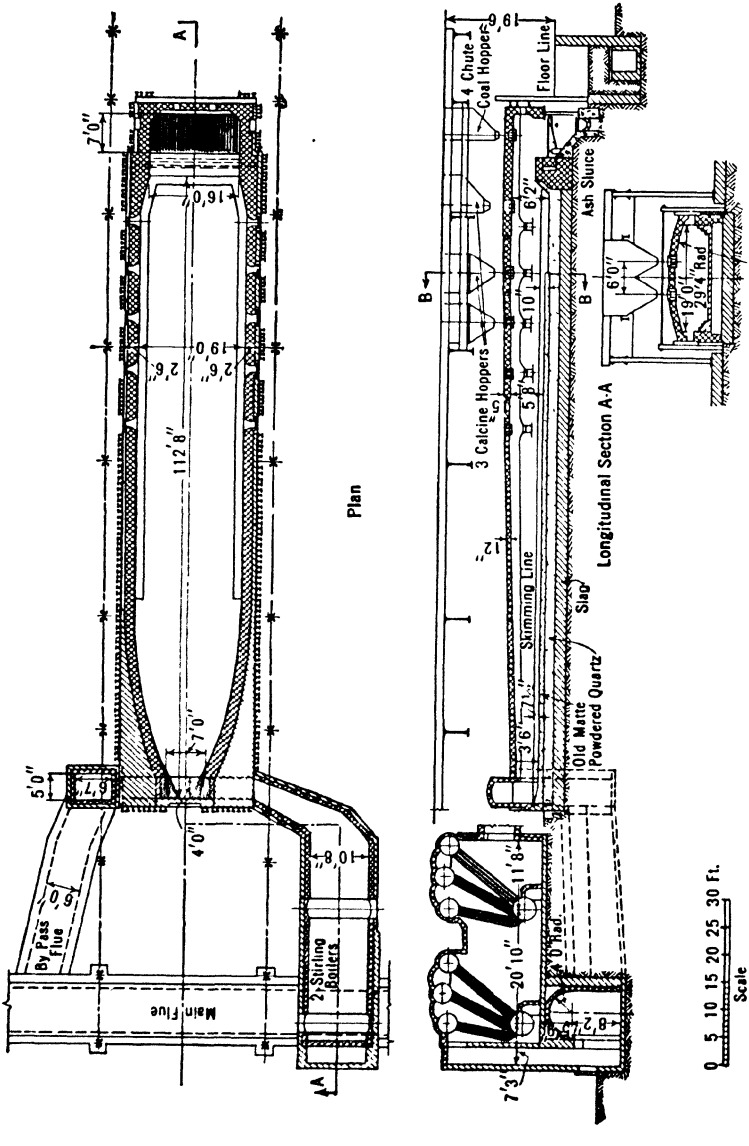


FIG. 2. Grate-Fired 112-foot Reverberatory Smelting Furnace Constructed at Anaconda in 1906.

Waste-Heat Boilers in Tandem

(Last, Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 64, 1933)

laboratory or hearth now occupied the entire space within the furnace walls. Choice of fuel was largely dictated by the location of the plant and cost and availability of the fuel; all three fuels are still in use at different places, and apparently there is no significant difference in their smelting efficiencies as calculated on their calorific powers. It was believed for a long time that the fuel used in a reverberatory must necessarily burn with a luminous flame, because much of the heat that the bath receives comes from radiation from the flame, and it was felt that a non-luminous flame would have such a low radiating power that its smelting efficiency would be low. Experience at Anaconda,[3] however, has shown that natural gas has a smelting efficiency per heat unit equal to that of the pulverized coal previously used; pulverized coal burns with a highly luminous flame, but the gas flame is non-luminous to such an extent that one can see from one end of the furnace to the other while the gas is on.

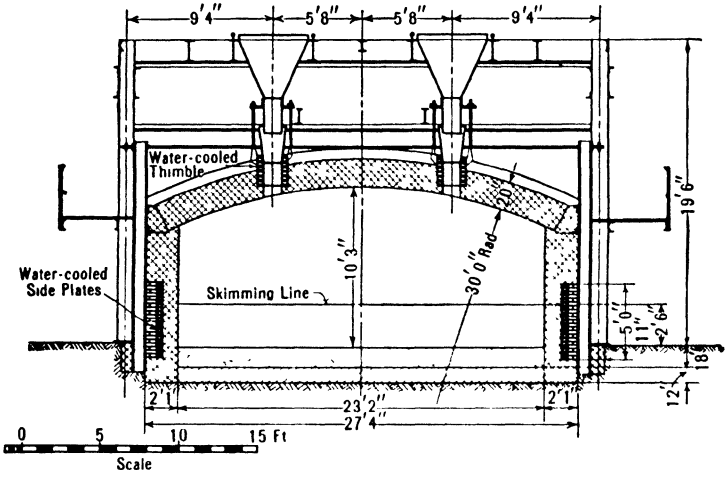
Coal-dust firing caused some trouble at first because ash and unburned particles fell on the bath and formed an insulating blanket. This had the effect of preventing the heat of the flame from reaching the bath, and the bath became chilled. It was found later, however, that this difficulty was caused by insufficient pulverizing of the coal and when the coal was sufficiently fine this blanket of ash did not form. When firing with coal dust, part of the ash is carried out the flue; the rest falls on the charge and eventually becomes part of the slag and must be taken into account in calculating the amount of slag-forming fluxes to be used. Fuel oil and gas, of course, contain no ash.

Another improvement in furnace design was the use of water-cooled side plates placed in the side walls of the reverberatory; the cross-section in Figure 3 illustrates how these side plates are located. These plates cool the side walls and hence prevent corrosion by the slag and the danger of the matte breaking out through the furnace walls. A system such as this serves to warn the operator if the walls are becoming thin, because then the water flowing out of the cooling plates is abnormally hot. At Anaconda it was found that the use of these side plates practically eliminated all trouble with matte break-outs and helped keep the furnace in better shape.

The method of charging a reverberatory matting furnace has been the subject of much research, and a perfectly satisfactory method of charging has never been found. Since hand charging through side doors on the early reverberatories was abandoned, it has been standard practice to charge through openings in the roof; one important devia-

[3] Laist, Frederick, op cit., p. 87.

tion from this has been the " gun feed " method of charging through the side walls. This is a recent development, and we shall consider it a little later. At first the charge hoppers were set near the center of the furnace roof, as shown in Figure 2, but later this method of *center charging* gave way to *side charging,* in which the calcine hoppers dis-



(*Last, Am Inst Min & Met Eng Trans, Vol 106, p 80, 1933*)

FIG. 3. Cross-Section of Anaconda Center-Charged, Water-Cooled Reverberatory Furnace of 1928.

charged through the roof close to the side walls. Thus the furnace charge piled up along the side walls, and this charge acted as its own fettling — protecting the walls from corrosion by the slag bath and helping to prevent break-outs. About 1924 the copper-smelting companies were confronted with serious litigation involving the right to use the method of side charging which had been previously patented. During the trial of the Carson case, the Anaconda company made some investigations relative to certain controversial points, and these served to throw a good deal of light on the general subject of the operation of reverberatory smelting furnaces. When side charging was first used, it was found that it was no longer possible to keep a deep pool of matte over the entire hearth — the matte pool froze over near the back of the furnace, and only a relatively small pool of matte was maintained near the front of the furnace. Although it had been thought that a deep bath was essential, it soon became evident that the " dry-hearth " technique was just as efficient as the previous practice. In studying the merits of side versus center charging, then, it was also necessary to study the effect of deep-bath versus dry-hearth

smelting, as both changes had been made at the same time. Several reverberatory furnaces were operated for a long time under different conditions, and the conclusion was reached that none of these factors had any appreciable effect on the smelting power of the furnace.[4] In other words, the important thing in reverberatory smelting is to maintain a constant evolution of heat and keep plenty of unsmelted charge in the furnace so that the flame and hot gases have something to work on at all times; otherwise it makes little difference how the furnace is charged or whether a pool of matte is maintained in it or not. Charging in different ways, and smelting with or without a deep bath of matte, may affect such things as the life of the furnace, dust losses, convenience in manipulation, and metal losses in slag, but they have no significant effect upon the actual smelting power of the furnace.

The Reverberatory Furnace Charge. The material fed into a reverberatory furnace will depend upon the type of ore, the nature of the concentrate produced from it, and the amount of preliminary treatment (drying and roasting) that it has received. The important facts to be considered with respect to the solid materials charged are:

1. The copper and sulfur content of the charge. This determines the grade and amount of the matte formed.

2. The nature of the gangue or waste materials in the ore. These must be fluxed and slagged off, and the amount and nature of this gangue material determines the amount of flux that must be used and the amount or *volume* of slag formed.

3. Whether the copper-bearing material has been roasted or not. In modern plants we find reverberatory furnaces operating on (*a*) roasted calcine, (*b*) dried concentrate, and (*c*) wet concentrates just as they come from the mill filters.

4. The particle size of the solid material.

5. The physical and chemical properties of the flux used.

In addition to the solid material fed to the reverberatories, in most plants it is also necessary to treat the slag from the converters. This is a ferrous silicate slag, high in iron, and containing about 4 per cent copper; this comes directly from the converters and is charged into the reverberatories in the liquid form. The reverberatory must also handle a certain amount of reverts — collected dust and fume, ladle skulls, and refinery slags.

Another material which finds its way to some smelters is *cement copper*, a finely divided high-grade precipitate of metallic copper obtained by the precipitation or *cementing* of copper from copper sul-

[4] Laist, Frederick, op. cit., p. 78.

fate solutions on metallic iron. When cement copper is being treated it usually forms part of the reverberatory charge.

Modern trends in concentration involve regrinding of middlings and concentrates with the subsequent production of finely divided high-grade flotation concentrate; this material presents many problems to the smelter. On the whole the furnace feed is becoming more basic as improved concentration decreases the amount of silica in the concentrates; converter slag was formerly useful as a flux because of its high iron content, but this is generally no longer true. The increasing basicity of furnace charges is largely responsible for the fact that siliceous refractories are being replaced by basic refractories in many reverberatory furnaces.

Roasting of finely divided concentrate produces a "wild" calcine which is difficult to handle without serious dust losses; these losses occur in the roaster itself, in transporting the calcine to the reverberatory furnace, and in charging the material into the furnace. Dust losses are particularly high when this "wild" calcine is charged through the roof of the furnace.

The Smelting Action of the Reverberatory. The principal function of the reverberatory, as we have noted, is to melt down the charge and permit the liquid slag and matte to segregate into two layers. In Chapter II we have considered the chemical reactions which take place during smelting; these are of two important types.

1. Formation of matte and slag by metathesis (double decomposition). Because of its strong affinity for sulfur, the copper on the charge forms Cu_2S, the stable copper sulfide. This copper may enter the furnace as a sulfide in concentrate or calcine; as an oxide in calcine, oxidized ore, or converter slag; or as metallic copper in cement copper — all eventually becoming sulfidized and entering the matte as Cu_2S. The rest of the sulfur on the charge is either volatilized as SO_2 or combines with iron to form FeS; the resultant liquid FeS is miscible with Cu_2S, and the solution of these two sulfides is the principal constituent of the matte.

2. Reactions which result in the formation of SO_2 and the consequent elimination of part of the sulfur on the charge. Some sulfur is eliminated by the direct action of the flame gases on the piles of charge, but this roasting action in the reverberatory is not great because there is usually not much excess air in the flame gases and because the material is not being stirred or rabbled. Other reactions which serve to eliminate sulfur by the interaction of constituents within the charge we have considered in Chapter II, Examples 4, 5, and 6. Sulfur elimination in the reverberatory depends upon the nature of the charge

and the amount of free oxygen in the flame gases. This elimination may range from practically nothing up to 30 per cent of the total sulfur on the charge. The sulfur elimination by the furnace must be known in order to calculate the grade of matte and the matte fall to be expected in any particular ore.

In many reverberatory furnaces infusible accretions are formed which tend to build up on the hearth of the furnace The most prevalent of these is magnetite, Fe_3O_4 The magnetite may be already present in the calcine or it may be formed by the partial reduction of Fe_2O_3, as for example

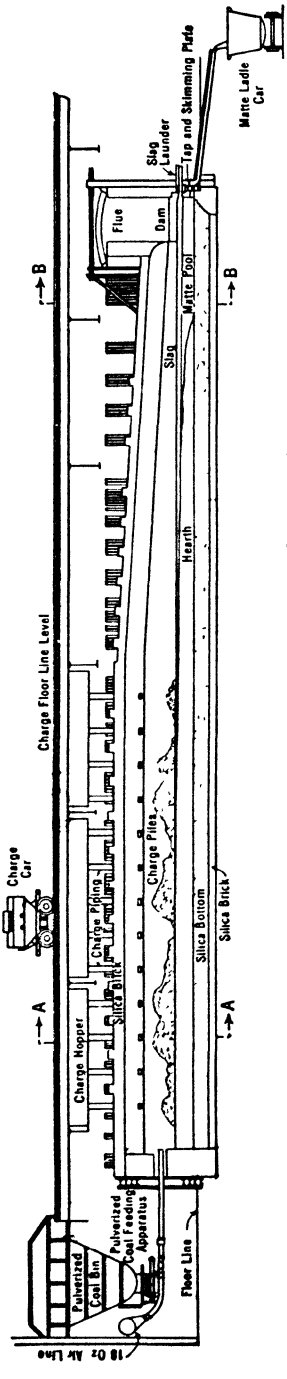
$$9Fe_2O_3 + FeS \rightarrow 6Fe_3O_4 + SO_2 + FeO$$

The first stage in the reduction of Fe_2O_3 takes place readily, but the Fe_3O_4 formed is highly refractory since it is both difficult to melt and to reduce to FeO in which form the iron can be slagged. Magnetite may be deposited by simply settling to the furnace bottom, or some of it may dissolve in the matte and then precipitate on the hearth after the bath has become saturated with it. It seems that liquid matte has some solvent action for magnetite because magnetite crystals have been found in frozen mattes However the deposit may be formed, there is a gradual building up of the layer of magnetite on the hearth of most operating furnaces, and very often it is this that determines the length of the life (*campaign*) of the furnace, because when the accretions become too thick the furnace must be shut down and the hearth rebuilt.

The greatest depth of these magnetite accretions is found in the back or smelting zone of the furnace, and in "dry-hearth" smelting the solid charge rests directly on this "magnetite hearth." A pool of matte and slag forms near the front of the furnace, but there is no deep bath of matte in the smelting zone Small pools of matte and slag accumulate on this "plateau" in the smelting zone, from which the liquids trickle down to the collecting pool near the front of the furnace. A cross-section of a coal-fired dry-hearth reverberatory is illustrated in Figure 4, and two of the diagrams in Figure 5 show the "magnetite hearth." The matte pool in this particular furnace held about 50 tons of matte; in a similar furnace operated with a deep bath of matte, the matte pool contained about 200 tons.

Construction of the Reverberatory Furnace. As we shall see when we consider some typical reverberatory furnaces, there are many differences in details of their construction. At this point we shall consider some of the general characteristics.

Furnaces are usually constructed of silica brick with a monolithic



(*Last, Am. Inst Min. & Met Eng. Trans., Vol. 106, p. 78, 1933*)

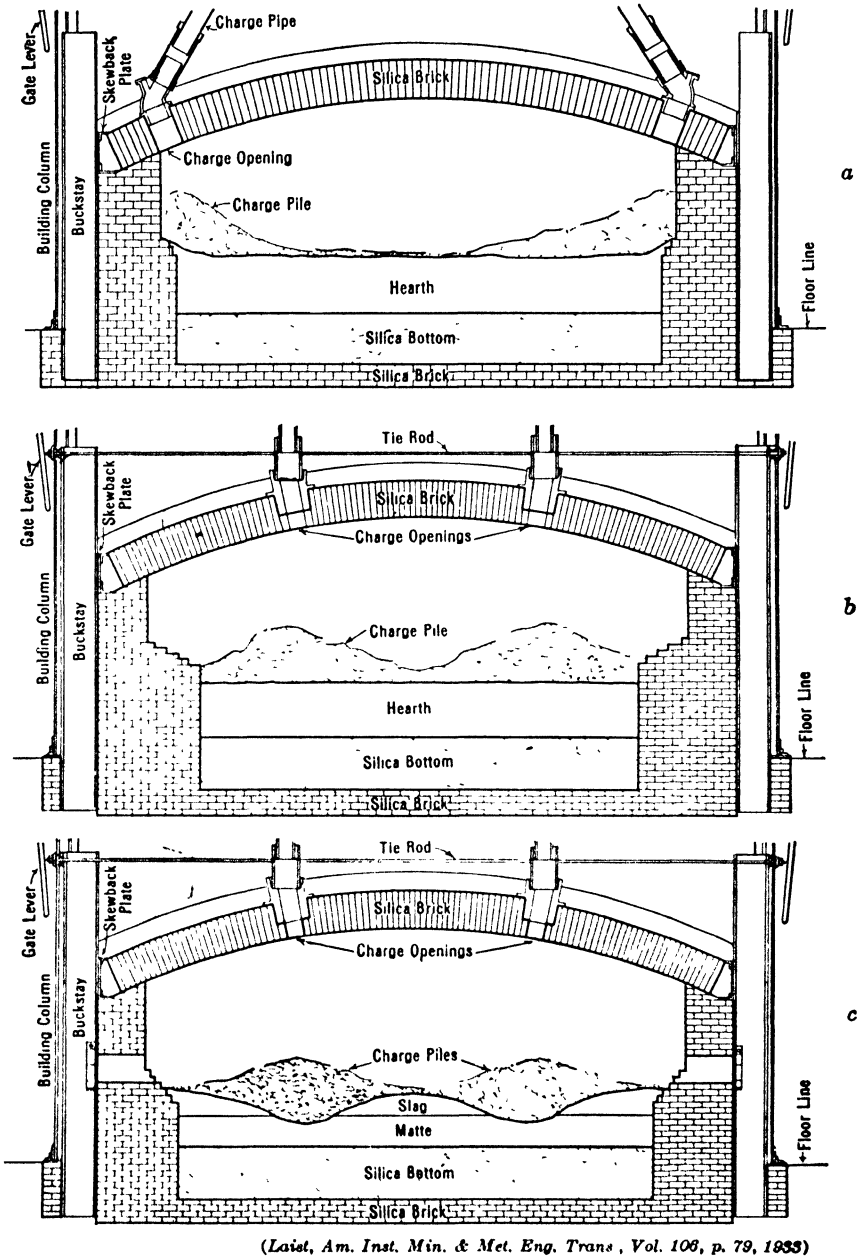
FIG. 4. Interior Longitudinal View of Side-Charged Reverberatory of About 1925.

Shows "dry hearth" and diminutive matte and slag pool at front end.

silica bottom; this bottom is built up over several courses of silica brick which in turn rest upon a solid foundation of concrete or poured slag. Steel buckstaves (usually I-beams) rise vertically along the sides of the furnace, and their lower ends are set firmly in the foundation. Steel tierods connect the buckstaves across the top of the furnace, and this combination of buckstaves and tierods holds the furnace together. Water-cooled hollow metal plates may be set in the side walls to cool and protect the refractory brick and keep the steelwork from buckling under the prolonged heating.

The Bottom. The furnace bottom or smelting hearth is usually constructed of silica sand or crushed quartz, formed into shape and sintered by the heat of the furnace; usually some slag or matte is added to help sinter the hearth. The liquid slag and matte in an operating furnace seep into the hearth, and magnetite also collects on the hearth; these substances replace the original material, and it is usually found on shutting down a furnace that the original hearth material has been completely replaced by matte, slag, and magnetite. Old hearth material is removed, crushed, and resmelted to recover the contained copper.

The Side Walls. Reverberatory furnace side walls are constructed of silica brick; they are usually quite thick near the bottom of the furnace and thinner near the top. Some furnaces have one or two courses of magnesite brick laid on the inner sides of the walls extending from the hearth to a level above the slag line. This mag-



(*Laist, Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 79, 1933*)

FIG. 5. Reverberatory Cross-Sections.

a, Shows "dry hearth" and charge piles resting on solid "magnetite" hearth. Side-charging.
b, Shows center-charging with "dry hearth", charge resting on solid "magnetite" hearth.
c, Center-charged, "deep-bath" furnace, charge floating on molten slag and matte bath.

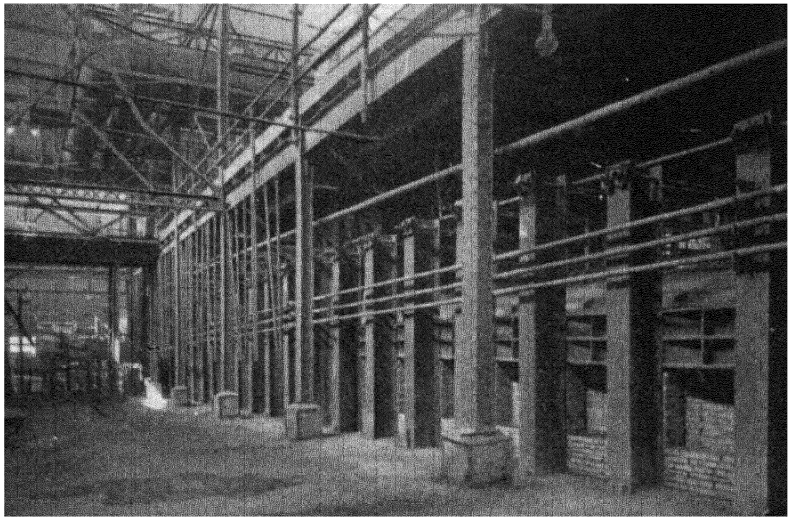


FIG. 6. Side View of Reverberatory Matting Furnace Looking Toward the Firing End.

In the background is the launder for charging converter slag into the furnace. Note the buckstaves, skewback plate, and tierods; also the panels in the side walls. These panels allow more brick to be added on the outside when the original brick has burned out.

nesite lining may not extend for the entire length of the furnace but may only line the *crucible* or the front portion of the furnace. When a new furnace is made ready for the first charge the side walls are fettled, and more fettling material can be added as needed by means of charging pipes near the side walls. In side-charged furnaces the charge tends to act as its own fettling material.

The Roof. The roof or *arch* of a reverberatory furnace is made of a single thickness of special bricks. Part of these bricks may be "straights," and part or all of the bricks are wedge shaped. These are set with the widest part on top so that they form a shallow arch. The arch sets against the *skewback plates* which run along both sides of the furnace and are fastened to the inner sides of the buckstaves. The weight of the arch rests on the side walls, and the thrust of the arch is taken by the skewback plates. Thus the arch is self-supporting and the width of the furnace is largely governed by the working strength of the arch brick at furnace temperatures. The maximum span which will support its own weight is about 30 feet; consequently the width of a furnace cannot be much more than 30 feet. The roof often slopes downward near the front of the furnace.

Sprung arches, such as have been described, are usually made of silica brick; their thickness may range from 9 to 20 inches. Recently some furnaces have been constructed with part or all of the arch made of magnesite brick. Magnesite brick arches are of the *suspended* type; special shapes of brick are used which hang from supporting rods above the furnace (Fig. 8). Thus the weight of the roof is carried by external support, and the thrust on the skewback plates does not hold the arch in shape as is the case with a sprung arch. Magnesite

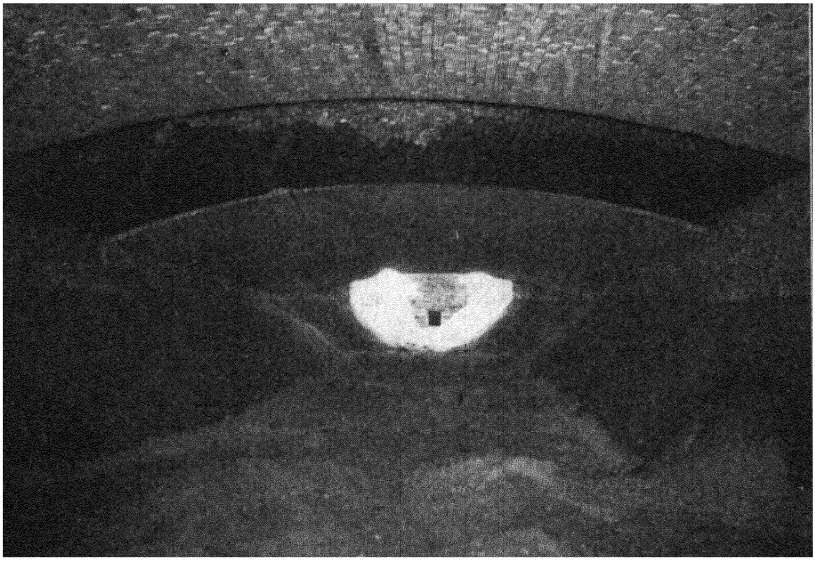


FIG. 7. Interior of a Reverberatory Furnace Looking Toward the Skim End. This furnace has a sprung arch roof and the fettling is in place along the side walls.

brick is denser than silica brick and shows less strength at high temperatures; so far it has not been feasible to build non-suspended (sprung) arches of magnesite brick over spans as wide as those used in these furnaces.

All refractories expand when heated, and in designing a furnace, allowance must be made for this expansion as the furnace comes to temperature. Usually the longitudinal expansion of the roof is taken up by means of suitable expansion joints — gaps which close up as the roof expands. These expansion joints show as breaks in a cross-section and may be noted in Figure 9. Lateral expansion may be taken care of by adjusting the tension in the tierods which cross the top of the furnace and connect the buckstaves on opposite sides.

Refractories. For many years silica brick was the standard refractory used in the construction of furnaces. Bottom, side walls, and arch were all made of this material. Today there are still many reverberatories which are of silica brick construction throughout. In other plants, however, basic magnesite refractories are being used for crucible linings and roof arches. In modern practice it is necessary to treat charges which are increasingly basic in their chemical composition and finer in size; these materials produce quantities of dust, and this basic dust (largely oxides of iron) reacts with the hot silica (acid) refractory to form fusible silicates. It is this corrosive action of basic material on siliceous refractories that has led to the use of basic refractories; these, of course, are not attacked by basic oxides.

Spalling, or the breaking of refractory material when subjected to sudden temperature changes or " thermal shock," is important because both magnesite brick and silica brick have rather strong tendencies to fail when subjected to sudden temperature changes; probably magnesite brick is the worse offender in this respect. Damage due to spalling may be minimized by careful operation of the furnace and the use of well made refractory brick.

Chrome brick is occasionally used in portions of the furnace subjected to severe corrosion by matte, slag, and dust. This refractory is highly resistant to corrosion; its principal disadvantages are its high cost and the fact that it will absorb matte and form a mass which is very difficult to smelt to recover the absorbed copper.

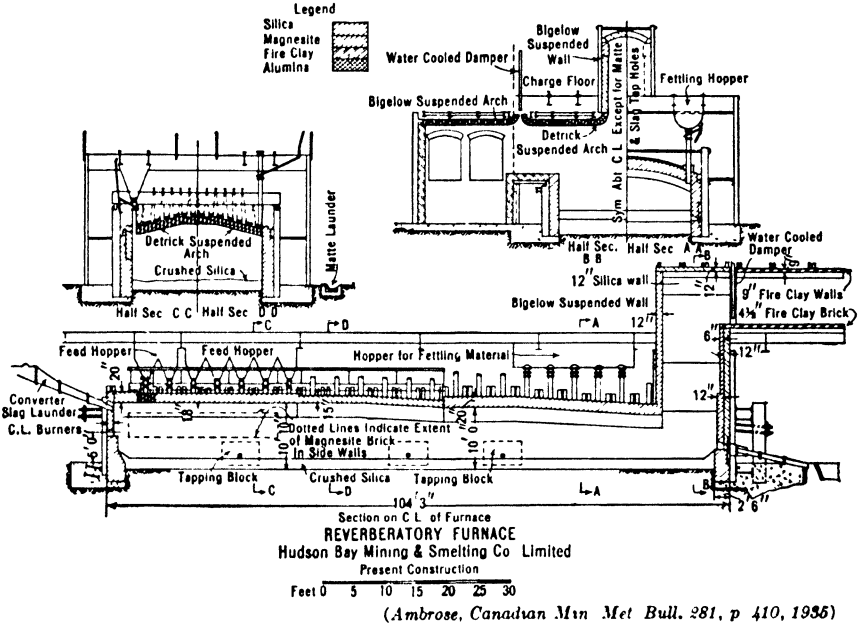
In an article on the application of refractories to the copper industry, Suydam[5] lists the following important conclusions:

1. The trend in the choice of refractories has been toward the more basic types as smelter feed has become more highly concentrated.
2. Fine grinding incident to flotation, and higher temperatures necessary to lower costs have imposed successively harder conditions, especially in the ore-melting reverberatory.
3. The tendency to increase furnace widths and temperature of firing makes almost imperative the selection of a refractory better suited to the service than is the commonly used silica brick.
4. Of known refractories, magnesite brick seem to possess the most desirable properties. Their high expansion characteristic, weight and cost have prompted careful increases in the proportion of magnesite substituted for silica in sprung arches of large span.
5. Nothing was known of the behavior of magnesite brick in suspended

[5] Suydam, A. G., Application of Refractories to the Copper Industry: Am. Inst. Min & Met. Eng. Trans., Vol. 106, p 277, 1933.

construction. Such a roof was provided over an experimental furnace and data gathered regarding the following points: period of safe heating and cooling; temperatures at which cold shapes could safely be installed; temperature gradient through brick; probable heat losses through the roof; over-all expansion; the effect of commonly used expansion joints and some information on the probable causes of spalling.

6. The probability of magnesite brick serving as a complete sprung arch over wide spans is considered in the light of such data as are available. Ideas as to the strength of magnesite brick at high temperatures may have been clouded by the results of tests under soaking heat conditions without due consideration of the mechanical strength of the refractory as actually used in practice, where a rather steep temperature gradient is had except in bottoms.



(*Ambrose, Canadian Min Met Bull. 281, p 410, 1935*)

FIG. 8. Reverberatory Furnace Showing a Suspended Magnesite Arch.

The life of siliceous refractories in reverberatory furnaces may be greatly extended by the method of "hot-patching" developed at the Clarkdale smelter. As described by Kuzell,[6] this method consists in spraying a water suspension of refractory material on the surface while the furnace is under full fire. The refractory material consists of quartz-sandstone pulverized to 78 per cent minus 200 mesh, and a

[6] Kuzell, C. R., Clarkdale Method of Hot-Patching Operating Furnaces: Am. Inst. Min. & Met Eng. Tech Paper 995 (Metals Technology), February 1939.

slurry of pulverized clay which is treated with live steam for several hours to insure complete dispersion and disintegration. The proper amounts of quartz and clay slurry are mixed in a concrete mixer, and the mix is then blown on to the refractory surface by means of a spray gun using a 1½-inch iron discharge pipe. An air pressure of 50 to 60 pounds is used on the spray gun when patching arches; for side wall and flue repairs lower pressures are used. The mix must be applied in successive thin layers, allowing sufficient time between applications to permit the heat of the furnace to set the refractory; an experienced operator can build a patch up to 6 inches thick. Since the adoption of this method at Clarkdale the furnace campaigns have been almost indefinitely extended, and when a reverberatory is shut down it is usually for external reasons and not because of failure of the refractories.

With respect to smelting practice on the North American Continent, the following excerpts from the annual review number of the February 1940 issue of Engineering and Mining Journal[7] are pertinent.

> Several differences were noticed between reverberatory furnace practice in the Southwest as compared with practice in Canadian plants. In the American plants, sprung arches of silica brick are used exclusively, whereas in Canada all copper and copper-nickel reverberatory furnaces have suspended magnesite roofs in the smelting zone at least, and many have suspended roofs for the full length of the furnace.
>
> A second notable difference is that in most of the American plants the cross-sectional area of the furnaces is uniform throughout their length, whereas in most furnaces in Canada the height of the roof at the firing end is increased to provide more area for combustion in the smelting zone, the cross-sectional area being decreased toward the front end.

Tapping of Slag and Matte. The withdrawal of matte is usually called "tapping," and the matte is removed through "tapholes" The removal of slag is known as "skimming," and the slag flows through a "skimming door." The term "skimming" originally meant the complete removal of slag preparatory to the tapping of the entire pool of matte; the term has lost its original meaning, as a certain amount of molten slag is retained at all times in modern furnaces — even in dry-hearth smelting there is always a good-sized pool of matte and slag in the front end of the furnace. The skimming door is a small opening in the wall of the furnace; it is closed by means of a clay dam when the flow of slag is to be stopped. In some operations,

[7] Boggs, W. B., Copper Metallurgy: Eng. and Min. Jour., Vol. 141, No. 2, p. 88, 1940.

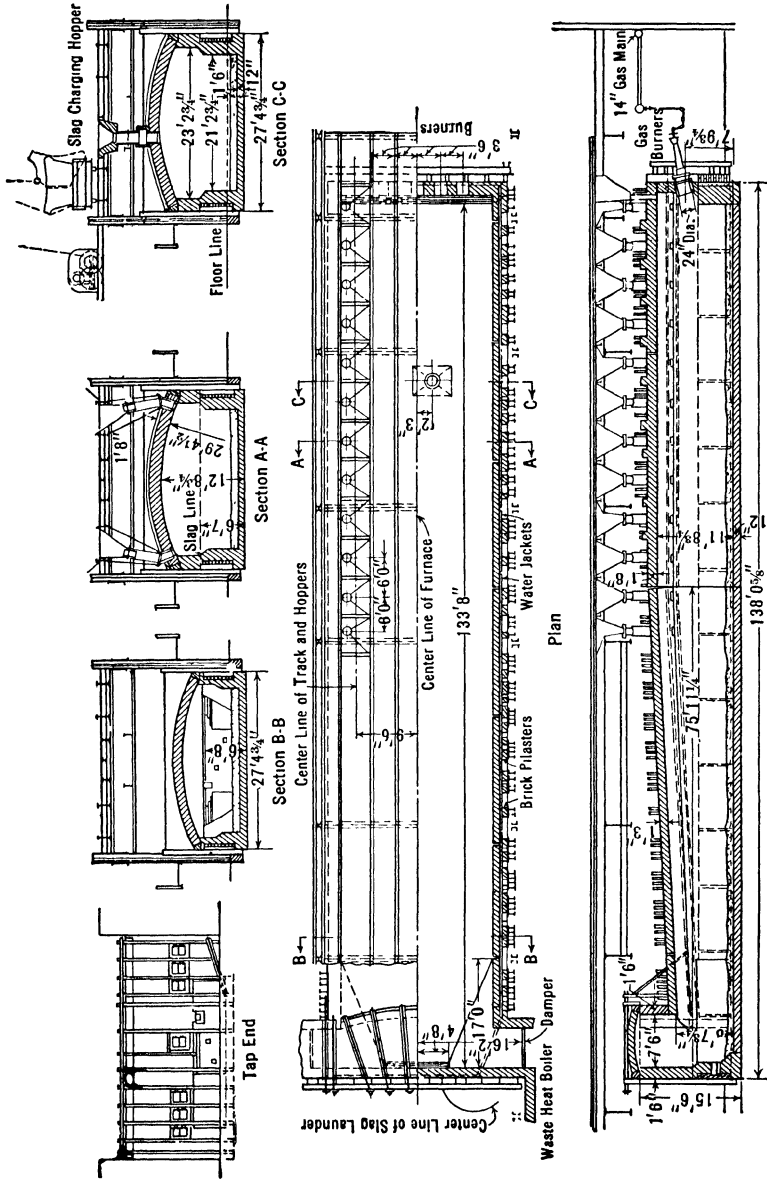


FIG. 9. Gas-Fired, Water-Cooled Anaconda Reverberatory Smelting Furnace of 1931 to Date.

(Last, Am Inst. Min. & Met Eng. Trans., Vol. 106, p. 83, 1933)

slag is skimmed intermittently by breaking and rebuilding the clay dam as occasion requires; in other operations where a large volume of slag is produced the slag flows continuously through the skimming door as long as the furnace is in operation.

The matte tapholes are located some 10 to 20 inches below the level of the skimming door; these are usually holes about 3 inches in diameter extending through the furnace wall; often there are two tapholes at different levels. These tapholes may be drilled through a refractory brick which is set in a metal plate in the furnace wall — these serve to cool the refractory and prevent corrosion of the taphole. The tapholes are closed by ramming a clay plug into the hole, and the furnace heat burns the clay into a hard mass; when the matte is to be tapped, a steel tapping bar is driven through the hole to open it.

Skimming doors and tapholes may be located in the front wall of the furnace or in either side wall; the exact location is often determined by the plant lay-out, and the skimming doors and tapholes are placed in such a position as to provide the maximum convenience in the subsequent disposal of the furnace products. Usually they are located in the front wall, or in the side walls near the front of the furnace, but when deep-bath smelting is used it is possible to tap matte through holes set in the side walls near the firing end of the furnace. It is sometimes advantageous to have the skimming door in the side wall rather than in the front wall. This is because there is always a certain amount of material dripping from the verb arch near the uptake where the furnace gases enter the flue; these drippings are formed by reaction of the dust from the charge with the silica of the refractory and contain considerable copper. If the slag is skimmed at the point beneath the verb arch, the slag will be contaminated with these drippings and the copper loss in the slag will be higher.

Wet-Charge Smelting. For the past 12 to 15 years the method of charging wet concentrates directly into the reverberatory furnace has been gradually developing, and today it is standard practice at several copper smelters.

Following the success of wet-charge feeding as worked out by A. D. Wilkinson at Cananea, it was decided in 1927 to try out this charging method at the International Plant at Miami, Arizona. Practice at the Miami plant is given in a paper by Honeyman[8] from which the following discussion is taken.

[8] Honeyman, P. D. I., Reverberatory Smelting of Raw Concentrates at the International Smelter, Miami, Arizona: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 88, 1933.

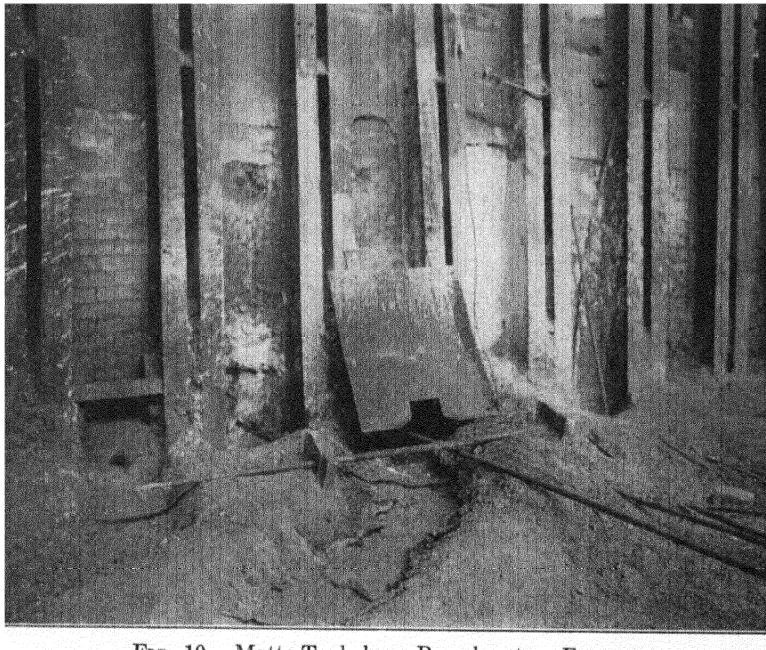


FIG. 10. Matte Taphole on Reverberatory Furnace.

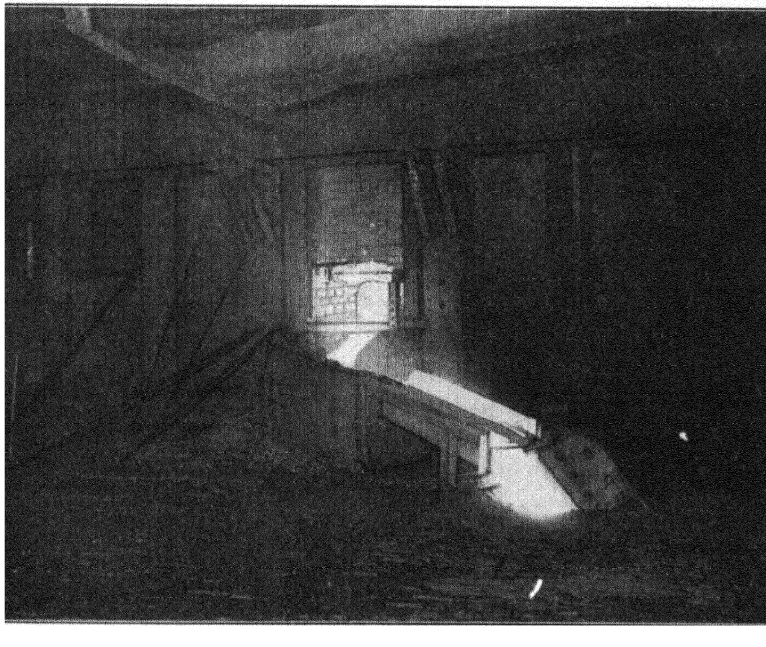


FIG. 11. Tapping Slag from a Reverberatory Furnace.

Figure 12 shows the plan and section of one of the Miami furnaces equipped for wet charging. The furnace feed is stored in charge bins under the feed floor, and these feed by way of a pan feeder to two drag chain conveyors which run above the charge pipes that pass through the arch near the side walls. These charge pipes are 8 inches in diameter and are spaced at 44-inch intervals; they are closed by means of gates which are controlled from the charging runway. The charge pipes cover the entire charging zone, which extends for 65 feet down the furnace. In charging the furnace all the slides covering the charge pipes are opened, and the conveyor is started; the operator starts at the firing end and feeds the charge into two or three holes until they are filled up, then he passes along to the next series of holes, and so on until he has covered the entire charging zone. Each charge pipe is equipped with a peephole through which the condition of the charge within the furnace may be observed; it is usually necessary for the charger to insert a short rod through the peephole and assist the flow of the charge into the furnace. The amount of material added in one charge will often exceed 60,000 pounds, and the charging ordinarily takes from 20 to 30 minutes. Charging is done about six times per 8-hour shift; the frequency and size of the charges will depend upon the nature of the charge.

Deep piles of charge are kept along the sides of the furnace in the charging zone at all times, and a pool of slag and matte is maintained between these charge piles. Note that a band of magnesite brick is set in the side walls to protect the slag line, extending through that part of the furnace where there are no charge piles to protect the walls. Water will react with hot matte with explosive violence, but it is found that there is little or no shooting caused by the contact of the wet charge with the matte, provided that a sufficient depth of molten slag is maintained above the matte pool. As a matter of fact, it has been found that matte can safely be tapped from the furnace directly under the charge piles, and the diagram shows a spare taphole located well back in the smelting zone. The taphole in the front of the furnace, however, is the only one that is used as a rule.

The average charge will contain 77 per cent flotation concentrates, 4 per cent cement copper, 7.5 per cent flux, and 11.5 per cent plant secondaries or reverts. Copper will run about 33 per cent, and sulfur about 25 per cent; moisture will average 11 per cent, and at times reach 15 per cent. Molten converter slag is returned to the furnace through a launder discharging through the middle of the bridge wall. The converter slag often reacts with the bath to produce a violent boiling action which may extend throughout the smelting zone; this assists

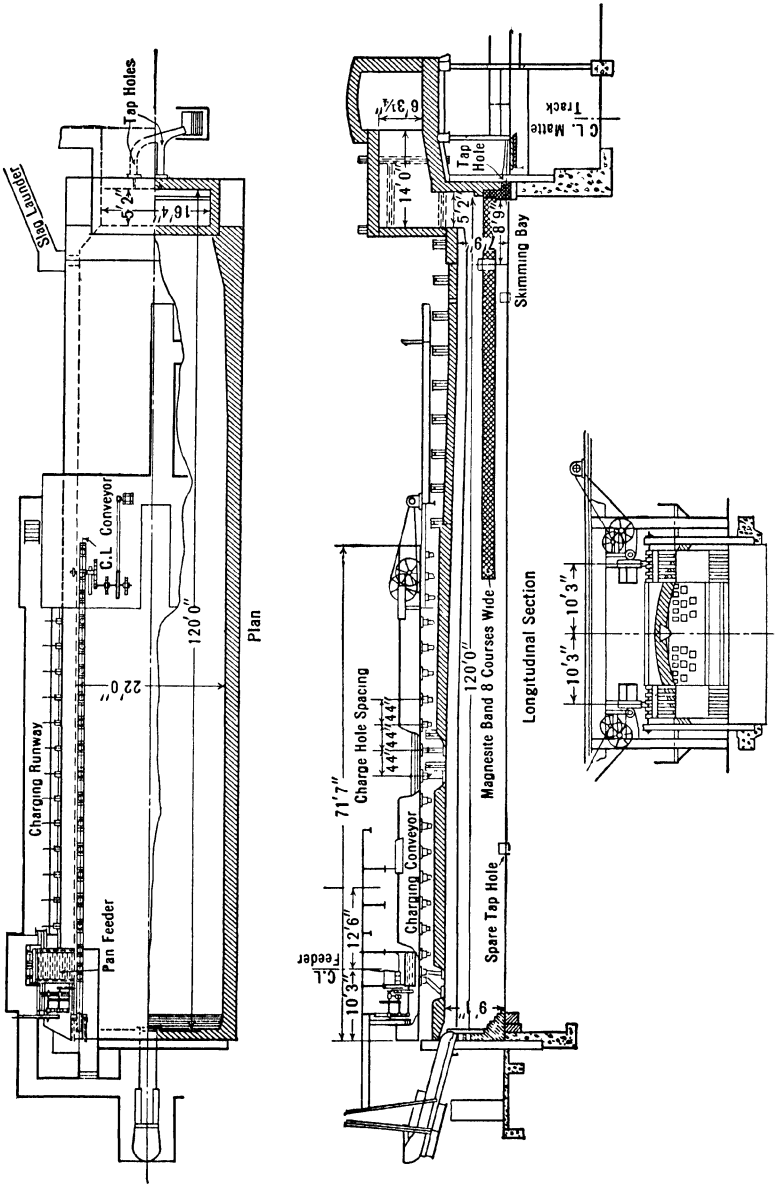
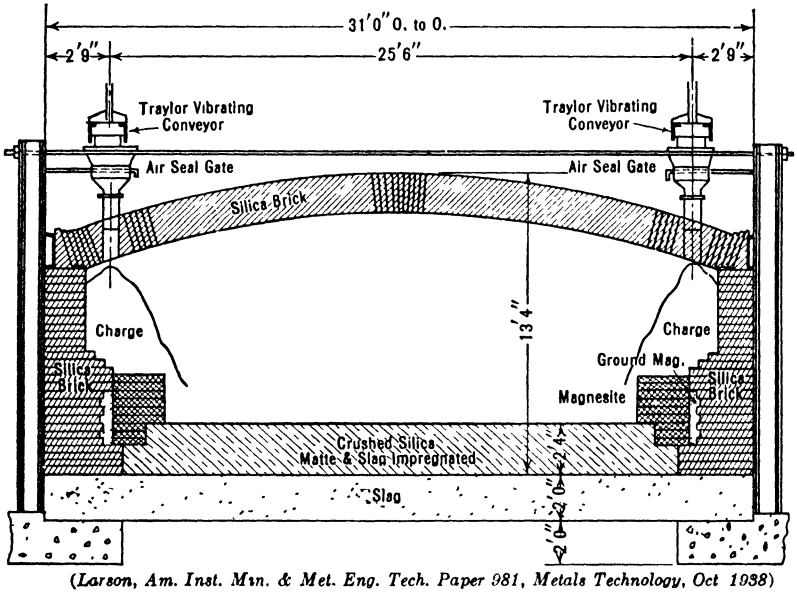


FIG. 12. Wet-Charged Reverberatory Furnace, International Smelting Company, Inspiration, Arizona.

(*Honeyman, Am Inst. Min. & Met Eng. Trans., Vol 106, p. 90, 1933*)

in mixing the surface charge with the molten bath and helps promote the smelting of the charge.

Another paper by Leonard Larson[9] describes the wet-smelting practice at McGill, Nevada. Figure 13 is a section through one of the reverberatory furnaces at McGill. Note that the walls and arch are of silica brick, and there is a shelf of magnesite brick set inside the side



(*Larson, Am. Inst. Min. & Met. Eng. Tech. Paper 981, Metals Technology, Oct 1938*)

FIG. 13. Section Through Wet-Charged Reverberatory at McGill, Nevada.

walls. This shelf runs for the entire length of the furnace, and extends above the slag line. The raw charge is dropped through the roof of the furnace onto this shelf which supports the charge along the side walls, and prevents undue sloughing of the wet charge into the furnace bath. There are 24 charge hoppers on each side of the furnace, and the charge holes extend through the arch near the side walls. The charge is brought to the charge hoppers by means of two Traylor vibrating conveyors; these conveyors are approximately 80 feet long, and are simply steel troughs which are vibrated longitudinally, the vibration causing the material to "crawl" through the trough. These troughs are equipped with spring gates so that the charge can be fed into any one of the charge hoppers; the hoppers have gates which are closed when not in use to prevent air entering the furnace. The ma-

[9] Larson, Leonard, Copper-Smelting Plant Remodeled for Direct Smelting: Am. Inst Min. & Met. Eng. Tech. Paper 981 (Metals Technology), October 1938.

terial from the reverberatory storage bins is brought to the vibrating conveyors by means of belt feeders.

The feed to the furnace averages about 8 to 9 per cent moisture; with both conveyors operating, about 100 tons of this material can be charged per hour. These vibrating conveyors have been in service since October 1934 and have proved entirely satisfactory for the feeding of wet charge to the reverberatory furnace.

At the new copper smelter of the Chino Copper Company at Hurley, New Mexico, blown in on May 2, 1939, wet-charge smelting is employed. Here, also, the material is charged by means of vibrating conveyors above the side walls of the furnace. The crucible of this furnace is lined with magnesite brick, and two sections of the roof near the gas outlet are made of firebrick; otherwise the furnace is made of silica brick throughout.[10]

The advantages of wet-smelting practices may be listed as follows:

1. The roasting plant is eliminated. This reduces the amount of equipment that must be maintained and the amount of handling necessary. Dust losses are greatly diminished, and this improves the cleanliness and the general working conditions of the plant.

2. Dusting within the furnace itself is greatly diminished, and consequently there is less wear on the refractories and less material to be caught in the dust-collecting apparatus and returned to the furnace. At Miami[11] during the period of calcine smelting, there was considerable dusting, and under these conditions a furnace seldom operated over 9 months without a shutdown for general repairs. After the adoption of wet-charging methods the furnace campaign has been extended to well over 2 years.

3. The accumulation of magnetite on the hearth is much less in a wet-charged furnace than in one smelting calcines. Probably the main reason for this is the absence of oxides of iron in the wet charges, as compared with the large amounts of Fe_2O_3 found in most calcines.

The disadvantages of wet-charge smelting are as follows:

1. The most obvious disadvantage, of course, is the fact that wet-charge smelting can be used only on relatively high grade feed. Many ores are difficult or impossible to concentrate sufficiently to be smelted directly to yield a satisfactory matte. For low-grade material it is better to eliminate some of the sulfur in the roasters so that the reverberatory will produce a higher-grade matte.

2. The wet-charged furnaces operating at present in southwestern United States, Mexico, and Africa are all located in climates where

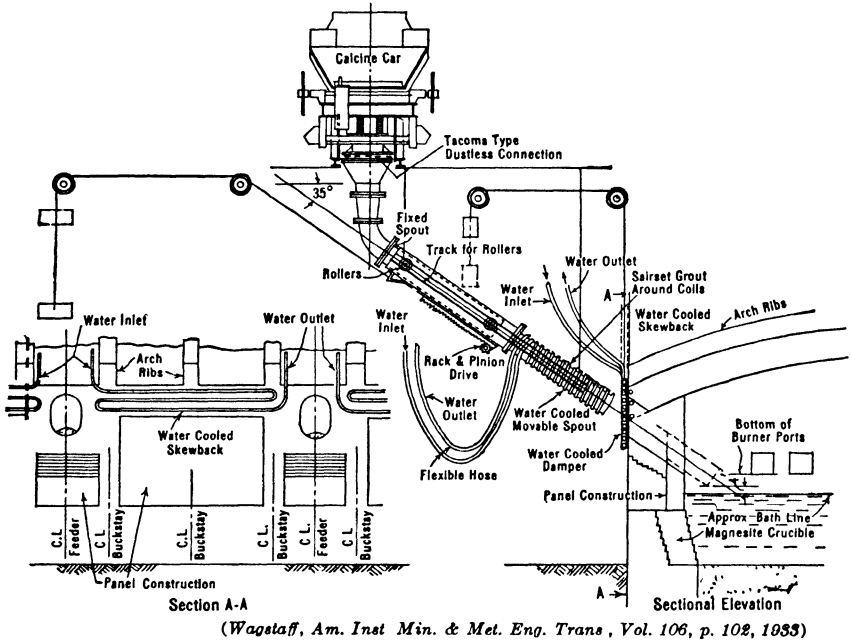
[10] Huttl, J. B., Chino Today: Eng. and Min. Jour., Vol. 140, No. 9, p. 29, 1939.

[11] Honeyman, P. D. I., op. cit.

there is little or no cold weather. Handling and feeding of wet concentrate during the winter in such places as Montana and Canada would probably offer many difficulties.

3. The fuel consumption per ton of charge smelted is, of course, greater when smelting cold, wet concentrate, than when smelting dry, hot calcine. If the concentrate were roasted, the burning of sulfides would provide some or all of the heat necessary to dry and heat the calcines, and less total fuel would be needed.

Laist[12] estimates that if wet charging were to be used at Anaconda to replace calcine smelting, it would require a 50 per cent increase in the amount of fuel used.



(Wagstaff, Am. Inst. Min. & Met. Eng. Trans, Vol. 106, p. 102, 1933)

FIG. 14. Principal Features of Gun Feeder and Construction of Side Wall.

Gun-Feed Furnaces. The following discussion is taken from a paper describing the gun-feed method of charging a reverberatory furnace as developed at Garfield, Utah.[13] A sketch of the equipment used is shown in Figure 14. This feeder is used for charging a furnace with hot calcine.

The gun feeder was designed to introduce the finely divided hot cal-

[12] Laist, Frederick, op cit., p. 81.

[13] Wagstaff, R. A., Development of Gun-Feed Reverberatory Furnaces at Garfield Plant of American Smelting and Refining Co.: Am. Inst. Min. & Met. Eng. Trans., Vol 106, p. 99, 1933

cines under the moving gas stream in the combustion zone and still have them spread uniformly over the hot bath of matte and slag. It was found that best results were obtained when the gun spout was inclined at an angle of 34° to 37° from the horizontal. The temperature of the furnace was so great that it was impractical to use a stationary feeder, and it was necessary to design a movable feeder which could be withdrawn after the charge had been dropped.

The gun proper is made up of two sections, the upper part or carriage, and the water-cooled nose. These two parts telescope together, with the carriage fitting inside the movable spout. The spout is moved in and out of the furnace by a rack and pinion drive. The gun carriage rides on tracks supported from above, and the calcine cars feed the calcine through the spout by means of a Tacoma dustless connection. Counterweights are used to allow easy movement of the gun in and out of the furnace. Water is fed through flexible hose to the coil surrounding the movable spout in order to keep it cool. When the gun is withdrawn, the opening in the wall is covered with a water-cooled damper or gate.

Five guns are used to a furnace, two on one side and three on the other; the charging ports are staggered to allow even distribution of the charge. One of the features of this method of feeding is that the operator must know the condition of his furnace at all times and feed the material at the proper time and place. The guns enter through the side wall, and there are no drop holes in the arch. This permits the building of a stronger arch and contributes materially to the life of the furnace. Note that this furnace has a magnesite crucible and that the skewback plates are water cooled.

The purpose of this development was to find a method of charging which would permit the continued use of deep-bath smelting and would eliminate the disadvantages caused by the method of center charging through the arch (as illustrated in Fig. 5). The gun feed introduces the hot calcine under the gas stream and spreads it over the bath with a minimum of dusting. The decrease in dusting, and the strengthening of the roof by the use of a ribbed arch and elimination of the drop holes resulted in much longer furnace campaigns. The average life of the center-feed furnace was 80 to 100 days, but with the gun-feed furnaces a campaign will last over 200 days.

Fuels. The three principal fuels used in copper matting reverberatories are pulverized coal, fuel oil, and natural gas, as we have already noted. These fuels are burned by means of special burners, which blow the fuel into the hot combustion chamber. All three fuels must be thoroughly and intimately mixed with combustion air so that rapid and efficient combustion is possible. Rapid and complete mixing of air and

fuel permits the fuel to be burned with nearly the theoretical amount of air, and this means that the flame will attain the maximum temperature; also such a flame will be short, and the maximum amount of heat will be liberated close to the burners where most of the unsmelted charge is found. As a rule, high-pressure *primary air* is introduced into the burner to disperse the fuel; the primary air is not sufficient for complete combustion, and *secondary air* is drawn in around the mouth of the burner to provide enough total air for combustion. Later we shall describe burners used for each of these fuels.

The important facts about fuels may be listed as follows:

1. *Cost and availability of the fuel* are often the principal factors in choosing the fuel to be used.
2. *The calorific power of the fuel,* or the amount of heat evolved when a unit weight or volume of the fuel is burned.
3. *The amount and nature of the ash* in coal.
4. *The calorific intensity of the fuel,* or the *temperature* attained when the fuel is burned.
5. *The amount of air required for combustion.*
6. *The amount and composition of the gaseous products of combustion.*

For copper smelting, of course, it is necessary that the fuel selected should be as cheap as possible and also that a continuous supply should be available so that operations may not be interrupted by temporary fuel shortages. When two or more fuels are available, comparison of cost is made primarily on calorific power, since in buying fuel the user is really purchasing heat units; but other factors such as convenience in handling and storing must also be considered.

TABLE 1

EQUIVALENTS OF VARIOUS HEAT UNITS

1 Btu	= 0 2520 Calorie
	= 252 calories
	= 0 2930 watt-hour
	= 0 5555 pound-calorie
1 Calorie	= 3.969 Btu
	= 1 163 watt-hours
1 kilowatt-hour	= 3411 Btu
	= 860 3 Calories
1 horsepower-hour	= 2545 Btu
	= 641 3 Calories
1 boiler horsepower	= 558.0 Btu per minute
	= 140 7 Calories per minute
(Btu per lb) × 0.5555	= Calories per kg (solid and liquid fuels)
(Btu per cu ft) × 8 90	= Calories per cubic meter (gaseous fuels)
1 barrel of fuel oil (bbl)	= 42 U. S. gallons

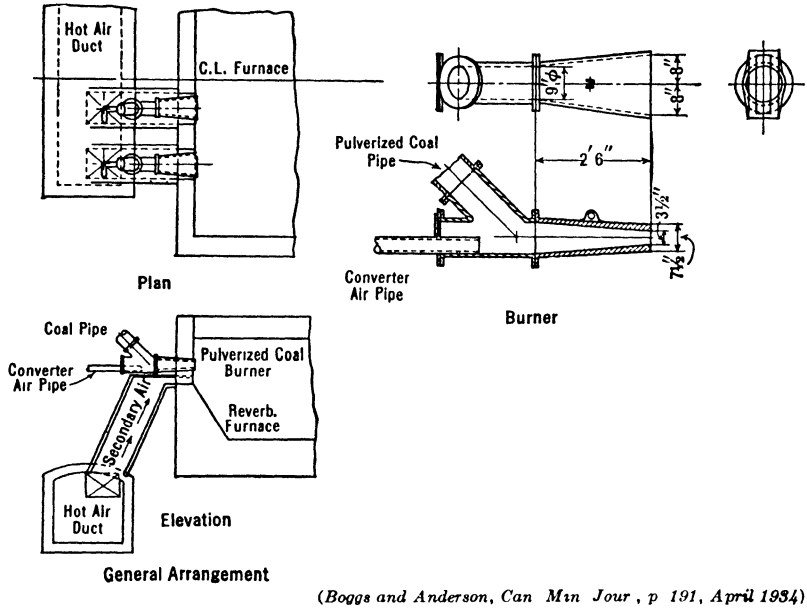
Pulverized Coal. The coal should be pulverized to the finest practicable state of division, which ordinarily means about 90 to 95 per cent minus 100 mesh and 80 to 85 per cent minus 200 mesh. Coal cannot be stored for any length of time after pulverizing because the large amount of surface exposed to the atmosphere results in considerable oxidation; the heat evolved may cause the particles to agglomerate or sinter together, or if enough air is available, the coal may take fire. Coal is pulverized as it is used, and although part of it may be stored for a while in surge bins or feeder bins, it is never allowed to stand for much more than 24 hours before it is used.

Almost any coal can be used for pulverizing; usually a good grade of bituminous coal is used for copper smelting. The coal is delivered in lump form, dried if necessary, crushed, and pulverized. The pulverizing may be done in ball mills, hammer mills, or similar equipment. Usually the pulverizing mill is traversed by a current of air which sweeps the particles out when they have been ground sufficiently fine, and the pulverized coal may be transported to the burners either by the use of screw conveyors or by blowing the air-coal mixture through a pipe. A feeder bin is sometimes located above the burners and kept full of pulverized coal; coal is fed from the bottom of the bin directly into the burners.

Figure 15 illustrates the pulverized coal burner used on the reverberatory furnace at Noranda. An air-coal mixture is fed into the burner through the inclined pulverized coal pipe and is struck by a horizontal blast of air from the " converter air " pipe. This air comes from the same blowers as the air used for the converters and enters the burner at a pressure of about 5 pounds per square inch About 35 per cent of the air required enters with the coal dust; this amount cannot be increased because the mixture would then be likely to explode. The converter air amounts to from 45 to 50 per cent of the total air, and the secondary air which enters below the burner amounts to about 15 or 20 per cent of the total. The secondary air comes from a preheater through a hot air duct and enters the furnace at a temperature of about 300° C. This burner mixes the coal and combustion air very thoroughly and gives a short hot flame.

Natural Gas. Natural gas makes a very good fuel for reverberatory smelting, but, of course, its use is limited to those localities which are served by pipe lines from natural gas fields. Natural gas consists largely of gaseous hydrocarbons; methane, CH_4, is usually the principal constituent together with ethane, C_2H_6, propane, C_3H_8, and ethylene, C_2H_4. The heavier hydrocarbons found in some natural gas are usually removed by condensation to form casing-head gasoline.

In addition to the hydrocarbons, natural gas contains small amounts of carbon dioxide, carbon monoxide, oxygen, and nitrogen. Natural gas will contain from 700 tc 1400 Btu per cubic foot and gives a high flame temperature.



(Boggs and Anderson, Can Min Jour, p 191, April 1934)

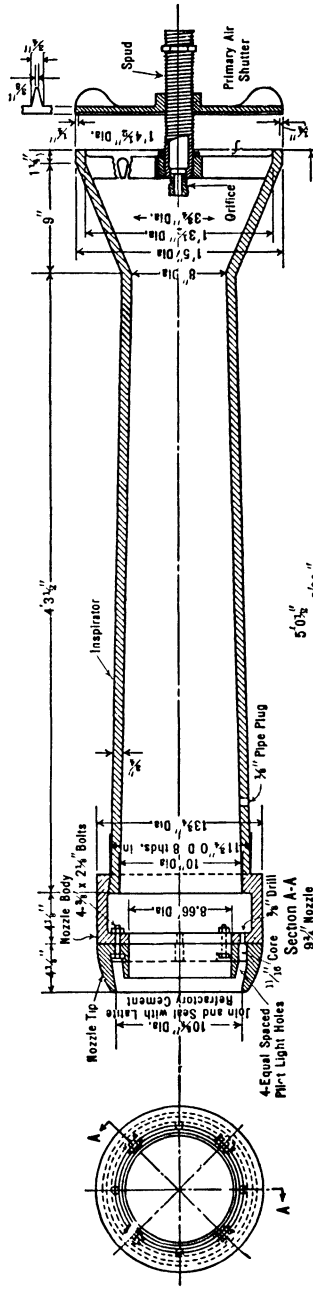
FIG. 15. Pulverized Coal Burner, Noranda Mines, Ltd.

Figure 16 is a section of the inspirator burner used for burning natural gas in the reverberatories at Anaconda, Montana. These operate exactly like Bunsen burners. Gas enters the burner from the gas manifold through a 2-inch nozzle at 20 pounds pressure and the injector effect of the gas stream draws primary air into the burner tube where the gas and primary air become mixed. As the mixture of gas and primary air issues from the mouth of the burner into the combustion chamber it meets the stream of secondary air drawn in around the burner mouth. The amount of both primary and secondary air can be controlled by means of shutters. (The shutters for regulating the secondary air can be seen in Figure 17.) There are five burners to each furnace, and each burner has a maximum capacity of 20,600 cubic feet per hour.

Fuel Oil. Fuel oil is a liquid solution consisting primarily of hydrocarbons, or of sulfur, nitrogen, or oxygen derivatives of the hydrocarbons. The fuel oil may be either crude petroleum or a product of the refining of petroleum; sometimes the lighter fractions, such as gasoline,

or the heavy fractions, such as grease, wax, or asphalt, are removed from the crude oil, and the " middle fraction " used as fuel oil. Fuel oil is a very good fuel, burns clearly, and gives a high flame temperature. The heating value varies somewhat, and will average around 6,000,000 Btu per barrel of 42 gallons.

As in the case of powdered coal, it is essential that the fuel oil be intimately mixed with the combustion air if the burning is to be rapid and efficient; to attain this end the oil must be atomized and the mixture of air and finely dispersed oil droplets sprayed into the combustion chamber. Viscous oils may require heating before entering the burners so that the fluidity may be increased enough to permit efficient atomization. The atomization of the fuel is an important factor in the combustion of oil and is essentially parallel to the pulverizing of coal. High pressure air or steam jets are used in some cases; in other cases the bulk of the atomization is performed by mechanical methods. For copper smelting a low-pressure burner is generally used; i.e. a burner which does not require high pressure air or steam to atomize the oil. The oil is heated to a temperature of 120° to 150° C and delivered through pipes to the burner at a pressure of about 50 pounds per square inch. When this oil issues from the pipe into the burner it has a low viscosity and high vapor pressure and is readily dispersed by means of low-pressure primary air (a few pounds per square inch). The dispersion of oil and primary

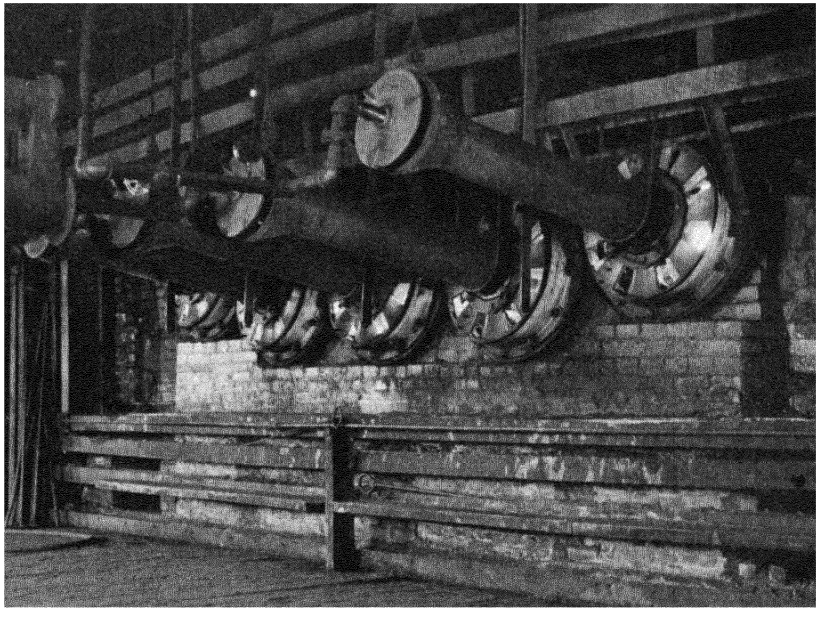


(Laist, Am Inst. Min & Met. Eng. Trans, Vol 106, p. 85, 1933)

FIG. 16. Section of Inspirator Gas Burner Used at Anaconda.

air enters the combustion chamber, where it meets the secondary air drawn in around the mouth of the burner.

Burners of all types are set in the end wall of the furnace, as shown by the various figures. At the Flin Flon smelter in Manitoba, auxiliary burners have been set in the side walls of the furnace near the back.



(Courtesy Anaconda Copper Mining Company)

FIG. 17. Natural Gas Burners on Anaconda Reverberatory Furnace.

One of these is set on each side of the furnace about 30 feet from the bridge wall and at an angle of 60° from the long axis of the furnace.[14] These have proved to be a valuable aid to the end burners both in increasing the tonnage treated and in smelting " floaters " on the slag bath.

It is difficult to give definite figures on the amount of fuel required to smelt a ton of charge, as this depends largely upon the nature of the charge itself. Table 2 gives the data on fuel consumption at six typical plants. Attention is called to a few important points illustrated by this tabulation.

1. The amount of fuel used in a reverberatory furnace is commonly expressed as the *fuel ratio,* or the amount of fuel (tons of coal, barrels

[14] Boggs, W. B., Copper Metallurgy Reveals Improvements: Eng. and Min. Jour., Vol. 139, No. 2, p. 70, 1938.

of oil, or cubic feet of gas) required to smelt a ton of dry charge; the fuel ratios can be calculated in each case from the data in Table 2. Sometimes the inverse ratio, or the number of tons of dry charge smelted per unit of fuel, is used. The earliest furnaces required about 0.50 ton of coal to smelt 1 ton of charge; modern reverberatories smelting hot calcines will consume as little as 0.12 ton of coal per ton of charge.

2. It will be noted that wet-charge smelting requires more heat units per ton of ore smelted than dry-charge smelting. However, only a part of the heat supplied is actually used in the furnace; part of it is used by the waste-heat boilers which are heated by the waste gases from the furnace. When wet charging is practiced there is a greater amount of heat abstracted by the boilers, and the *net* heats actually used for smelting will not differ as much as the gross heats. Table 3 on page 114 will illustrate this point.

Note that there is a much greater waste-heat steam recovery in the wet-charged furnace per ton of charge smelted. In this particular case, when the fuel used in drying is included, the net heat required for smelting 1 ton of charge is actually less in the wet-charge smelting than in the other two methods.

3. Two examples in Table 2 deal with furnaces at Anaconda at the time the change was made from coal to gas firing. Note that there is very little difference in the number of Btu required per ton of charge smelted. The natural gas appears to be slightly more efficient than coal when comparing the gross or high calorific powers of the two fuels, and the difference is even greater when the low or net calorific powers are compared.

4. Table 2 illustrates the effect of the charge on the gross fuel consumption of the furnaces. At Noranda, for example, 2,430,000 Btu is required per ton of charge; the charge is 93 per cent hot calcine and the secondary air is preheated. On the other hand, at Miami the charge is 81 per cent wet concentrate and cement copper, and here 5,600,000 Btu is required per ton of charge.

The temperature in reverberatory furnaces is usually about 1400° to 1700° C in the smelting zone or firing end and 1100° to 1300° C at the flue end. The high temperature of the gases entering the flue means that a good deal of the heat evolved in combustion is not utilized in the furnace itself; and it is standard practice to pass the flue gases through waste-heat boilers and convert this heat into steam which can be used for various purposes around the plant.

The distribution of the heat evolved in a reverberatory furnace is important; this is usually shown by means of a *heat balance* such as

TABLE 2

FUEL CONSUMPTION OF SOME REVERBERATORY FURNACES

Plant	Fuel Used	Charge		Tons of Dry Solid Charge Smelted Per Unit of Fuel Burned	Calorific Power of Fuel Used	Btu Used Per Ton of Dry Charge	Approximate Size of Furnace (feet)
		Type	Amount Per Furnace Day (dry tons)				
Miami, Arizona[a]	Fuel oil	Wet	500. 77% of charge is wet concentrate; 4 0% is cement copper.	1 11 bbl of fuel oil.	6,206,000 Btu/bbl	5,600,000	120 by 22
Anaconda, Montana[b]	Natural gas	Dry	613 plus 122 tons of molten converter slag. 51.1% of solid charge is hot calcine	0 284/1000 cu ft of gas	1,043 Btu/cu ft (gross) 955 Btu/cu ft (net)	3,680,000 (gross) 3,360,000 (net)	134 by 27
Do.[c]	Pulverized coal.	do	587 plus 118 tons of molten converter slag 51 5% of solid charge is hot calcine	6.35/ton of coal.	11,750 Btu/lb (gross) 11,360 Btu/lb (net)	3,700,000 (gross) 3,580,000 (net)	134 by 27
Noranda, Quebec[d]	Pulverized coal Secondary air preheated to 300° C.	do.	1,193 plus 650 tons of molten converter slag 93% of solid charge is hot calcine.	9 40/ton of coal	11,400 Btu/lb	2,430,000	105 by 30

Plant	Fuel Used	Charge		Tons of Dry Solid Charge Smelted Per Unit of Fuel Burned	Calorific Power of Fuel Used	Btu Used Per Ton of Dry Charge	Approximate Size of Furnace (feet)
		Type	Amount Per Furnace Day (dry tons)				
McGill, Nevada[e]	Pulverized coal.	Wet	1,013	5.20/ton of coal	12,015 Btu/lb	4,660,000	127 by 28
Roan Antelope, Rhodesia[f]	Pulverized coal Secondary air preheated to 200° C	do	340	6.44/ton of coal	13,640 Btu/lb	4,240,000	100 by 25

[a] Honeyman, P. D I, op cit, p 88, Honeyman, P. D I, and Faust, P A, Waste-Heat Boiler Practice at Miami Am. Inst Min & Met. Eng. Trans., Vol 106, p 253, 1933.
[b] Laist, Frederick, op cit, p 85
[c] Idem, p 85
[d] Boggs, W. B, and Anderson, J N, The Noranda Smelter: Am. Inst. Min. & Met. Eng Trans, Vol 106, p. 165, 1933.
[e] Larson, Leonard, op cit.
[f] Wraith, C. R., Smelting Operations at Roan Antelope Copper Mines, Ltd.. Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 202, 1933.

TABLE 3[a]

FUEL CONSUMPTION WITH THREE METHODS OF CHARGING AT MIAMI, ARIZONA (Oil Firing)

	1931; 6 Month Period; Wet Charge	1924; One Year Period; Dry Charge	1926; One Year Period; Partial Roast
Gross fuel ratio per ton dry solid charge at reverberatories	0 902 bbl	0 667 bbl	0.577 bbl
Equivalent waste-heat steam recovery	0.470	0.263	0 219
Net fuel ratio per ton dry solid charge at reverberatories	0 432	0 404	0 358
Drier fuel consumption	...	0 105	0 077
Net total plant fuel ratio per dry ton smelted	0 432	0 509	0.435

[a] Honeyman, P D I, op cit

that given in Table 4. Of course, this distribution will be different for various furnaces and will depend upon such factors as the nature of the charge, flux, and fuel; whether the charge is wet concentrate, dried concentrate, or hot calcine; temperature and composition (hence total heat content) of matte and slag; temperature of the flue gases; nature of refractories used in walls and arch; and whether combustion air is preheated or not. Table 4 is a heat balance for a coal-fired reverberatory

TABLE 4[a]

HEAT BALANCE ON AVERAGE RESULTS, REVERBERATORY SMELTING, 6 MONTHS ENDING JUNE 30, 1920

	Btu per Furnace Day	Per Cent
Input:		
Coal	1,827,676,000	94 63
Heat in calcine	103,680,000	5 37
Total	1,931,356,000	100.00
Output:		
Slag	335,820,000	17.40
Matte	96,000,000	4.97
Limestone (decomposition)	96,567,800	4.99
Boilers	579,406,800	30.00
Waste gases	347,644,100	17 94
Radiation, conduction, and other losses	475,917,300	24.70
Total	1,931,356,000	100.00

[a] Laist, Frederick, op. cit., p. 73.

smelting hot calcine. Note that about 48 per cent of the total heat passes out in the gases and that 30 per cent is absorbed by the boilers; in wet-charge smelting this figure would be even greater.

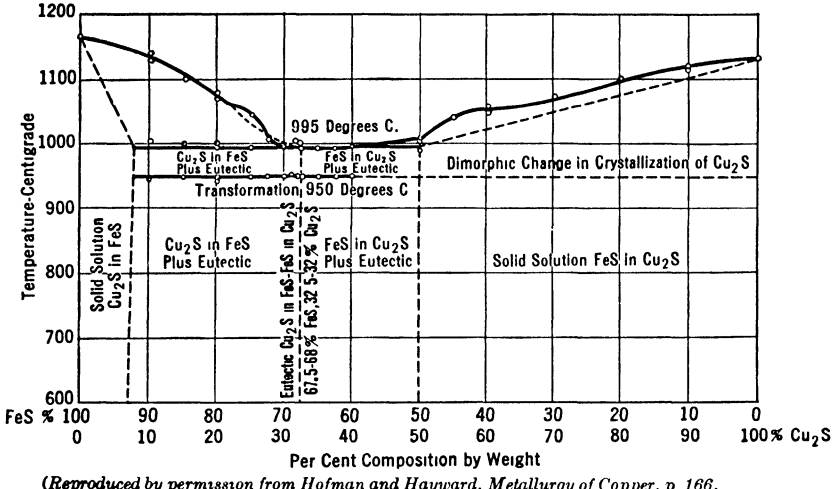
The Products of the Reverberatory Furnace. Three products are removed from a reverberatory smelting furnace — matte, slag, and flue gas. The matte is of course the most important economic product, but the slag and flue gases are probably of greater importance in the furnace and plant operation. We shall take up the subject of matte and slag presently; after taking up converting and fire refining we shall devote a separate chapter to the consideration of flue gases.

MATTE. We have already had occasion to refer to copper matte and have indicated that it consists essentially of artificial sulfides of copper and iron. The two sulfides which are stable at furnace temperatures are FeS and Cu_2S. In Chapter II we assumed that these were the only substances present and made our calculations accordingly. These two liquid sulfides are soluble in one another in all proportions.

The matte produced in copper smelting may range in grade from about 20 to 80 per cent copper. The solidified matte resembles in color and luster the massive form of the natural sulfide minerals. Low-grade mattes (20 to 50 per cent copper) show a dull bronze color on a fresh fracture, mattes containing about 60 per cent copper have a bluish-purple color, and mattes containing more than 70 per cent copper are almost white. High-grade matte which approaches the composition of Cu_2S is called *white metal.* Many high-grade mattes also contain visible stringers of metallic copper or "moss copper." Mattes range in specific gravity from about 4 8 to 5 6, the gravity increasing with the copper content. Molten matte will contain as total sensible heat from 350 to 400 Btu per pound; this of course will depend upon the temperature and composition of the matte. A figure of 375 Btu per pound was used in computing the balance shown in Table 4. Pure Cu_2S melts at 1100° C, and FeS at 1193° C; other mattes melt at lower temperatures, and according to the diagram of Carpenter and Hayward (Fig. 18), mattes containing from 30 to 50 per cent Cu_2S melt at about 1000° C.

Figure 18 is an equilibrium diagram between the compounds Cu_2S and FeS. It appears from the figure that FeS is quite soluble in Cu_2S in the solid state, that Cu_2S is less soluble in solid FeS, and that a eutectic of the two solid solutions exists. This diagram does not indicate the presence of any other compounds. Other investigators have published results which do not entirely agree with the deductions which would be drawn from Carpenter and Hayward's diagram (Fig. 18).

Gibb and Philp[15] reported the presence of the stable compound $5Cu_2S \cdot FeS$ in mattes, and in a more recent paper Avetisian[16] reports that the only stable compound formed is $2Cu_2S \cdot FeS$. It would seem that there is as yet no complete analysis of the system Cu_2S-FeS.



(Reproduced by permission from Hofman and Hayward, Metallurgy of Copper, p 166, McGraw-Hill Book Co, New York, 1924)

FIG. 18. The Cu_2S-FeS Equilibrium Diagram.

It is likely that even complete knowledge of the Cu_2S-FeS binary system would be inadequate, and it would probably be necessary to have an analysis of the 3-component, Cu-Fe-S system for complete interpretation. Figure 18 is determined from melting point data, and the liquidus (upper) curve gives us the melting points of mattes of different compositions.

Although our previous assumption that copper matte consists of Cu_2S and FeS in varying proportions is sufficiently accurate for many purposes, it is not strictly true; matte is a more complex substance than this would indicate. We shall not have space to consider all the investigations which have been made on the composition of mattes but shall merely present a few important facts.

1. As a rule the combined percentages of copper, iron, and sulfur in matte will equal or exceed 95 per cent.

2. The sulfur content of matte is usually less than would be expected theoretically, by calculating the amount required to form Cu_2S and

[15] Gibb, Allan, and Philp, R. C., The Constitution of Mattes Produced in Copper Smelting· Am. Inst. Min & Met. Eng Trans., Vol. 34, p. 665, 1906.

[16] Avetisian, C. K., Copper Matte Composition: Eng. and Min. Jour., Vol. 133, No. 12, p. 627, 1932, and Vol. 134, No. 1, p. 27, 1933.

FeS with all the copper and iron present. One reason for this is that some of the iron may be present as magnetite (Fe_3O_4) or copper ferrite ($CuO{\cdot}Fe_2O_3$). Another reason is that sulfur appears to volatilize from the FeS, leaving behind metallic iron which is soluble in the remaining FeS. This excess iron can react with Cu_2S thus:

$$Cu_2S + Fe \rightarrow 2Cu + FeS$$

and this reaction may account for the moss copper found in some mattes.

3. Matte may contain up to 10 per cent magnetite. It is not clear whether this substance is actually soluble in molten matte or not. Magnetite has a specific gravity of 5.1, which means that its density lies between the maximum and minimum densities of mattes; it will settle out through low-copper mattes, but it will float on high-copper mattes and be removed with the slag. In any event there is not much difference in density, and especially when the matte has about the same density as magnetite (Cu 30 to 40 per cent) we should expect to find the magnetite mechanically entrained in the matte.

4 Many mattes contain metals other than copper and iron in important amounts. When there is zinc on the charge, part of the zinc will enter the matte as ZnS; some copper mattes contain from 2 to 5 per cent zinc (Table 5). In the smelting of nickel-copper ores all the nickel enters the matte as a sulfide, and as an approximation we may consider that these mattes consist of $Cu_2S + FeS + NiS$, just as we considered copper matte to be $Cu_2S + FeS$. Sometimes the formula Ni_3S_2 is given for the nickel sulfide, but there probably is no such compound, and this represents the approximate composition of a solution of Ni in NiS. In lead smelters, the copper is usually collected in a matte, and these byproduct mattes will contain considerable lead as PbS and as metallic lead.

5. The other elements found in matte may be considered impurities, as the percentages are usually small. These will be determined by the nature of the charge and may include small amounts of cobalt, nickel, arsenic, antimony, bismuth, and lead. Arsenic and antimony are only slightly soluble in matte and when present in any quantity these elements form a *speiss* which is insoluble in matte and separates from it in a distinct layer. Speiss is primarily an artificial arsenide or antimonide, just as matte is an artificial sulfide. The formation of speiss is uncommon in reverberatory copper smelting; in most cases the small amounts of arsenic and antimony on the charge are dissolved in the matte. Most mattes also contain small amounts of SiO_2, CaO, and other slag-forming substances.

6. All commercial mattes are excellent solvents for the precious metals — gold, silver, and the platinum group metals — and all these metals on the charge will be efficiently collected by the matte. Practically the only possibility of losing any precious metals in copper smelting is in producing such a small amount of matte that it does not have an opportunity to come in contact with all the precious metals and collect them; the operator always aims to produce a matte of low enough grade and large enough volume to collect all the precious metals.

The amount of matte produced expressed as percentage of the total charge is known as the *matte fall;* the per cent of copper (or copper + nickel for copper-nickel mattes) is the *grade* of the matte. For some of the mattes shown in Table 5 the theoretical amounts of iron and sulfur have been calculated according to the method of Chapter II, assuming that the matte consists only of Cu_2S + FeS (and ZnS in case *g*) ; the theoretical figures are given in parentheses. Note that the actual iron assay checks closely with the theoretical but that the chemical assay for sulfur is always lower than the theoretical. This is especially evident in the low-grade mattes *b* and *g*; apparently this is because a large part of the iron is present either as an oxide or as metallic iron dissolved in the iron sulfide.

Slag. Table 5 also gives the composition of a number of slags formed in reverberatory smelting; in each case the corresponding slag and matte are from the same operation. Note that in general these slags contain from 30 to 38 per cent silica, 45 to 52 per cent FeO, 5 to 8 per cent Al_2O_3, and 1 to 5 per cent CaO. Essentially these slags are molten solutions of ferrous silicates in which are dissolved smaller amounts of other basic oxides (Al_2O_3, CaO, and MgO). Slag from the Roan Antelope deviates quite markedly from the average composition.

Requirements of a Slag. We have already noted that one of the functions of the reverberatory furnace is to permit slag and matte to separate as completely as possible; the ideal slag is the one which promotes the cleanest separation. Such a slag must have the following characteristics:

1. Low specific gravity. The slag must, of course, be lighter than the matte, and the greater the difference in density (viscosity remaining the same) the more rapid and complete will be the separation of the two liquids. Reverberatory slags will range in specific gravity from 2.8 to 3.8, the heavier slags being those which are highest in iron. For the common slags containing 45 to 50 per cent FeO the specific gravity will usually be 3.3 to 3.5.

TABLE 5

ASSAYS OF SOME TYPICAL MATTES AND SLAGS FROM REVERBERATORY SMELTING

Mattes

Plant	Per Cent				
	Cu	Fe	S	Zn	SiO_2
Miami.[a]	45 9	26 0	25 2	...	....
		(27 0)	(27 0)	...	....
Noranda.[b]	19.3	48 3	22.5	...	....
		(48 0)	(32 5)	...	....
Roan Antelope.[c]	78.73	0 58	19 5	...	0.14
		(0 75)	(20 5)	...	....
Andes.[d]	45 88	....	...	...	....
McGill.[e]	31.54	....	....	...	.
Anaconda.[f]	42 00	....	. .	.	..
Flin Flon.[g]	22.00	41 4	24 5	4.2	...
		(40 0)	(32 8)	.	. . .

Slags

	Cu	SiO_2	Al_2O_3	FeO	CaO	MgO	S	Silicate Degree
Miami[a]	0.52	34 5	7 7	49 8	1 26	..	. .	1 22
Noranda.[b]	0.27	37 9	8 5	46 7	1 7	1.9	1.1	1 29
Roan Antelope.[c]	1.20	47 3	14 7	13 7	11.4	2 9	...	1.75
Andes.[d]	0.60	30.9	7 2	50 9	2 5	,.	0 8	1 07
McGill.[e]	.. .	36 1	5 2	48 8	5 7	.	.	1 29
Anaconda[f]	0 50	32 0	8 0	52 0	1 5			1 07
Flin Flon.[g]	0 36	36 5	5 1	41 3	1 7	4 7	0 4	1 39

[a] Honeyman, P D I , op cit , p 88

[b] Boggs, W B , and Anderson, J. N , op cit , p 165

[c] Wraith, C R , op cit , p 202

[d] Callaway, L A , and Koepel, F N , Metallurgical Plant of the Andes Copper Mining Company: Am Inst Min & Met Eng Trans , Vol 106, p 690, 1933.

[e] Larson, Leonard, op cit

[f] Bender, L. V , Development of Copper Smelting at Anaconda: Eng. and Min. Jour , Vol. 128, No 8, p 301, 1929

[g] Ambrose, J H , The Flin Flon Copper Smelter· Canadian Inst Min Metallurgy, Bull 281, p 418, September 1935

2. Low melting point. The slag must be completely molten at the furnace temperature. In early practice the slag was skimmed through side doors in the furnace by means of rakes and rabbles; such a slag could be removed even if not completely molten, although, of course, these slags were not as *clean* (free from copper) as could be desired. In modern practice, however, the slag flows from the furnace, and it must be completely molten.

3. Low viscosity. Slags must be sufficiently fluid to flow easily from the furnace and to permit entrained globules of matte to settle rapidly. A slag may have a low melting point and low density, but if the liquid is " thick " or viscous the separation of slag and matte will not be clean.

4. Low solubility for matte and metal. Most reverberatory slags have practically no solvent power for liquid matte or for metallic

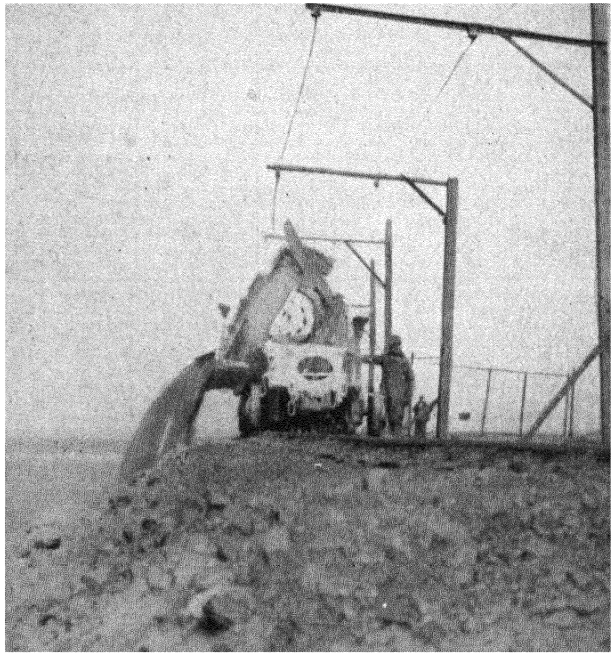


FIG. 19. Dumping Reverberatory Furnace Slag.

copper, but there is some evidence that a very small amount of sulfide may be in true solution in silicate slags. Oxidized copper, however, dissolves readily in slags; the copper oxide forms either copper silicate or copper ferrite, and these compounds dissolve readily in other silicates. The loss of copper in slag is high in any smelting operation where oxidized copper is present in the charge.

Slag Composition. The various acid and basic oxides which make up slags form " alloys " with one another, and equilibrium diagrams can be constructed which indicate the melting points of slags of various compositions, the nature of the solid phases formed, etc; these diagrams are essentially the same as those which are so widely used in the study

of metallic alloys. Practically all copper slags, however, contain at least four important components (FeO, SiO_2, CaO, and Al_2O_3), and the analysis of four-component systems by the method of equilibrium diagrams is difficult and tedious. There has never been a complete theoretical investigation of copper slags, and it is doubtful if such an investigation would be worth the effort. Years of experience have determined the approximate slag composition which gives the best results, and, fundamentally, the method of selecting a slag composition is to use one which has already worked successfully.

Silicate Degree. Slags are often classified according to their *silicate degree,* which is defined as the ratio of the weight of oxygen in the acid oxides in the slag to the weight of oxygen in the basic oxides, i.e.:

$$\text{Silicate degree} = \frac{\text{Weight of oxygen in acid}}{\text{Weight of oxygen in bases}}$$

The following names are given to slags according to their silicate degree.

Silicate Degree	Slag Name
<1.0	Subsilicate
1.0	Monosilicate or singulo-silicate
1.5	Sesquisilicate
2	Bisilicate
3	Trisilicate

For example, the simple slag $CaSiO_3$ or $CaO{\cdot}SiO_2$ has two atoms of oxygen in the acid (SiO_2) and one atom of oxygen in the base (CaO). Hence the silicate degree is $\frac{2}{1} = 2$, and the slag is a bisilicate. The slag Ca_2SiO_4 or $2CaO{\cdot}SiO_2$ has a silicate degree of $\frac{2}{2} = 1$; this slag is a singulo-silicate. For all practical purposes, SiO_2 is the only acid radical in copper slags; Al_2O_3 may act as either an acid or a base (forming respectively aluminum silicates or metal aluminates), but it behaves as an acid only in very basic slags. In all our copper slags we shall consider Al_2O_3 as a basic oxide. Consider the three slags:

Composition	Per Cent SiO_2
$CaO{\cdot}SiO_2$	51 8
$FeO{\cdot}SiO_2$	45 5
(CaO, FeO) SiO_2	45.5 to 51.8

All these are bisilicates, but the per cent of silica is not the same in each slag. In the (CaO, FeO)$\cdot SiO_2$ slag the per cent of silica may range between 51.8 and 45.5, depending upon how much of the CaO is replaced by FeO. In other words, two slags having the same silicate degree need not have the same *weight percentage* of silica, but they do

have the same *molecular ratio* of SiO_2 to basic oxides. The fact that the *amount of oxygen* is used as a basis of calculation takes care of valence changes in the metal radical, since oxygen has a constant valence of two. Thus an aluminum bisilicate would have the formula:

$$Al_2Si_3O_9 \quad \text{or} \quad Al_2O_3 \cdot 3SiO_2$$

Let us now calculate the silicate degree of the Noranda slag in Table 5 for one more illustration. The analysis as given does not add to quite 100 per cent because some of the minor elements are not reported. We shall calculate the silicate degree on the basis of the analysis of the five principal oxides as given. One pound of this slag will contain

0.379 lb of SiO_2
0.085 lb of Al_2O_3
0.467 lb of FeO
0.017 lb of CaO
0.019 lb of MgO

The weight of oxygen in the acid $= 0.379 \times \frac{32}{60} = 0.202$ lb.

The weight of oxygen in the bases is

Al_2O_3	$0.085 \times \frac{48}{102}$	$= 0.040$ lb
FeO	$0.467 \times \frac{16}{71.8}$	$= 0.104$ lb
CaO	$0.017 \times \frac{16}{56}$	$= 0.005$ lb
MgO	$0.019 \times \frac{16}{40.3}$	$= 0.008$ lb
	Total	0.157 lb

$$\text{Silicate degree} = \frac{0.202}{0.157} = 1.29$$

The silicate degree indicates the relative acidity of a given slag, and the comparison of slags by means of the silicate degree is actually based on the assumption that equivalent amounts of one base may be substituted for another without affecting the properties of the slag. This, of course, is not true — calcium silicate and ferrous silicate are quite different substances — but within the rather narrow limits of

composition found in copper slags, the silicate degree is a useful criterion.

Most copper slags approach the composition of a sesquisilicate (silicate degree = 1.5) as an average. The silicate degree may range from 1.0 to 2.0 but seldom passes either limit. The calculated silicate degrees are listed in Table 5; for these slags the values lie between 1.07 and 1.75.

Some Properties of Copper Slags. Copper smelting slags are black and have either a stony or a glassy appearance; slags which are rapidly cooled are glassy. As we have already noted, these slags are fairly heavy (specific gravity 2.8 to 3.8).

Copper slags are usually discharged from the furnace at 1100° to 1300° C, and the slag must be molten and free-running at this temperature. The exact temperature of the melting point of different slags is difficult to obtain. The *formation temperature* of a given slag is probably of more importance than its actual melting point; this formation temperature is the temperature at which molten slag will form from the mechanical mixture of solid oxides on the charge. It is always higher (usually 100° to 300° C) than the melting point determined on a sample of the formed slag, and the coarser the pieces of slag-forming oxides the higher the formation temperature will be. In an operating furnace, the actual mechanism of slag formation is essentially the *dissolving* of the oxides ("earthy" material) in the pool of slag which is always maintained.

As a general rule the more acid slags have a greater viscosity. Basic slags are "thin" and fluid; acid slags are "thicker" or more viscous. Basic slags are more corrosive to furnace refractories than acid slags.

Copper slags as discharged from the furnace will contain from 500 to 600 Btu of sensible heat per pound of slag; for the heat balance in Table 4, a figure of 579 Btu per pound was used. As is true of mattes, this value depends upon the temperature of discharge and the composition of the slag.

Copper Losses in Slag. As the slag from the smelting furnace is discarded and any copper contained in it is lost, the question of the manner in which copper is carried in the slag is of great importance. There are three principal ways in which copper can be carried out in slag, viz.:

1. Oxidized copper (oxides, carbonates) form copper silicates and ferrites which are soluble in the molten silicate slag.

2. Silicate fusions appear to have a slight but definite solvent power for sulfides, so that some of the matte may be actually dissolved in the slag.

3. Small particles of matte may be mechanically entrained in the slag and swept out of the furnace with the slag stream before they have an opportunity to settle.

In a recent paper on this subject, Jackman and Hayward[17] report that most of the copper found in reverberatory slags is in the form of small irregular pellets of sulfides; metallic copper may be present at times, but it is of minor importance. They found no proof of the presence of copper silicate in the slags studied.

It appears that when there is little or no oxidized copper on the charge, the copper lost in the slag is largely in the form of sulfide pellets. These can be identified in the solidified slag, but it may be noted that this fact does not indicate whether they were dissolved or mechanically entrained, because it is likely that sulfides which were soluble in the liquid slag would separate out when the slag solidified. Probably both factors contribute to the presence of sulfides in slag.

The presence of oxidized copper on the charge usually leads to higher slag losses, because unless this copper can be either sulfidized or reduced to metallic copper it will dissolve in the slag. At Roan Antelope (see Table 5) the concentrate carried 2.40 per cent Cu_2O, and the original slag from the smelting contained 2.25 per cent copper, largely because of the slagging of the copper oxide. Later 3.0 per cent by weight of fine coal was added to the concentrate before charging; this served to reduce the oxide to metallic copper and lowered the slag assay to 1.20 per cent copper.[18]

As a general thing, the copper content of reverberatory slags will range from 0 20 to 0.60 per cent; in a few slags it will go above 1.0 per cent. The copper assay of slag is roughly proportional to the per cent of copper in the matte — the richer the matte the higher will be the copper content of the slag. This would be expected from the discussion given above. To illustrate this point the data in Table 5 have been plotted in Figure 20. The copper content of the Roan Antelope slag is higher than might normally be expected even with such high-grade matte; two contributing reasons for this are (1) the presence of oxidized copper in the concentrate, and (2) the viscosity of the high-alumina slag produced.

The total copper loss in slag depends upon both the copper content of the slag and the amount of slag produced (*slag volume*), and of course both are important. Roan Antelope, for instance, finds it more profitable to make a slag of 1.20 per cent copper (Table 5) than to

[17] Jackman, R. B., and Hayward, C. R., Forms of Copper Found in Reverberatory Slags: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 111, 1933.

[18] Wraith, C. R., op. cit., p. 215.

lower the copper content by changing the slag composition. The use of more limestone flux would make the slag less viscous and would decrease its copper assay, but the volume of slag would increase. Wraith[19] states that in this instance the amount of copper lost in the viscous slag of high copper content and low volume is less than is lost in a fluid slag of low copper content and larger volume.

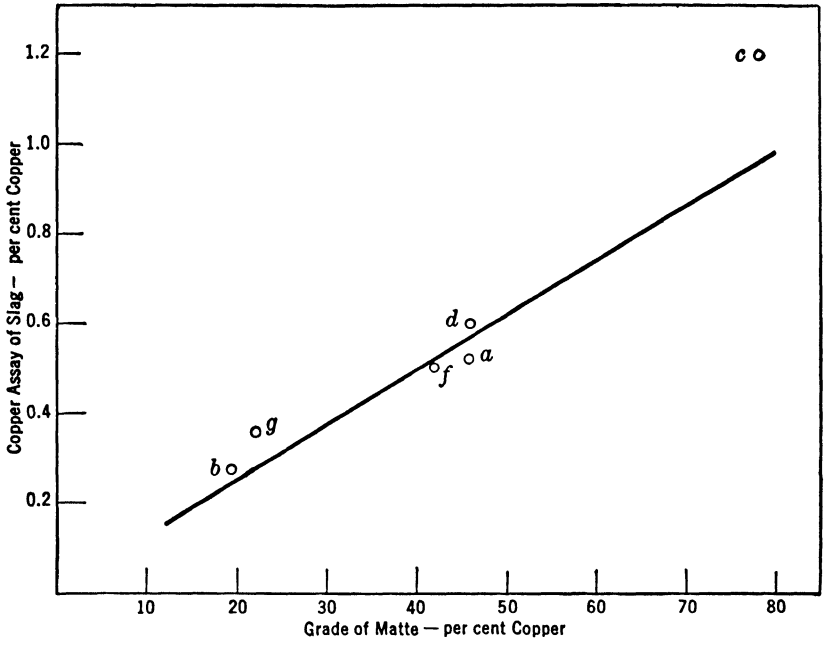


FIG. 20. Variation of the Copper Assay of Slags with the Grade of the Matte.

Letters refer to the plants in Table 5

Fluxes. In order that the slag shall have the desired composition it is often necessary to add *flux* to the furnace charge; sometimes the flux is charged directly into the reverberatory, but when the material is roasted the flux may be added at the roasters. The most satisfactory way of fluxing a reverberatory charge is to mix ores and concentrates of different composition so that the gangue minerals are present in the correct proportion to form a suitable slag. Thus Noranda[20] uses a siliceous copper ore to flux the high-iron ores and calcines; this combination produces a suitable slag (Table 5) without the use of any other flux. Very often, however, it is necessary to use a *barren flux,* i.e., a material which carries no copper. The disadvantages of

[19] Wraith, C. R., op. cit., p. 215.

[20] Boggs, W. B., and Anderson, J. N., op. cit., p. 165.

this are obvious, because every ton of barren flux charged displaces a ton of copper-bearing material and therefore decreases the smelting capacity for calcine or concentrate and increases the slag volume. Be that as it may, in most cases it is necessary to add a certain amount of barren flux to obtain a proper slag composition. The most common flux used is limestone, which contributes CaO to the slag. The other important oxides (FeO, SiO_2, and Al_2O_3) are usually present in the smelting charge. In modern plants there is seldom a deficiency of FeO, and when SiO_2 is needed it is usually supplied as siliceous ore; Al_2O_3 is never added intentionally, as it makes the slag viscous, and is generally an undesirable constituent of slags.

Slag Disposal. The liquid slag tapped from the furnace may be either (1) collected in slag pots which are then hauled to the slag dump where the slag is poured or (2) allowed to flow directly into a large volume of water in a launder; the slag is granulated and sluiced to the dump. Slag may be used occasionally for such purposes as furnace foundations, but practically all slag is sent directly to the dump and discarded. Some of the slags produced by the smelting of oxide ore in the southwestern United States in the early days (1881–1890) contained enough copper (2.5 to 4.5 per cent) so that it later became possible to resmelt them to recover the contained copper. Present-day copper slags are probably too lean to be resmelted, but when ore supplies become exhausted it may be necessary to find some way to recover the copper in these slag dumps — possibly by leaching or concentration, if the copper is in such a form as to make these methods feasible.

Charge Calculations. We shall consider a simplified example to illustrate the method used in proportioning the various components of the reverberatory furnace charge so that when the charge melts, slag and matte of the desired composition will be formed. We shall confine our illustration to one particular type of calcine, namely a high-iron, low-copper material which will be smelted to a low-grade matte. The smelting of high-grade calcine, or wet concentrate, would require a different type of charge, but the method of calculation would be the same.

Materials to be charged to the furnace are usually stored in bins from which weighed amounts can be drawn as desired; the exception to this is hot calcine, which usually comes directly from the roasters. Proper amounts of each material are then either transported to the furnace in charging cars or else fed onto the conveyor belt system which serves the furnace. In some plants the charge is *bedded*, i.e., a large pile of material is built up containing layers of the different

constituents of the charge in their proper proportions; this material is then excavated in such a way that those proportions are maintained and is charged into the furnace.

EXAMPLE 1

Let us assume that we have available a low-copper, high-iron calcine of the following composition:

	Per Cent
Cu	8 0
S	12.7
SiO_2	17.0
Al_2O_3	3.0
Fe	46.7

Also there is available an ore containing quartz in large quantity, pyrite, and chalcopyrite. The composition of this ore is as follows:

	Per Cent
Cu	1.0
S	17.2
SiO_2	65.0
Al_2O_3	2.0
Fe	14.8

Pure limestone can be secured for fluxing purposes if needed Of the sulfur in the calcine we can expect a 10 per cent loss by volatilization, and 50 per cent of the sulfur in the siliceous ore will be volatilized. Let us neglect dust losses and copper losses in the slag; we shall also assume that the matte will consist of FeS and Cu_2S.

Let us first calculate the relative amounts of the two materials we should use to secure a 20 per cent matte.

Assume

100 lb of calcine
x lb of siliceous ore

Then the total copper will be $8.0 + 0.010x$ lb and total sulfur to the matte will be

$$0.9(12.7) + 0\,5(0.172x) = 11.4 + 0.086x$$

A 20 per cent matte will contain (Chapter II)

	Per Cent
Cu	20.0
S	32.3
Fe	47.7

Therefore

$$\frac{8.0 + 0.010x}{11.4 + 0.086x} = \frac{20.0}{32.3}$$

$$12.9 + 0.01615x = 11.4 + 0.086x$$

$$x = 21.5$$

Hence the charge should consist of 21.5 lb of the siliceous ore for every 100 lb of calcine.

Let us see what sort of slag analysis this charge would give

Total weight of copper on charge = 8 0 + 0.010(21 5) = 8.215 lb

$$\frac{8.215}{y} = \frac{20}{47.7} \text{ where } y = \text{no. of lb of iron to matte}$$

$$y = 19.6$$

Total iron to slag = 46.7 + (0.148 × 21.5) − 19.6 = 30.3 lb and the slag will be made up as follows:

FeO	= 30 3 × $\frac{72}{56}$	= 39 0 lb	= 53.1%
SiO_2	= 17.0 + (0.65 × 21.5)	= 31.0 lb	= 42.2%
Al_2O_3	= 3.0 + (0.02 × 21.5)	= 3.4 lb	= 4 6%
		73.4 lb	99.9%

The weight of the matte would be:

$$\frac{8\ 125}{0.20} = 40.63 \text{ lb}$$

and the matte fall

$$\frac{40\ 63}{121\ 5} \times 100 = 33.5\%$$

If we have only these two substances to smelt, and if it is desired to have a 20 per cent matte, then only one combination can be used, namely the one arrived at previously. However, this combination yields a rather acid slag Let us calculate the silicate degree.

$$O_2 \text{ in } SiO_2 = 0\ 422 \times \frac{32}{60} = 0\ 225 \text{ lb}$$
$$O_2 \text{ in FeO} = 0.531 \times \frac{16}{72} = 0.118 \text{ lb}$$
$$O_2 \text{ in } Al_2O_3 = 0.046 \times \frac{48}{102} = 0.022 \text{ lb}$$

Total O_2 in bases = 0.118 + 0.022 = 0.140

$$\text{Silicate degree} = \frac{0.225}{0.140} = 1\ 61$$

This slag might be too acid; this could be remedied by (1) adding a little limestone flux, or (2) cutting down the amount of siliceous ore used. The latter remedy would affect the grade of the matte somewhat, but that would probably be more desirable than to add a barren flux. The Al_2O_3 content is low enough so that it is probably unnecessary to add lime; if, however, there were more Al_2O_3 on the charge, the addition of some lime would probably be called for. Let us cut the amount of siliceous ore to 18 lb and see how this affects the grade of matte and the slag analysis.

The total copper on the charge will now be

$$8.0 + 0.01(18) = 8.18 \text{ lb}$$
$$8.18 \times \frac{32}{128} = 2.04 \text{ lb of S as } Cu_2S \text{ in matte}$$

Total weight of sulfur to matte will be

$$11.4 + (0.086 \times 18) = 11.4 + 1.55 = 12.95 \text{ lb}$$
$$12.95 - 2.04 = 10.91 \text{ lb of S as FeS in matte}$$
$$10.91 \times \frac{88}{32} = 30.0 \text{ lb of FeS in matte}$$

Total weight of matte = 30.0 + 8.18 + 2.04 = 40 22 lb

$$\frac{8.18}{40.22} \times 100 = 20.3\%, \text{ grade of matte}$$

$$\frac{40\ 22}{118} \times 100 = 34.1\% = \text{matte fall}$$

The change in the amount of fluxing ore alters the matte fall and grade of matte only slightly Let us see what happens to the slag

Total iron on charge = 46.7 + (0.148 × 18) = 49.36 lb
Iron to matte = 10 91 × $\frac{56}{32}$ = 19 1 lb

49.36 − 19 1 = 30.26 lb of Fe to slag

FeO	= 30.26 × $\frac{72}{56}$	= 39 0 lb	= 54.8%
SiO_2	= 17.0 + (0 65 × 18)	= 28 7 lb	= 40 4%
Al_2O_3	= 3 0 + (0.02 × 18)	= 3 4 lb	= 4.8%
		71.1 lb	100.0%

The silicate degree of the new slag would be

O_2 in SiO_2 = 0 404 × $\frac{32}{60}$ = 0.215 lb
O_2 in FeO = 0 548 × $\frac{16}{72}$ = 0 122 lb
O_2 in Al_2O_3 = 0 048 × $\frac{48}{102}$ = 0 023 lb

Total O_2 in bases = 0 122 + 0.023 = 0.145

$$\text{Silicate degree} = \frac{0\ 215}{0.145} = 1\ 48$$

This is probably a more suitable slag, and it might be advisable to make the slag still more basic and bring the silicate degree down to 1.2 or 1.3, it is evident from the calculations made so far that the amount of the fluxing ore could be decreased considerably without affecting the matte grade very much

Finally, let us determine what the grade of the matte would be if we were to smelt the calcine alone, i e., use an acid flux of pure silica, so that no copper or sulfur would be introduced from the flux.

Weight of Cu = 8.0 lb
Weight of S in Cu_2S = 8.0 × $\frac{32}{128}$ = 2.0 lb
Total S to matte = 11.4 lb
S to FeS = 11 4 − 2 = 9 4 lb
Weight of FeS = 9.4 × $\frac{88}{32}$ = 25 8 lb
Total weight of matte = 25.8 + 8.0 + 2.0 = 35.8 lb

$$\frac{8.0}{35.8} \times 100 = 22.3\% = \text{grade of matte}$$

Hence the maximum grade of matte possible would be 22.3 per cent Cu; if the volatilization loss of sulfur were 10 per cent, as we have assumed, no higher-grade matte could be produced from this calcine.

The calculations and assumptions made so far illustrate the method used in proportioning the charge to a reverberatory smelting furnace;

these have been intentionally simplified so that the principles involved might not be obscured by too much arithmetic. In an actual problem, the calculations would be longer and more tedious because of a number of factors which we have omitted. Let us briefly consider some of these.

1. An actual ore or calcine would show more constituents than we have indicated; these would include such substances as CaO, MgO, and MnO, which would go to the slag; possibly some zinc and lead which would be distributed between the matte and slag; small amounts of antimony and arsenic which would be partly volatilized and partly dissolved in the matte; and tin, cobalt, nickel, etc, and precious metals, which would go into the matte. Small amounts of basic oxides may be counted as FeO or CaO; thus MnO may be figured as if it were FeO, and as the molecular weights are almost the same (70.93 and 71.84), it may be assumed that these two bases replace one another pound for pound. The molecular weight of CaO is 56 against 40.3 for MgO, so that one pound of MgO is chemically equivalent to $56.0/40.3 = 1.39$ pounds of CaO. Thus a flux containing 30 per cent CaO and 10 per cent MgO could be considered as containing $30 + (10 \times 1.39) = 43.9$ per cent *equivalent* or *summated* lime, which is often written ΣCaO.

2. Not only would the analysis of each component of the charge be more detailed than we have indicated, but there would be other materials charged besides calcines and flux. Possibly there might be two or more different calcines, some direct smelting ore, and cement copper precipitate. Certainly there would be a considerable tonnage of reverts of one kind or another. With such a low-grade matte there would be a large tonnage of molten converter slag to be returned to the reverberatory for removal of its copper content. This converter slag would contain all the iron in the matte in the form of an iron silicate slag formed in the converters; the silica content of this slag would probably be lower than that desired for the reverberatory slag, so that it would be necessary to add more siliceous flux than that required for the iron in the calcines. In addition to the converter slag, flue dust, matte skulls from the ladles, custom ores, refinery products, etc, would have to be charged into the reverberatory from time to time. The effect of all these materials upon the matte and slag would have to be considered.

3. If powdered coal were used for fuel, the coal ash would enter the charge and become part of the slag. Part of this ash would fall directly on the charge and part of it would pass into the flue to return eventually with the flue dust.

4. With a low-grade charge such as this, the slag volume would be high, and the slag would have to be as low in copper as possible. Probably, in a case like this we would expect the slag to run not over 0.3 per cent copper. The fact that the matte is of low grade will insure a low-grade slag provided the slag is fluid enough; this probably would be the factor which determines whether or not a lime flux would be used, for the lime would not be added unless the values saved by making a cleaner slag were greater than the cost of diluting the furnace charge with barren flux. Taking the figures from the first part of the example, we find that with a slag assaying 0.2 per cent Cu, we would lose $73.4 \times 0\,002 = 0\,15$ pound of copper out of 8.125 pounds, or a loss of 1.84 per cent; with a slag containing 0.6 per cent Cu the loss would rise to $73.4 \times 0.006 = 0.44$ pound, or 5.4 per cent of the total copper on the charge.

5. We have assumed that all the iron on the charge becomes FeO and is slagged as such. With such a high-iron charge, it is certain that there would be a good deal of magnetite entering the furnace from both the calcine and the converter slag. If this were not reduced to FeO by the sulfides on the charge, part of it would settle through the low-density matte and accumulate on the furnace bottom and the rest would be removed with the matte and slag. The amount and disposition of the magnetite would be of great importance in the operation of the furnace.

6. There are several ways[21] of calculating furnace charges, ranging from a precise and formal algebraic method to a simple cut-and-try procedure. The latter is probably most commonly used, as the problem is usually one of making slight changes in existing charges rather than calculating an entirely new charge.

7. Let us consider briefly how the reverberatory furnace practice is tied up with other operations. The calcine is the type that would result from the roasting of ore or concentrate high in pyrite, pyrrhotite, or both. Unless the ore minerals were unusually fine grained it should be possible to mill such an ore to give a much higher grade of concentrate by rejecting a large part of the iron sulfides; the low copper content of this calcine suggests that (1) the ratio of concentration is probably low — perhaps the milling is designed simply to reject gangue minerals and remove the bulk of the sulfides — or (2) a considerable amount of heavy sulfide ore goes directly to the roasters without milling. This would indicate that copper is not the only metal to be recovered but that there is considerable gold associated with the

[21] Butts, Allison, Textbook of Metallurgical Problems, McGraw-Hill Book Co., New York, 1932.

iron sulfides. The collecting of the gold would require a reasonably high matte fall.

In other words, this particular example illustrates the type of smelting we should expect for a heavy sulfide copper-gold ore. If copper was the only valuable mineral we would expect a different method of treatment, either (1) the bulk of the iron sulfides would be rejected in the mill to give a richer feed to the smelter or (2) a method would be devised to recover the iron and sulfur in the pyrite as well as the copper. It would also be possible to make a high-copper concentrate from an ore of this type if it were feasible to recover the gold from the sulfides in the mill tailing — for example by regrinding and cyanidation.

With such a heavy fall of low-grade matte a relatively large converter installation would be required to provide sufficient capacity. There are three stages at which iron and sulfur can be rejected — (1) in the mill, (2) in the roasters and reverberatory, and (3) in the converters, and the process should be adjusted so that the combination of these produce the desired results with the minimum total cost. Of course the practice should be adjusted so that all existing equipment (roasters, reverberatories, and converters) operates at full capacity.

If the siliceous ore contained considerable gold, this would be another incentive to make a large amount of low-grade matte because this would consume more of the siliceous ore both in the reverberatory and in the converters. Thus the mining practice would have its effect on smelting, for the smelting practice might be altered as the supply of the siliceous ore increased or decreased.

The roasting practice will depend upon a number of factors. It may be desirable under some conditions to secure a low-sulfur dead roast which yields a relatively cool calcine, or it may be preferable to remove less sulfur and produce a "hot" calcine (in which the sulfides are still burning) and thus introduce more heat into the reverberatory. The amount of iron oxides formed in roasting must also be considered, for if the calcine is too highly oxidized there may be too much magnetite formed in the reverberatory.

Thus it may be seen that the operation of the reverberatory depends upon a number of factors — roaster and converter capacity, milling methods, mining practice, metal prices, and fuel costs, to name only a few. Changes in any of these may bring about corresponding changes in smelting practice.

Examples of Practice. We have already cited figures on fuel consumption, slag and matte composition, and furnace construction at several plants. Before we leave the subject of reverberatory smelt-

ing let us briefly recapitulate the essential features of the practice at two smelters which employ different smelting techniques.

Flin Flon.[22] There is one reverberatory furnace (Fig. 8) at the Flin Flon smelter in Manitoba. The furnace is 104 feet 3 inches by 25 feet 6 inches, outside measurements, and 101 feet 3 inches by 21 feet 6 inches inside the brickwork. The bottom is built of crushed silica, side walls of silica brick with a magnesite brick insert in the smelting zone, and the arch partly of silica brick (sprung arch) and partly of magnesite brick (Detrick suspended arch). The furnace has a hammerhead design, and the gases turn at right angles in both directions at the flue end into two 768-horsepower Stirling waste-heat boilers.

The calcine and flue dust are fed by means of feed hoppers which discharge through pipes along the side walls near the firing end. Matte is tapped through Anaconda-type water jackets set in one side wall; a cast-copper plate is set in each water jacket, and in the center of this plate is a magnesite brick 5 inches square and 2½ inches thick. A 2-inch hole through this brick is the taphole. Three water jackets are provided, but only the two nearest the burner wall are used. Slag is skimmed from the furnace through the front wall; it runs through a 12-foot launder into 225-cubic-foot cast-steel slag pots which are hauled to the slag dump. Converter slag is charged into the furnace through a launder set in the firing end above the burners.

Pulverized coal is used as fuel, and there are four burners. The charge consists principally of calcine, plant reverts, and liquid converter slag. The charge requires a siliceous flux and most of this enters the circuit at the roasters and converters. The furnace charge is low in copper, and a low-grade matte is produced; the analyses and amounts of the various smelter products are given in Table 6. At the end of 1934 the furnace was handling 1040 tons of solid charge per furnace day.

Roan Antelope.[23] The Roan Antelope smelter at Luanshya, Northern Rhodesia, has one reverberatory furnace which is 100 feet by 25 feet, inside dimensions. Construction is silica brick throughout. Side walls are 2 feet thick and 7 feet high. The arch is 18 inches thick for a distance of 65 feet from the burner wall and 15 inches thick over the remainder of the furnace. A Stirling waste-heat boiler is connected to the uptake of the furnace, and this boiler utilizes 52 per cent of the heat value in the coal burned.

[22] Ambrose, J. H., The Flin Flon Copper Smelter: Canadian Min. Met Bull. 281, p. 402, September 1935.

[23] Wraith, C. R., Smelting Operations at Roan Antelope Copper Mines, Limited: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 202, 1933.

TABLE 6

FLIN FLON

Typical Assays

	Cu	Zn	Pb	Fe	SiO_2	Al_2O_3	MgO	CaO	S
Calcine	8 00	4.1	0.7	31.0	20.9	2.3	4.6	1.4	13.3
Roaster flue dust	7.43	4.2	...	28.5	18.3	...	...	...	....
Roaster Cottrell dust	6.86	4.2	...	23.6	20.0	...	...	...	...
Converter slag	1.50	...	...	39.8	30 0	4 4	1.0	1.7	...
Flux	....	...	...	3.0	74.0	12.5	0.6	3.5	...
Reverberatory slag	0.36	4.0	0.2	32.1	36.5	5.1	4.7	1.7	0.4
Matte	22.00	4.2	1.6	41.4	...	...	...	...	24.5

Weight of Material Charged During 1934 (325 furnace days)

Roaster products	252,453 tons	
Other pay material	6,490	
Recharged material	11,377	
Flux direct	66	
Total solid charge		270,386 tons
Liquid converter slag		162,522
Total solid and liquid charge		432,908 tons
Coal burned	32,019 tons	
Coal, per ton of solid charge	11 8 per cent	
Matte produced	126,284 tons	
Matte fall, per cent of solid charge	46.7 per cent	
Slag produced	251,469 tons	
Slag produced, per cent of total solid and liquid charge	58 7 per cent	

This is a wet-charged furnace, and the principal constituent of the feed is a high-grade flotation concentrate which is primarily a mixture of chalcocite (Cu_2S) and a shale gangue. Limestone is used as flux. The charge is fed into the furnace through 6-inch pipes which extend vertically downward from the overhead hoppers into holes in the roof adjacent to the side walls. There are 12 charge pipes on each side spaced at 5-foot intervals. Slag is skimmed through an opening in the front wall of the furnace, and the sill of the skimming door is 24 inches above the lower matte taphole, and the surface of the slag may be raised 6 to 12 inches by means of temporary clay-mud dams built across the skimming openings. Molten slag is laundered into

200-cubic-foot cast-steel ladles in which it is hauled to the dump. There are two tapholes for matte, one directly above the other. The tapping block consists of a magnesite brick cast in a block of copper and is set in the side of the furnace 75 feet from the burner wall; two 3-inch holes are drilled through the brick at 9-inch centers. These holes are sealed with a clay dolly in the usual manner; they are usually opened by burning out the hole with an oxygen lance; sometimes a tapping bar is used. In order to prevent the formation of heavy skulls of frozen matte in the ladles it is desirable to tap the matte as quickly as possible, and when the matte does not flow as rapidly as desired from one taphole, both are opened. As a rule a 22-ton matte ladle can be filled in less than 10 minutes.

TABLE 7

ROAN ANTELOPE

Typical Assays

	Cu	SiO_2	FeO	CaO	Al_2O_3	MgO	S
Concentrate	58 67	13 4	3 90	0 10	4 12	0 70	16 02
Limestone	. .	0.6	0 17	52 30	1 02	2 04	.....
Matte reverts	78 73	.	0.58(Fe)	..	...	....	19.52
Reverberatory flue dust	31.22	19.82	4.59	3.13	11 37	0.35	5.7
Converter flue dust	73.29	0 88	0 69	0 22	1 32	....	11.41
Reverberatory slag	1.20	47.3	13.7	11 4	14.7	2 9	.....
Matte	78.73	0 14	0 58(Fe)		. ...	. .	19.52

Operating data, February, 1933

Dry charge per furnace day	340	tons
Coal consumed per day	52.7	do.
Fuel, per cent of charge	15.5	per cent
Flux, per cent of concentrate	6.5	do.
Flux, per cent of charge	5 09	do.
Slag, per cent of charge (excluding reverts)	25.5	do.
Slag, per cent of charge (including reverts)	21 22	do.
Silicate degree of slag	1.704	
Matte fall, per cent of charge	70.0	per cent

The matte reverts amount to about 3.3 per cent of the weight of the charge. Flue dust is added at irregular intervals and is not considered part of the regular charge.

The fuel used is pulverized coal and there are four burners. The analysis and relative amounts of material charged and produced are given in Table 7. It is interesting to contrast these with the figures

in Table 6. Roan Antelope slag differs from most other reverberatory slags, as we have noted (Table 5), in that it is higher in Al_2O_3 and SiO_2 and lower in iron; the copper assay of the slag is high, but the slag volume is low. The large amount of shale gangue accounts for the high Al_2O_3 content of the slag.

The charge is high in copper, the matte is almost pure Cu_2S, and the matte fall is very high. As there is practically no iron in the matte, there is no converter slag to return to the reverberatory.

The two examples cited were chosen because they illustrate what might be called two extremes in reverberatory practice. One smelts a low-grade charge high in iron to produce a low-grade matte, and the other treats a high-grade charge and produces an exceptionally high grade matte. Practice at most other plants will generally lie somewhere between these limits, although there are smelters which produce matte as low in copper as the Flin Flon matte or lower.

We have devoted the major part of this chapter to reverberatory matte smelting for the reason that this is by far the most prevalent type of copper smelting. We shall now consider briefly the other types of copper smelting that are used.

MATTE SMELTING IN THE BLAST FURNACE

Introduction. For many years the blast furnace had been widely used for matte smelting, but since 1910 it has gradually been displaced by the reverberatory. This change has been largely due to the fact that more and more copper has been produced in the form of finely divided concentrate, which can be more readily handled in the reverberatory furnace. At Anaconda, for example, both blast furnaces and reverberatories were used from the beginning, but as the milling methods improved, the superiority of the reverberatory became evident; in January 1919 the blast furnaces were shut down and the plant dismantled.

The Blast Furnace; General. The blast furnace is a shaft furnace and contains a vertical column of the charge to be smelted; as the charge is smelted down the liquids formed settle to the bottom, from where they can be removed; new material is charged at the top in quantity sufficient to keep the charge level relatively constant, and as material is fused at the bottom of the column, the column descends and more new material is charged on top.

The fuel for the blast furnace is almost invariably coke, and it is charged from the top along with the ore and flux. In the side walls of the furnace are located the *tuyères* through which the air or *blast* enters the furnace; the tuyères are always located near the bottom of

the furnace but are high enough above the bottom so that any liquids which collect in the furnace can never rise above the tuyère level.

Blast furnaces have different shapes; iron blast furnaces are circular with the tuyères spaced evenly around the circumference, whereas lead and copper blast furnaces generally have rectangular cross-sections with tuyères along both sides but not on the ends. The walls of iron blast furnaces are constructed of refractory brick; non-ferrous blast furnaces usually have steel water jackets for the walls of the lower portion, and the upper walls may be constructed of refractory brick or they may consist of a second tier of water jackets. Blast furnaces may have an *internal crucible* directly beneath the tuyères where the liquids collect and separate into layers, or the liquids may flow out of the furnace together directly beneath the tuyères and pass into an *external crucible* or *forehearth,* where the separation takes place. Copper blast furnaces for matte smelting usually have external crucibles.

Before describing the copper blast furnaces, let us consider some of the general characteristics of blast furnace smelting.

1. The hottest part of the blast furnace is the region just above the tuyères, or the *smelting zone.* The oxygen in the blast combines with the fuel in the smelting column as soon as it enters the furnace, and it is here that the heat of combustion is liberated In iron blast furnaces the air is preheated before entering the tuyères, but non-ferrous furnaces usually employ a cold blast.

2 The diameter of a circular furnace, or the width of a rectangular furnace, is determined by the distance the air blast will penetrate the charge. It is essential that the rising gases be distributed evenly throughout the cross-section of the column.

3. The smelting action in a blast furnace is essentially a reaction between the solids in the charge column and the stream of gas formed by the combustion at the tuyères; the nature of this action will be determined by the make-up of the solid charge and the composition of the gases. In reduction smelting (iron, lead, and oxidized copper) an excess of coke is used and the combustion gases therefore contain large amounts of CO and the furnace is said to have a *reducing atmosphere;* this plays an important part in reducing the oxides to the elemental metal. When a small amount of coke and an excess of air are used the combustion products contain free oxygen and the furnace has an *oxidizing atmosphere;* the gases then act to oxidize the solid matter in the charge. The relative amounts of fuel and air used must be adjusted according to the nature of the smelting done.

4. Sufficient oxidizable material (carbonaceous fuel, sulfides, or both)

must be present before the tuyères so that the heat generated will be sufficient to raise the temperature well above the formation temperature of the slag. Slag and either reduced metal or unoxidized sulfides (matte) become liquid in the smelting zone and trickle down to collect in the crucible.

5. Part of the heat generated in the smelting zone is carried out as sensible heat in the molten products; the remaining heat is carried upward in the hot gases. A good deal of this heat is absorbed by the relatively cold solids in the upper part of the charge, so that the temperature of the solids rises as they descend in the furnace, and the temperature of the gases decreases as they rise toward the furnace top. In reducing smelting a part of this heat is absorbed by endothermic reactions such as (for reduction smelting of copper oxides)

$$CuO + CO \rightarrow Cu + CO_2 - 33{,}140 \text{ Cal}$$
$$Cu_2O + CO \rightarrow 2Cu + CO_2 - 28{,}040 \text{ Cal}$$

Also if carbonates are present either as ore minerals or as flux, they will decompose endothermically, viz.:

$$CuCO_3 \rightarrow CuO + CO_2 - 6{,}200 \text{ Cal}$$
$$CaCO_3 \rightarrow CaO + CO_2 - 39{,}900 \text{ Cal}$$

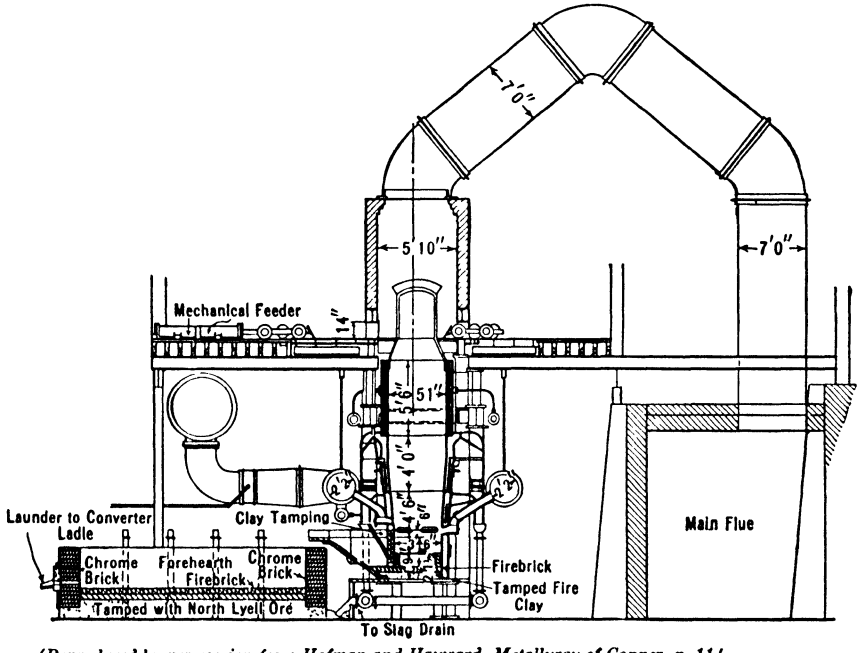
The solids and gases at the top of the smelting zone should be cool; when the upper part of the column becomes abnormally hot, the condition is known as *overfire*. Overfire causes the charge to soften while still high up in the furnace and increases the formation of *accretions* which adhere to the furnace walls and interfere with the proper descent of the charge.

6. The fact that blast furnace smelting is essentially the reaction between a column of solids and an uprising current of hot gas imposes certain limitations on the physical properties of the charge. In the first place the charge must not contain much fine material, for two reasons: (1) A good part of the fine material would not stay in the column but would be immediately carried out of the furnace by the gas current, and (2) the fine material that did get into the column would tend to pack and form regions through which the gases would not pass, and thus the gas current would "channel" and leave portions of the charge cold and unsmelted.

Also the solid particles on the charge must not be too large because the reaction with the gases can take place only at the surface, and large lumps would therefore smelt very slowly. The porous sinter produced by the Dwight-Lloyd machine makes ideal blast furnace

feed because the pieces can be penetrated by the gases and also because the incipient fusion in the Dwight-Lloyd machine gives a " presmelted " or " predigested " material which smelts readily. Coke is the ideal blast furnace fuel because it is strong enough not to crush under the weight of the charge column and because its porosity aids in rapid combustion. Charcoal is occasionally used for blast furnace smelting; although porous, it is not as mechanically strong as coke and is generally much more expensive. Non-porous fuels such as wood or lump coal burn much too slowly to make suitable blast furnace fuel. Some experiments have been made in which powdered coal was blown in through the tuyères, but this practice has not been adopted to any extent.

With these general operations in mind, let us turn our attention to the copper blast furnace for smelting to matte — this will be oxidizing smelting. Later we shall mention the reduction smelting of oxidized copper ores in the blast furnace.



(Reproduced by permission from Hofman and Hayward, Metallurgy of Copper, p. 114, McGraw-Hill Book Co., New York, 1924)

FIG. 21. Section Through a Copper Blast Furnace.

The Copper Blast Furnace. Figure 21 is a cross-section of a copper blast furnace and Figure 22 shows another furnace in construction. Most furnaces have a height and width of the same order of magnitude

as those shown in Figure 22. These furnaces, however, may vary considerably in length. As a rule the width at the tuyères will range from 42 to 56 inches, and the length from 266 inches to 1044 inches. This last figure (87 feet) represents the length of a furnace used at Anaconda previous to 1918; this was the largest copper blast furnace in the world.

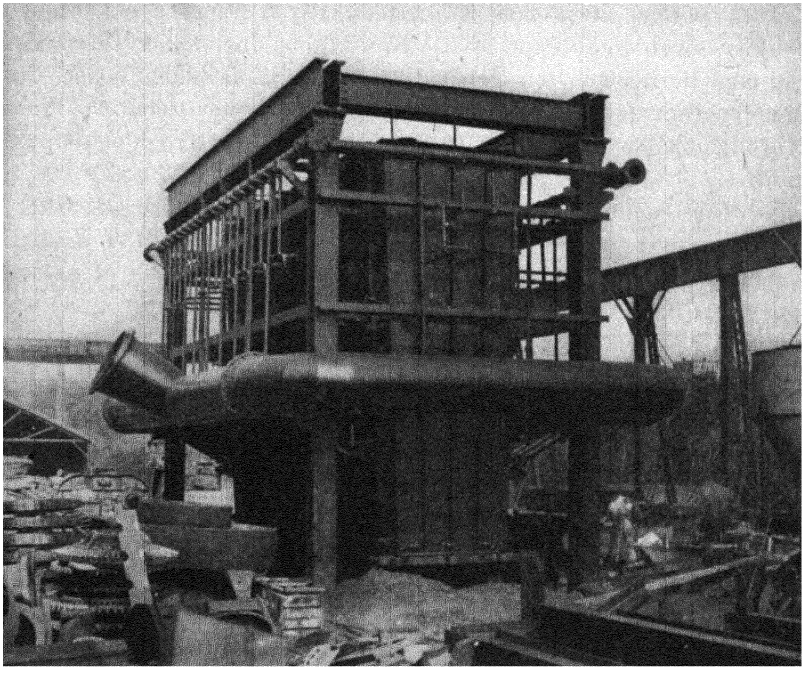


FIG. 22. Copper Blast Furnace Under Construction.

These furnaces have vertical ends and sloping or *boshed* sides; the crucible is shallow and the slag-matte mixture is discharged through a raised spout which traps the blast and keeps it from blowing out of the taphole. The liquids usually flow continuously from the spout into the refractory-lined forehearth; slag overflows the forehearth and matte is tapped from the bottom (Fig. 21).

The side walls of the furnace are made of hollow steel or cast-iron water jackets through which water is kept circulating. The pipes which circulate this cooling water can be seen in Figure 22. The tuyères pass through the side walls and are connected by means of tuyère pipes to the large *bustle pipe,* which takes the air from the blowing engines. The top is closed and connected with the flue system

for the removal of the waste gases. Side doors in the upper part of the furnace are used for charging. The furnace shown in Figure 22 has the customary two tiers of water jackets. The water jackets are usually surmounted by a brick superstructure which contains the charging doors and confines the gases until they enter the flue.

A depth of charge column of 10 to 14 feet is commonly used, and the blast pressure will range from 10 to more than 60 ounces per square inch. The tuyères usually have circular openings which range from 2 to 6 inches in diameter, and there may be from 24 to 150 tuyères to a furnace, depending upon the length of the furnace and the size of the tuyère openings.

Chemistry of Matte Smelting. The reactions which take place in the blast furnace depend upon the nature of the charge, amount of coke used, and the volume of the blast. If it is desired to simply melt the charge down to matte and slag, after the manner of the reverberatory, then sufficient coke is used to provide the necessary heat, and the volume of the blast is regulated so that there is not quite enough oxygen present to burn all the carbon to CO_2. This gives a slightly reducing atmosphere in the furnace, and except for the distillation of free-atom sulfur in pyrite and chalcopyrite, there is little or no sulfur loss, and the sulfides, gangue, and fluxes melt down in the smelting zone and form layers of matte and slag.

If the blast supplies oxygen in excess of that required by the carbon in the fuel, the furnace atmosphere will be oxidizing and the oxygen will attack the iron sulfides present, thus:

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2 + 223{,}980 \text{ Cal}$$

$$2FeS_2 + 5O_2 \rightarrow 2FeO + 4SO_2 + 340{,}760 \text{ Cal}$$

The copper sulfides will not oxidize to any extent as long as some iron sulfide remains; if any copper sulfide were oxidized it would immediately be converted back to sulfide by metathesis with the iron sulfide.

The additional oxygen serves to oxidize the iron and cause it to enter the slag, and this serves to eliminate both iron and sulfur and hence raises the grade of the matte. For a given percentage of fuel on the charge, the grade of matte can be regulated within limits by regulating the volume of blast.

In the smelting of massive pyrite ores, the practice of *pyritic smelting* was developed to smelt copper ore in the blast furnace without the use of any carbonaceous fuel. This method was used at Mount Lyell, Tasmania, and other places where massive pyrite ores occurred. Pyritic smelting has not been practiced for many years, but a brief dis-

cussion of the method will aid in an understanding of the more modern practice.

Two things were essential to successful pyritic smelting — (1) a " pyritic ore," i.e., a massive pyrite ore containing copper in the form of disseminated chalcopyrite, and little gangue, and (2) a flux of almost pure silica. These materials were fed into the furnace and the iron sulfide burned to FeO, and the FeO then combined with the free SiO_2 to form a ferrous silicate slag. Both the combustion and the slag-forming reactions were exothermic and together they supplied enough heat for smelting.

In the pyritic furnace a column of infusible quartz extended from the bottom to the top of the smelting column; in the upper part the solid sulfides were present, but as the charge moved down in the furnace the sulfide melted and became oxidized and the FeO formed immediately reacted with the incandescent quartz to form slag. Thus the pieces of silica in the smelting zone were gradually eaten away by the corrosive action of the FeO, and as they disappeared they were replaced by more flux moving down in the smelting column. The slag and unoxidized sulfides (iron and copper) were withdrawn from the bottom of the furnace.

The pyritic process was economical in that it required no extraneous fuel, but this apparent advantage was actually a weakness because it gave no flexibility to the process When coke is used as fuel it is possible to use more or less fuel as required, and, except for the minor effect of the coke ash on the slag, the composition of charge and flux need not be changed. On the other hand, in pyritic smelting the ore and flux served as its own fuel, and if the composition of these changed so that they could not provide enough heat for smelting, the process would not work. The bulk of the silica on the charge had to be present as " free " or uncombined SiO_2 because the heat of the reactions such as

$$2FeO + SiO_2 \rightarrow Fe_2SiO_4 + 22{,}000 \text{ Cal}$$

aided in the smelting. If the silica present in the gangue or flux were already combined with bases, then there would be no heat of combination, but these silicates would still have to be melted down.

Consequently, as it became necessary to smelt ores which were not ideally suited for pyritic smelting, the practice was modified to the extent of adding some coke to the charge (0.5 to 6.0 per cent by weight), and the method was then known as *partial pyritic smelting.* When the amount of coke used increases above 2 or 3 per cent of the weight of the charge, the process loses the characteristics of true

pyritic smelting and approaches the type of smelting that is used at present. In the modern blast furnace the principal fuel is coke; the oxidation of iron sulfides serves to raise the grade of the matte formed, and their combustion together with exothermic slag-forming reactions contribute considerable heat to the smelting operation, but these are not the principal sources of heat. It may be noted that one kilogram of FeS_2, if oxidized to FeO and SO_2 and the resulting FeO combined with free silica, will yield about 1500 Cal of heat; a good grade of coke should have a calorific power of better than 7000 Cal per kilogram. Moreover, in pyritic smelting most of the "free-atom" sulfur in pyrite was distilled off in the upper part of the furnace and did not reach the smelting zone, where its heat of combustion would be useful.

The slag and matte formed in blast furnace smelting do not differ significantly from the slags and mattes that we have discussed previously. Following are brief descriptions of some blast furnace operations.

Mount Lyell, Tasmania.[24] Smelting at Mount Lyell, Tasmania, began in 1896 and passed through various stages of development of pyritic and partial pyritic smelting to present simple smelting of raw and sintered concentrate, high-grade siliceous ore, and returned converter slag.

The Mount Lyell blast furnace is 42 by 126 inches at the tuyères and 13 feet 10 inches from tuyères to feed floor. A blast pressure of 20 to 30 ounces per square inch is used, and the furnace smelts about 300 tons of new copper-bearing material per day. The charge is high in copper, and a 50 per cent matte is produced. Part of the flotation concentrate is mixed with flue dust and crushed limestone and is sintered on two Dwight-Lloyd machines; the remainder of the concentrate is charged directly into the blast furnace. Analysis of the charge constituents and slag are given in Table 8.

The converter slag must be allowed to solidify before it can be returned to the blast furnace; it cannot be added in the liquid form as is customary in reverberatory smelting.

Tennessee Copper.[25] The present-day treatment of the massive sulfide ores at Copperhill, Tennessee, is interesting in that the ores are treated to recover the contained iron, sulfur, copper, and zinc in the form of marketable products. This practice is a great improvement

[24] Metallurgical Operations at Mount Lyell, Tasmania, Eng. and Min Jour., Vol. 130, No. 1, p. 12, 1930

[25] Tennessee Copper Works Toward Maximum Economy: Eng. and Min. Jour., Vol. 138, No. 10, p. 40, 1937

TABLE 8

MOUNT LYELL

Product	Per cent							
	Cu	S	Fe	FeO	Al_2O_3	SiO_2	CaO	$BaSO_4$
Sinter	20.5	12.6	27.6	....	....	17.8	....	....
Raw concentrate	18.3	33.8	28.2	....	4.3	10.2	....	....
High-grade North Mount Lyell ore	17.0	....	9.8	....	4.1	47.2	....	6 3
Slag	0 45	. ..	...	53 1	5.89	33.4	3 13	[a]0 70

[a] BaO.

The relative amounts of each material on the charge are as follows:

	Pounds
Sinter	1050
Raw concentrate	1850
Converter slag	800
North Lyell ore	300
Coke, about 9 0 per cent of solid charge	325–350

on the previous method, which employed principally blast furnace smelting; in 1916, there were seven blast furnaces used and today only one remains. The principal function of this furnace is to supply matte for the converter, and all the copper concentrates are smelted in the converter. We shall take up the direct smelting of concentrates in the converter in the next chapter. If it were not for the fact that some liquid matte is needed for the converter operation, blast furnace smelting would probably be abandoned completely; and a good deal of the iron which now passes into the blast furnace slag could be thrown into the iron concentrates. This blast furnace may eventually be replaced by a reverberatory furnace.

The crude ore is first subjected to hand picking, and the high-grade material removed serves as blast furnace feed. The mill feed is then treated by selective flotation to produce concentrates of the following average composition:

Iron concentrates 54.0 per cent Fe, 40.0 per cent S
Zinc concentrates 50.0 per cent Zn
Copper concentrates 20.0 per cent Cu, 35.0 per cent Fe, 35.0 per cent S, 3.5 per cent SiO_2, 2.0 per cent Zn

The zinc concentrates are sold to a zinc smelter and the copper concentrates are smelted in the converter which treats the blast furnace matte The iron concentrates are first roasted down to 6.5 per cent

sulfur in Wedge roasters; the calcine is then mixed with coke breeze and sintered on Dwight-Lloyd machines to give an iron oxide sinter containing only 0.05 per cent sulfur. This sinter is then sold for smelting in the iron blast furnace.

All SO_2 in the gases goes to a sulfuric acid plant, and of the gas delivered, 60 per cent comes from the roasters, 25 per cent from the blast furnace, and 15 per cent from the converter. Actually it is the requirements of the acid plant which determine the smelter practice.

The blast furnace used at Copperhill is 22 feet by 4 feet 8 inches at the tuyères and runs with a 16-foot column and 30-ounce blast. The matte produced contains approximately 12 per cent copper and 24 per cent sulfur; the furnace has a maximum capacity of 1000 tons of charge per 24 hours but normally treats about 650 tons made up approximately as follows:

	Tons
Ore from Burra Burra and Eureka mines	500
Ore from Fontana mine	50
Quartz flux	60
Coke	40

The coke used makes up about 6.0 per cent of the charge. The average analysis of the charge is Cu, 2.5 per cent; Fe, 33.0 per cent; S, 25.0 per cent; SiO_2, 18.0 per cent. The Fontana ore is richer in copper (about 7.0 per cent) than the other ores, but it contains talc, which makes it harder to smelt.

Converter slag is not resmelted, but the molten converter slag is poured into the forehearth of the blast furnace where the entrained matte settles out.

Coniston.[26] The Coniston smelter of the International Nickel Company (near Sudbury, Ontario) employs four blast furnaces to treat coarse magnetic ore from the Frood mine and both coarse and fine magnetic ores from the Creighton mine. These ores are massive sulfides high in copper and nickel and low in silica. The furnaces make a copper-nickel matte whose grade varies from time to time depending upon the ore being smelted.

Coarse ore is charged directly to the blast furnace, and fine ore, flue dust, and limestone are sintered on six Dwight-Lloyd machines, the sinter then going to the blast furnaces. The blast furnaces are 50 by 240 inches at the tuyères and have settlers or forehearths 18 feet in diameter. The furnace water jackets extend down only to the top of the crucible;

[26] Canadian Min. Jour., p. 683, November 1937.

the furnace crucibles (" bottoms " of the furnaces) are lined with magnesite brick, and the settlers also. The breast jackets and spouts on the furnaces are made of cast iron and are water cooled. Molten converter slag is returned to the blast furnace settler.

These three examples illustrate the use of the blast furnace for matte smelting. Blast furnaces are seldom thus employed and then only under special conditions; the bulk of the copper-bearing feed (finely divided concentrate) which reaches most copper smelters is not suited for blast furnace smelting. The blast furnace is cheaper to construct than a reverberatory and for a small installation may prove cheaper to operate than the reverberatory when everything is taken into account. For large installations, however, the reverberatory is the standard.

ELECTRIC SMELTING

The smelting of copper concentrates for matte in electrically heated furnaces has been practiced in Europe, but in the Western Hemisphere the cost of electric power has been too high to compete with fuel heating. Electric smelting has been confined to a few remote regions of the world where water power is abundant and fuel is expensive. Technically, the electric smelting furnace offers many interesting features not found in the fuel-fired reverberatory, and it may well be that in the future more use will be made of this technique.

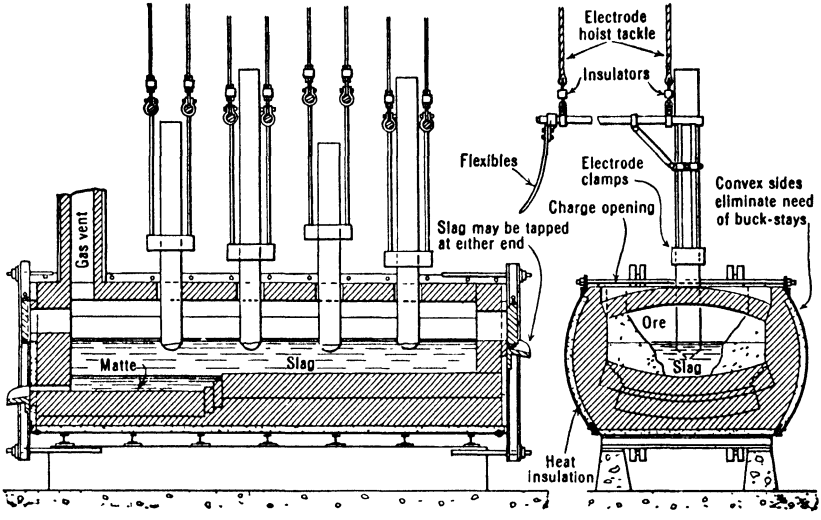
The discussion which follows is taken from an article by M. Sem,[27] of Oslo, Norway, and deals with the use of electric smelting in Norway and Finland.

Figure 23 is a diagrammatic sketch showing one of the early Westly smelting furnaces, and this illustrates the principles involved. Actually the furnace is simply a melting furnace, and heat is supplied by the current carried in on the carbon electrodes which pass through the roof and dip into the slag bath. The heat is generated by the resistance the bath offers to the heavy amperage current brought in by the electrodes; as the smelting progresses, the electrodes slowly burn away, and provision is made to lower them as required. The charge enters through the roof of the furnace and melts down to slag and matte. The slag can be tapped from either end, and the matte collects in a sump at one end of the furnace, from which it can be tapped as required.

The chemistry of the electric smelting process is essentially the same as in reverberatory smelting; matte and slag are formed in the same

[27] Sem, M., Electric Smelting with the Westly Furnace: Eng. and Min. Jour., Vol 140, No. 1, p. 47, 1939.

way, and the interaction of the various components of the charge results in the elimination of more or less of the sulfur as SO_2 gas. The principal drawback to the use of electric smelting is the cost of electric power, as we have noted, and the method can only be used at present where the cost of power is unusually low. Another objection to electric smelting has been the fact that most of the furnaces were small and



(Sem, Eng and Min. Jour., Vol. 140, No. 1, p. 47, 1939)

FIG. 23. Diagrammatic Sketch of the Early Westly Electric Smelting Furnace.

had rather low capacities; this second disadvantage has been largely overcome, and it is now possible to build electric furnaces of such a size that they have a capacity comparable with that of the standard reverberatory.

The largest closed electric smelting furnace in the world was put into operation at Imatra, Finland, in 1936. This furnace has an outside diameter of 10 meters and is heated by a 3-phase current carried on three Soderberg electrodes each 1.4 meters in diameter and weighing about 15 tons. Power consumption ranges between 500 and 600 kwhr, and electrode consumption is from 2 to 3 kg of electrode per ton of charge. The furnace is lined with magnesite and has separate tapholes for slag and matte; the slag may flow continuously, and the matte is tapped into a ladle through water-cooled tapholes.

The furnace is charged mechanically from overhead hoppers and handles from 240 to 250 tons of cold charge per day plus the molten converter slag. The raw material is a concentrate containing about 20 per cent copper; part of the concentrate is roasted and part is

charged raw. The matte produced has an average grade of about 50 per cent copper; the slag will assay from 0.3 to 0.6 per cent copper, depending upon the grade of the matte.

Some of the advantages of electric smelting may be listed as follows:

1. The fact that fuel is not used means that the thermal efficiency of the furnace is much greater than that of the reverberatory. There is no great volume of high-temperature combustion gases passing out of the furnace to carry away as much as 50 per cent of the heat generated. Of course most of this heat is abstracted by waste-heat boilers in modern reverberatories, but the heat is not confined to the furnace itself as it is in the electric furnace.

2. The absence of the large volume of combustion gases which sweep through a fuel-fired reverberatory gives the electric furnace a quiet atmosphere which greatly reduces dust losses and the corrosion and abrasion of refractories caused by the impact of a current of hot dust-laden gas.

3. There are no combustion gases to dilute the SO_2 gas evolved from the smelting charge, and hence there is a much smaller volume of gas to handle and it is much richer in SO_2. This is a very important factor when the gas is to be treated to remove the sulfur.

4. Present-day furnaces show reasonably low power and electrode consumption, the slag losses are low, and the operation is simple and reliable.

All the smelting methods we have considered up to this point have been processes of matte smelting. We shall now proceed to consider two smelting methods which yield metallic copper directly — smelting of native copper concentrates and the reduction smelting of oxide copper ores and concentrates.

SMELTING OF NATIVE COPPER

The Lake Superior district is the only place in the world where native copper has been found in great abundance, and it is here that we find the only application of native copper smelting. The following discussion is taken from an article describing the smelter of the Calumet and Hecla Consolidated Copper Company on Torch Lake, Michigan.[28]

The concentrates coming to the smelter consist of metallic copper plus some gangue minerals. There is also a certain amount of copper oxide (from the ammonia leaching plant) which is smelted with the native copper. Except for the reduction of the copper oxide precipitate

[28] Lovell, E. R., and Kenny, H. C., Present Smelting Practice: Mining Cong. Jour., p. 67, October 1931.

the operation is simply one of melting the copper and fluxing the gangue minerals.

Large pieces of mass copper from the mines and mills go directly into the furnace. Gravity and flotation concentrates are stored in bins until they are needed; then they are bedded and mixed in the proper proportions. The gravity concentrates from the conglomerate lode have a ferruginous gangue; the amygdaloid concentrates have a gangue containing silica and some alumina; and all the flotation concentrates have a gangue which is siliceous and high in alumina as well. The various concentrates are intimately mixed in such proportions that the gangue minerals are self-fluxing and about 5 per cent of coal or coke screenings is added to the mixture.

Two such mixtures are made up and stored in separate bins. One is high grade and contains about 75 per cent copper, the other is low grade and averages about 40 per cent copper. The amount of each mixture to be added to the furnace charge depends upon the immediate demand for copper from the melting furnace. Limestone flux is added with the mass copper. The copper oxide is stored in a separate bin and is mixed with 8 per cent of coal screenings before being charged.

The melting furnace is a reverberatory furnace resembling the furnaces used in matte smelting. All furnaces are equipped with water-cooled cast-iron side plates to prevent break-outs. Skewbacks and charge-hole jackets are made of deoxidized copper and are also water cooled. The slag is skimmed through tapping openings on one side of the furnace, and a tapping slot for copper is on the opposite side; there is one slag tap near each end of the furnace, and the copper taphole is located near the burner end. Furnace foundations are of solid concrete, and the furnace bottom is a silica-brick inverted arch 18 or 20 inches thick; under the bottom proper is another inverted silica-brick arch. The use of burned-in silica or sand bottoms has not been successful. The furnace is fired with pulverized coal and is charged through holes in the center of the roof.

It is customary to charge a certain number of holes every 2 hours, or at longer intervals, depending upon the rapidity of melting at various points along the furnace. While the charging is going on, slag is being drawn off more or less continuously, starting as soon as the slag becomes sufficiently fluid — usually 4 to 6 hours after the first charge. The furnace atmosphere is kept slightly reducing, and this, together with the coal mixed with the concentrates before charging, serves to prevent oxidation of the copper and consequent slag loss. Approximately 14 hours before the copper is to be tapped from the furnace, charging is stopped and the piles of concentrate are allowed to melt

down. Before the piles are flat, air is blown below the surface of the bath for 4 to 6 hours to assist in bringing up unmelted material from the bottom; this tends to oxidize the bath, but as long as a blanket of fine coal remains on the bath there is little danger of excessive slag losses due to oxidation of the copper. No slag is tapped while the air is being blown, but after the blowing is stopped the slag is allowed time to separate, and tapping is then continued. From 2 to 4 inches of slag is allowed to remain on the surface of the bath, and the copper is tapped from beneath it.

Molten copper is not as easily handled as molten matte — its melting point is higher, and its specific heat is so low that unless the molten copper is heated well above its melting point it will solidify and form skulls in the ladles and launders. For this reason it is the custom to melt practically the entire charge before tapping copper, because it is almost impossible to raise the molten copper above its melting point if any unmelted copper remains in the furnace. The slag is granulated and pumped to the waste slag dump, and the copper flows from the melting furnace directly to the fire refining furnace. The oxide copper precipitate mentioned above is usually charged in this refining furnace rather than in the melting furnace.

The plant contains two melting furnaces and two refining furnaces. Usually only one of each is in service and the others are kept ready for use whenever the necessity arises. The average daily capacity of the melting furnace is about 280 tons of concentrates, which will produce about 120 tons of slag; the holding capacity of the furnace is about 500 tons of molten copper. At the maximum firing rate the furnace will consume about 75 tons of coal a day. Analyses of slag and melting furnace copper are:

Melting Furnace Copper	
	Per Cent
Cu	98.7
Fe	1.0
S	0.2
As	0.04

Slag	
	Per Cent
SiO_2	42.5
FeO	30.0
Al_2O_3	13.0
MgO	2.3
CaO	8.0
Cu	0.60

The slag would not be considered desirable in a matting furnace because of the high Al_2O_3 content, although the silicate degree is about right (1.4). It is sufficiently fusible, however, at the higher temperatures employed in the copper melting furnace.

It was previously the custom to resmelt the slag in a blast furnace

to remove the copper, but, as firing with pulverized coal and mixing coal with the charge were practiced, the copper content of the slag is held low enough so that resmelting is not required.

SMELTING OF OXIDIZED COPPER ORES

Introduction. The smelting of ores containing the oxidized copper minerals rather than sulfides differs from the smelting of sulfide ores in two respects — (1) the process is one of reduction smelting and (2) the product is metallic copper and not matte. The copper produced by reduction smelting is quite impure and is often called *black copper*. The ore minerals may be oxides (cuprite, tenorite), carbonates (malachite, azurite), or silicates (chrysocolla); the carbonates break down to copper oxide and CO_2 in the furnace, and the copper silicate is decomposed by more active bases (CaO, FeO) to yield copper oxide and calcium or iron silicate. Thus all these compounds eventually behave like copper oxide, and the essential chemistry of the process involves the reduction of the oxide to metallic copper.

As we shall see directly, the smelting of oxidized copper ores has never been as satisfactory as matte smelting. The most successful way of treating oxidized copper ore is by leaching, and today most of the ores from the great oxide ore bodies are being treated by leaching. One exception is the high-grade oxide ore from Katanga in the Belgian Congo, and here also a large leaching plant has been built to treat certain classes of ore. It is likely that leaching will some day displace smelting completely for all classes of oxide ore in the Katanga district.

Early Arizona Practice. In the early days in Arizona, high-grade oxidized ores were smelted directly in blast furnaces. These furnaces were water-jacketed throughout; some were rectangular in cross-section, but most of them were circular furnaces. Some analyses of smelting ores, slags, and the black copper produced are given in Table 9.

This type of smelting had two principal disadvantages; the copper loss in the slag was very high and the copper produced was quite impure and required considerable refining. Eventually this practice was abandoned, and the high-grade oxide ores were mixed with sulfide ores and concentrates and smelted to matte — a procedure which was also applied to some of the high-grade slags which had been sent to the dump from the blast furnaces. Low-grade oxide ore was treated by leaching.

Note that the slag losses were high — always well over 1.0 per cent and in one smelter almost 4.0 per cent CuO. Part of the copper was present as grains of metallic copper, but most of the copper in the slag was there as copper silicate caused by the slagging of copper oxide be-

TABLE 9[a]

ANALYSES OF ARIZONA OXIDE COPPER ORES

Locality	Cu	SiO_2	FeO	MnO	CaO
Longfellow	38.80	11 15	10 40	....	....
Do.	21 67	17.25	.....	7.43	....
Do.	17.17	26 80	13 76	7.49	....
Coronado	21.95	48 90	12 09	....	....
Do.	11 17	67 00	8 88		....
Old Dominion	15 17	35 3	28 7	.	22 2

ANALYSES OF ARIZONA BLAST FURNACE SLAGS

Smelter	Cu	CuO	SiO_2	FeO	MnO	CaO	MgO	Al_2O_3	S
Copper Queen	2 10		24 67	44 85	0 39	10 92	1 75	15 57	0 28
Do.	0 15	1.02	30 06	53 36	11 10	.	..	...	...
Detroit	..	.. .	34 34	32 27	8 05	10 13	2 30	11 64	.
Do.	1 82	. .	29.50	37 08	1 13	9 02	7 44	14.07	0 30
Prince	1 64	. .	27 16	34 62	0 49	17 42	3 51	14 70	0 33
Old Dominion	. ..	3 76	27 23	51 30	1 65	5 14	2 54	5 22	.
United Verde	0 18	2 59	35 79	37 89	. .	12 98	0 75	8 29	..
Bisbee	1 32		28 0	29 0		9 0	..	27 0	

ANALYSES OF ARIZONA BLACK COPPER

Smelter	Cu	S	Fe	As	Sb	Bi	Insoluble
Prince	95 00	0 44	4.23	.	. ..	. .	0 51
Old Dominion	98 91	0 64	0 12	0 057	0 008	0 010	0.065
Do.	98 27	0 60	0 73	0 039	0 019	trace	0 060
Do.	98 24	0 53	0 80	0 054	0 021	0 006	0 007
Do	97 52	0 69	0 97	0 052	0 014	trace	0 180

[a] Hofman, H O , and Hayward, C R , Metallurgy of Copper, p 247, McGraw-Hill Book Co , New York, 1924

fore it could be reduced. Some of the analyses indicate the amounts of the copper present as elemental copper and as oxide; where only the copper is given this refers to the total assay and most of this copper is present as the oxide.

Practice at Katanga.[29] The ores of Katanga are oxidized ores with a gangue that is highly siliceous and low in iron; most of the gangues are quartzitic or schistose, a few ores have a dolomite gangue. The principal ore minerals are malachite and chrysocolla with minor amounts of other oxidized copper minerals. The ores vary widely

[29] Roger, E., La Métallurgie du Cuivre et du Cobalt au Katanga: Cong. Internat. des Mines, de la Métallurgie, et de la Géologie Appliquée (Sect. Mét.), pp. 441–456, 6me sess., Liége, June 1930.

in grade. Much ore is available which contains more than 15 per cent copper, and other ores contain as little as 4 per cent copper.

The Union Minière du Haut Katanga operates the mines and metallurgical plants of the district, and we shall discuss the metallurgical operations in the order of their adoption.

In considering the methods to be used in treating these ores it was decided to use reduction smelting in water-jacketed blast furnaces; these were used on the rich ore from the Mine de l'Etoile, which ran about 15 per cent copper.

In 1911 there was one such blast furnace in operation in the smelter at Lubumbashi, from 1911 to 1914 two more were constructed, and in 1915 another extension was made which brought the total to seven. The first three furnaces constructed consisted of a single stage of water jackets surmounted by a brick superstructure; the dimensions at the crucible and the tuyères were 1 20 by 4 88 meters (47 2 by 192 inches). There were 8 water jackets (4 2 by 0 6 meters) on each side, and each was pierced by two tuyères, making a total of 32 tuyères per furnace. The tuyère openings were each 127 square centimeters in cross section (equivalent to a circular opening about 5 inches in diameter). The last four furnaces had two stages of water jackets and a crucible 1 12 by 6 10 meters (44 1 by 240 inches); the total height of the water jackets was 4 35 meters, and the charging floor was 0 82 meter above the top of the upper stage of water jackets These furnaces each had 40 tuyères 127 square centimeters in cross-section — two in each of the 20 lateral water jackets on the lower stage. These furnaces had internal crucibles and employed a blast pressure of 80 to 110 millimeters of water.

Later, changes were made in the size and shape of the furnaces; the section at the tuyères was increased to 1 57 by 6 10 meters (62 0 by 240 inches), and the number of tuyères was cut in half. The new tuyères had an opening of 190 square centimeters (about 6 3 inches in diameter), but this increase was not enough to give the same total tuyère area as before. This reduction in tuyère area had a beneficial effect on the smelting rate.

The reactions which take place in these furnaces are relatively simple; in the upper part the charge is dried, and carbonates in the ore and flux are decomposed into CO_2 and the metallic oxides; reduction of oxides takes place farther down in the furnace, and in the smelting zone above the tuyères the molten slag forms; metal and slag then trickle down to collect in the crucible, from which they are tapped. The copper oxides are reduced to the metal together with some of the oxides of iron and cobalt (if present). The resulting metal contains

about 97 or 98 per cent copper. A small amount of matte forms because there is a little sulfur on the charge and this comes principally from the coke used as fuel.

In smelting these ores it was necessary to use a temperature high enough to insure reduction of the copper oxides, but if too much fuel were used the temperature would be so high and the reducing action so strong that too much iron would be reduced from the iron oxides on the charge. It was therefore necessary to adopt a type of slag which would have a formation temperature between 1150° and 1300° C. The slags which have been used in these furnaces are sesquisilicates of lime and iron containing from 40 to 45 per cent SiO_2. Slags which have been successfully used over a period of years have compositions between the following limits:

	Per Cent
SiO_2	40 to 45
Al_2O_3	6 to 8
FeO	14 to 19
CaO	14 to 21
MgO	5 to 8

Since the gangue minerals are generally siliceous, basic fluxes are required; limestone and dolomite are used for the lime and oligonite and hematite to supply the iron.

The annual capacity of these blast furnaces is about 1,000,000 tons of charge; the annual production of metal from the blast furnaces from 1918 to 1927 is listed below.

TABLE 10

ANNUAL PRODUCTION, IN METRIC TONS, FROM KATANGA BLAST FURNACES

1918	20,239	1923	56,220
1919	23,019	1924	79,697
1920	18,962	1925	81,081
1921	30,464	1926	72,328
1922	43,362	1927	72,621

Note that the total output in 1925 was more than four times the 1918 production. This was made possible by changes in the furnace design and by the selection of higher grade material for the furnace charge. Some of the important facts about the smelting during two different periods are given in Table 11.

The question of copper losses in the slag has been a matter of much concern, as the blast furnace slags carry from 1.5 to 2.5 per cent

copper. Efforts to decrease the slag losses have followed two lines — (1) to reduce the slag volume and (2) to reduce the copper assay of the slag.

The first of these has met with considerable success, and the method employed has been simply to select higher grade feed for the furnaces. This not only gives a greater yield of copper per ton of ore smelted and requires less coke but, as there is less gangue on the charge, less flux is required and the slag volume is diminished accordingly. Table 11 shows that the weight of flux required has been cut in half; the weight of the slag produced was reduced from 120 per cent of the weight of the ore to 80 to 95 per cent.

TABLE 11

BLAST FURNACE SMELTING AT KATANGA

	1911–1920	Since 1928
Per cent of Cu on charge	8 to 9%	14 to 15%
Tons of total charge (ore and flux) per hour	10 7 tons	20 to 24 tons
Tons of ore per ton of produced metal	8 4 tons	5 0 tons
Weight of flux; per cent of weight of ore	70 to 90%	40 to 50%
Weight of coke; per cent of total charge	24%	17 to 20%
Tons of coke per ton of metal produced	3 5 tons	1 5 tons
Tons of total charge per ton of metal produced	14 5 tons	7 6 tons

Efforts to lower the copper content of the slag have not been so successful. At one time forehearths or settlers were used on the theory that this would diminish slag losses by permitting suspended globules of copper to settle out. The forehearths did not give the desired effect, however, because most of the copper in the slags was chemically combined as copper silicate and was not present as mechanically entrained copper. After several trials, the use of forehearths was abandoned. Better reduction of copper could be attained by using more coke and thus having a more vigorous reducing action; but as it was necessary to have considerable iron oxide on the charge to insure a fusible slag, this procedure would reduce too much metallic iron. The use of powdered coal blown through the tuyères was also attempted in order to secure better reduction of the copper; but these experiments were not successful, and the practice was abandoned.

In general these blast furnaces are operated to give a high tonnage of metal containing 96 to 98 per cent copper and as free as possible from iron and cobalt. The total slag loss does not exceed 10 per cent of the copper on the charge, and it is not economical to try to cut this loss at the expense of furnace capacity or grade of copper produced.

In spite of the large output of copper from the blast furnaces it was

realized that blast furnace smelting was not suited for all types of ore in the district. Economical blast furnace smelting demanded coarse high-grade ores to produce copper with the minimum slag losses and coke consumption and maximum furnace capacity. Accordingly, other means had to be developed to take care of (1) ores too low in grade for the blast furnace and (2) rich ores that were too finely divided to go directly to the blast furnaces.

Sintering. The fine ores and concentrates which were continually increasing in amount led to the installation of two Dwight-Lloyd sintering machines between 1923 and 1925. The charge to these machines was mixed with 9 to 11 per cent of its weight of coke breeze and sintered to make blast furnace feed. These two machines require just about as much coke breeze as is obtained by screening the coke for the blast furnaces, and no more sintering machines have been installed Fine ores and concentrates which are not sintered are smelted in reverberatory furnaces.

Concentration In Chapter I we have given a brief description of the Panda concentrator and have noted that both gravity and flotation concentrates are produced. These concentrates are then either smelted in reverberatory furnaces or sintered and charged to the blast furnaces. In addition to the more or less standard methods of concentration the Union Minière has developed a process of reducing at low temperature copper minerals in crushed ore to metallic copper and then removing the metallic copper by flotation. On certain low-grade ores this method gives a concentrate assaying 65 per cent copper and 0.5 per cent tails, with a recovery of 90 per cent.[30]

The production of the two mills of the Union Minière in 1936 was as follows:[31]

Panda mill:

11,450 tons of 33 2 per cent gravity concentrates.
50 500 tons of 35 0 per cent gravity concentrates
71,800 tons of 29 8 per cent flotation concentrates.

Prince Leopold works:

63,700 tons of 30 5 per cent concentrates.

Reverberatory Smelting. The constantly increasing supply of finely divided concentrates at Katanga led to the construction in 1922 of an experimental reverberatory furnace at the Lubumbashi smelter. Two years of work with this furnace demonstrated the feasibility of smelting

[30] Roger, E , op cit , p 449.

[31] Minerals Yearbook, 1938, p. 103, U. S Bur. Mines.

oxide ores and concentrates in the reverberatory. In 1927 a new smelter containing four reverberatory smelting furnaces was put in operation; the new smelter was located near the Panda concentrator.

These furnaces are 33 by 6 meters (108 by 19.7 feet), interior dimensions, and are of silica brick construction throughout. Firing is done with pulverized coal and there are five burners to each furnace; combustion air is preheated to 180° C by means of the heat left in the furnace gases after they pass through the waste-heat boilers.

Fluxes are crushed to 6 millimeter size and thoroughly mixed with the copper concentrates and ores together with about 7 to 10 per cent by weight of fine coal; this serves as the reducing agent for the copper oxide. The charge is dried more or less completely in 8 Wedge-type 5-hearth furnaces fired with powdered coal burners. When flotation concentrate is being smelted the charge must not be completely dried or the dust losses in the furnace are excessive, and the charge piles in the furnace tend to slide down into the bath.

Side-charging is employed, with the charge entering through holes in the roof and piling up along the sides of the furnace. The reduced copper and slag melt down and form a pool in the furnace from which they can be drawn as desired. It is necessary that the material shall not slide off the piles and float on the bath — if this happens some of the unsmelted charge may be carried off with the slag.

The slags formed are slightly more siliceous than those produced in the blast furnaces. Better settling conditions in the furnace permit the use of a more siliceous (and more viscous) slag, which cuts down on the amount of basic flux needed. The reverberatory slags are also somewhat lower in copper than the blast furnace slags when copper of similar quality is being produced. Furnace slag is granulated in water.

Table 12 gives some of the data characteristic of reverberatory practice at Katanga.

Some of the advantages of reverberatory smelting over blast furnace smelting at Katanga are as follows:

1. It permits the direct treatment of fine ores and concentrates which could not be smelted in the blast furnace without preliminary sintering.

2. Slag losses are less, and the recovery of metal is usually higher in the reverberatory than in the blast furnace.

3. Although the total consumption of fuel is greater than in blast furnace smelting, the coal is sufficiently cheaper than coke so that the fuel cost per ton of charge smelted is lower for reverberatory smelting than for the blast furnace. Moreover, about 35 to 40 per cent of the heat of the combustion coal is recovered by the waste-heat boilers.

TABLE 12

REVERBERATORY PRACTICE AT KATANGA

	Experimental Furnace	Panda Smelter	
	1925	1928	Sept 1929
Smelting rate, tons per hour	7.9 tons	8.4 tons	11.2 tons
Copper content of ore and concentrate, per cent	24 80%	27 79%	29%
Copper content of charge, per cent	16%	19%	23%
Coal, per cent of charge	45 80%	40%	31 7%
Coal, tons per ton of metal produced	3 20 tons	2 40 tons	1 45 tons
Daily production of metal; tons per furnace	28 tons	35 tons	60 tons

4. Blast furnace smelting demands selected ores of 15 to 20 per cent copper, and such a process requires (for coke manufacture and other purposes) about 2.5 tons of coal per ton of copper produced from 20 per cent ore. The concentrator and reverberatory furnaces, on the other hand, will operate on lower grade ores and require only about 1.7 tons of coal per ton of copper produced; also part of the heat is converted into steam power which can be used in mill and smelter.

Leaching. In addition to the pyrometallurgical operations, the Union Minière has installed a large copper leaching plant. We shall have occasion to discuss this in a later chapter.

OTHER SMELTING METHODS

We shall mention here two papers dealing with methods of copper smelting; these have not yet had commercial application, but they indicate other approaches to the ideal which is back of such processes as pyritic smelting and direct smelting in converters, i.e., to use as advantageously as possible the heat of combustion of the sulfide minerals, or to make the sulfides smelt themselves (*autogenous* smelting).

Shaft Roasting and Reverberatory Smelting.[32] In the spring of 1931 an experiment was made at Anaconda in which a down-draft roasting shaft (essentially a flash or suspension roaster) was mounted over a small reverberatory so that the hot calcine discharged directly into the smelting furnace. The hearth of the reverberatory was 3 by 21 feet and the roasting shaft was 3 feet square and had an effective height of 20 feet. The shaft discharged through an opening in the

[32] Laist, Frederick, and Cooper, J. P., An Experimental Combination of Shaft Roasting and Reverberatory Smelting: Am. Inst. Min. Eng. Trans., Vol. 106, p. 104, 1933.

center of the roof about 7 feet from the burner wall. Dry concentrate mixed with the necessary flux constituted the feed to the roaster.

When operated without the shaft, on calcine at a temperature of 492° F, the reverberatory smelted 16,678 pounds per 24 hours with an oil consumption of 797 gallons. The roaster-reverberatory combination smelted 40,552 pounds of cold dry concentrate per hour with an oil consumption of 262 gallons. After making due allowance for the calcination ratio (change in weight due to roasting) of the concentrates, it may be said that the use of the shaft increased the capacity of the smelting furnace 2½ times and decreased the fuel consumption by 60 per cent These are results obtained from 30 8-hour shifts with the reverberatory alone and 30 8-hour shifts with the roaster-reverberatory combination.

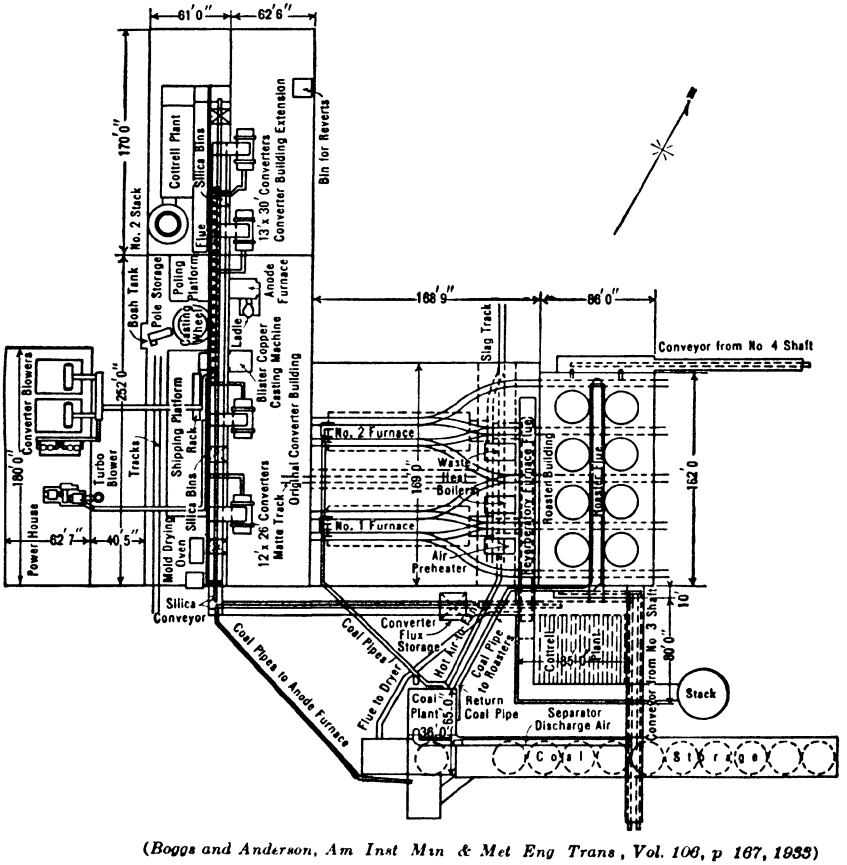
Laist and Cooper are of the opinion that such an installation on a standard reverberatory, with the shaft roasters dropping calcine through the roof along the side walls of the reverberatory, might reasonably be expected to increase the smelting capacity from 1½ to 2 times without any material increase in fuel consumption. Other factors might weigh against the practical use of such a combination; for example, in certain cases the copper content of the concentrates will be so high that all the sulfur is needed for the matte, and such concentrates could not be roasted before smelting.

Autogenous Smelting. In an article published in 1936 Mr. T. E. Norman[33] has discussed the theoretical aspects of smelting copper concentrates without the use of extraneous fuel. It appears that the maximum temperature attained in ordinary flash roasting in air is not high enough for the direct formation of liquid matte and slag from the calcine; this is because the large volume of inert nitrogen in the combustion air absorbs too much of the heat. If, however, the suspension roasting is carried out in an atmosphere of 40 to 95 per cent O_2 (air contains 21 per cent O_2 by volume), then there is less material to absorb the heat evolved and a higher " flame temperature " is attained — high enough that properly fluxed concentrates would issue from the roaster not as solid particles of calcine but as drops of molten sulfides and slag together with superheated particles of acid and basic oxides which would react to form liquid slag at the first opportunity.

The bulk of this article consists of an extended consideration of the production and distribution of heat in copper roasting and smelting,

[33] Norman, T. E., Autogenous Smelting of Copper Concentrates with Oxygen-Enriched Air: Eng. and Min. Jour., Vol. 137, No. 10, p. 499, 1936, and Vol. 137, No. 11, p. 562, 1936.

and Mr. Norman shows that, at least theoretically, it is possible, by burning copper concentrates in an oxygen-enriched atmosphere, to generate sufficient heat to fuse the roasted product to slag and matte. These calculations were based on published analyses of the concentrates which serve as smelter feed at three large smelters — Noranda, Flin Flon, and Anaconda.



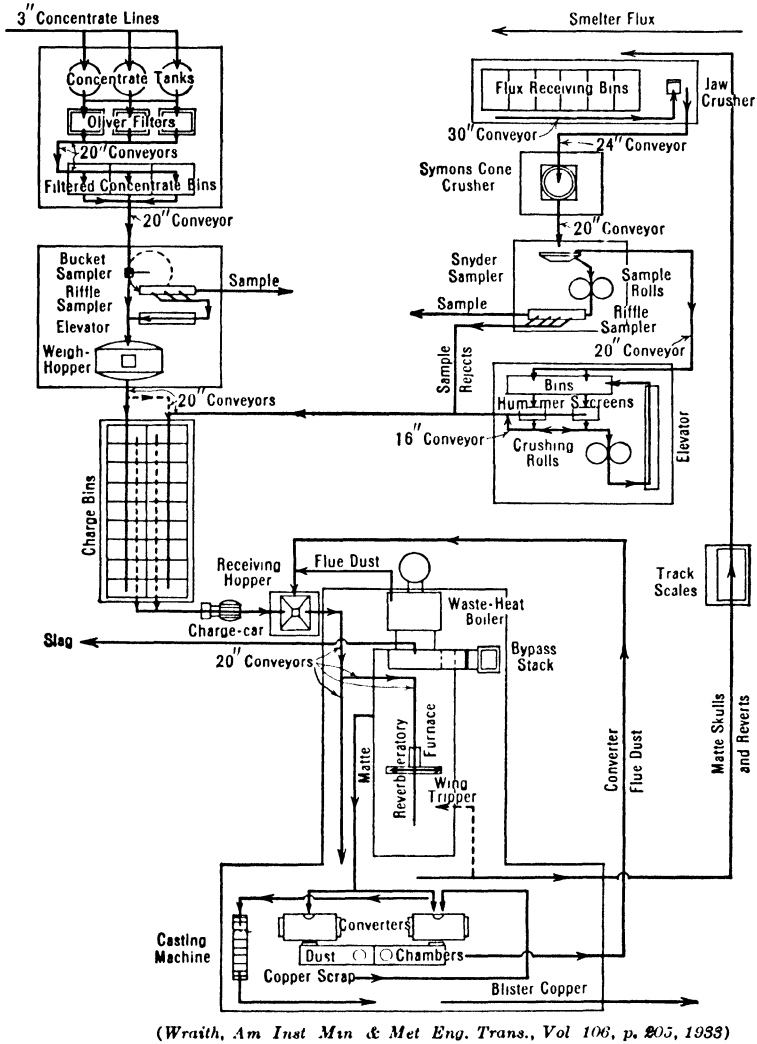
(Boggs and Anderson, Am Inst Min & Met Eng Trans, Vol. 106, p 167, 1933)

FIG. 24. Layout of Smelter, Noranda.

No actual experiments were made, but on the basis of other published work on copper roasting and smelting, Mr. Norman discusses some of the problems that would arise in carrying out these ideas in practice. The smelting might be done in a down-draft roasting shaft (similar to the method used by Laist and Cooper), or it might be possible to use a countercurrent system in an up-draft shaft.

Although such a system would not require extraneous fuel such as

coal or fuel oil, it would require a supply of oxygen. Provided that a suitable furnace could be designed which would be as satisfactory as



(Wraith, Am Inst Min & Met Eng. Trans., Vol 106, p. 205, 1933)

FIG. 25. Flowsheet, April 1933, Roan Antelope Smelter.

present equipment, the factor that would be of primary importance would be the relative costs of fuel and oxygen.

SMELTER FLOWSHEETS

Figures 24 and 25 show the layout or flowsheet of two different smelters; these are more or less typical arrangements.

CHAPTER V

CONVERTING

INTRODUCTION

The operation of matte smelting produces an artificial sulfide or matte, and in this chapter we shall consider the problem of treating this matte to produce metallic copper. The standard method (*converting*) in modern practice is to oxidize the iron and sulfur in a *converter* by blowing air through the molten matte; sulfur goes off in the gases as SO_2 and the iron is oxidized and slagged off. The liquid metallic copper remains in the converter. Before proceeding to a discussion of converting, let us consider the history of the process and some of the older methods of treating matte

Most of the successful methods for converting matte to metallic copper have been oxidation processes in which the iron and accompanying sulfur (FeS) are oxidized and removed and subsequently the Cu_2S is oxidized to yield SO_2 and metallic copper. There will not be any appreciable oxidation of copper sulfide until practically all of the iron sulfide is gone, and this is the fundamental fact upon which the success of converting matte depends.

The Welsh Process. The Welsh process was employed at Swansea, Wales, for many years, and until the invention of the converter, this method and its modifications constituted the standard treatment for matte. It never had any great application in the United States because shortly after copper production became important in this country the converting process was invented and was speedily adopted. Prior to this, however, a great deal of the copper produced in the United States was shipped to Wales in the form of matte.

The Welsh process involved a series of carefully controlled roasting and melting operations. The matte was first crushed and given a partial roast; this roast was controlled so that the bulk of the iron would be oxidized but so that there would not be an excessive formation of the higher oxides of iron. The roasted matte was then melted with silica or siliceous ore on the hearth of a small reverberatory. The iron was removed in a slag (which was usually returned to a blast furnace for smelting) leaving in the furnace a high-grade matte (white metal) containing 70 per cent copper or better.

Sometimes a single roast and fusion would produce this rich matte; other times it was necessary to employ several partial roasts and fusions. Repeated roasts and fusions were helpful in removing arsenic, antimony, and other volatile impurities.

The white metal (essentially Cu_2S with a small amount of FeS) was cast into pigs and treated by the process of *blister-roasting.* The pigs of white metal were melted down on a hearth under an oxidizing flame; as the sulfides melted some oxidation took place at the surface and the iron sulfide and part of the copper sulfide oxidized:

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

However, the copper oxide formed would immediately react with more copper sulfide (roast-reaction) to liberate metallic copper.

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

By the time fusion was complete there would be three layers of liquid in the furnace — metallic copper on the bottom, a layer of molten Cu_2S above this, and a film of slag on top. This slag was formed from the small amount of FeO in the matte, silica sand from the furnace bottom, and the sand from the casting floor which clung to the pigs of matte. The slag was carefully skimmed and returned to the previous smelting operation, leaving the layers of copper and matte in the furnace.

The oxidation of liquid matte by scorification (surface oxidation) proceeds very slowly, so no attempt was made to oxidize more of the molten Cu_2S. Instead, the fire was lessened and the charge allowed to *set* or solidify; bubbles of SO_2 evolving from the liquid forced their way through the cooling surface so that the crust solidified with numerous protuberances which gave a large surface for oxidation. After the charge had set, it was again heated to fusion and the accompanying oxidation formed more copper oxide, which in turn reacted with copper sulfide to contribute more copper to the molten layer on the bottom. This alternate freezing and melting was continued until practically all of the sulfide was gone and the bath had the oily, sea-green surface characteristic of metallic copper. The blister-roasting process would continue for 24 to 48 hours; at the end the temperature was raised to complete the reactions, any remaining slag was skimmed, and the copper was tapped into sand molds. Small amounts of SO_2 gas escaping from the metal as it solidified caused blisters to form on the surface; hence the name *blister copper,* a term which is also used for the product of the modern converter.

Although the converter operation is entirely different in method, as we shall see later, the essential chemistry and sequence of operations are exactly the same as in the Welsh method.

The Bottoms Process. If in the blister roasting process the oxidation is regulated so that about 10 per cent of the contained copper is reduced to the metallic state, the metallic copper will remove the bulk of the impurities — arsenic, antimony, silver, and particularly gold — as these are more soluble in liquid copper than in liquid matte. If such an oxidized charge of matte is tapped from the furnace the slabs of metallic copper are found under the first pigs of matte cast, and these *copper bottoms* can then be worked up to recover the concentrated gold. The matte remaining is purer than the original and yields a higher grade of copper for the market.

The universal use of electrolysis for purifying copper has rendered obsolete the bottoms process as well as a number of other complex and ingenious methods formerly used to recover precious metals from matte. In modern converting the gold and other precious metals in the matte pass into the copper and are later removed by electrolytic refining.

Development of Converting. Early attempts were made to oxidize matte by the simple process of blowing air through the molten matte, and the successful application of converting or bessemerizing to the refining of pig iron lent additional stimulus to these efforts. Between 1850 and 1855 the converting process was invented in England by Sir Henry Bessemer, and it was developed independently in the United States by William Kelly at about the same time After 1860 the process of converting pig iron to steel rapidly attained great importance.

The bessemer converter is a pear-shaped refractory lined steel vessel with a row of tuyères in the bottom. It is charged with molten pig iron and a blast of cold air is blown through the bath to oxidize the metalloids (C, Si, Mn). The first attempts to use the bessemer technique for converting copper matte resulted in failures, and a successful technique was not developed until the problems peculiar to matte converting had been worked out. A few of the significant differences between matte converting and the converting of pig iron are listed below.

1. Cold air can be blown through liquid pig iron, and instead of chilling the metal it actually heats it up because of the heat liberated by the oxidation of the iron and impurities. The same thing is true of liquid matte but not of liquid copper. The oxidation of metallic copper is slow and the amount of heat liberated is small; consequently a blast of cold air will cause liquid copper to freeze rapidly and seal up the tuyères. This meant that the bottom-blown converter could

not be used, because as soon as liquid copper formed in the bottom of the converter it would freeze and clog the tuyères. Copper converters are side-blown, and provision is made to allow the metallic copper to collect below the tuyère level.

2. About 20 tons of pig iron can be blown in a matter of 18 to 20 minutes, and the impurities oxidized form a comparatively small volume of slag; this is because the pig contains only about 4 or 5 per cent of impurities to be oxidized and together with the iron loss only about 7 to 8 per cent of the metallic bath is removed as gases and slag. Matte converting, on the other hand, takes a much longer time because there is so much material to oxidize. A 30 per cent copper matte, for instance, contains about 40 per cent iron and 30 per cent sulfur; thus in 10 tons of matte it is necessary to oxidize 4 tons of iron and 3 tons of sulfur, and there remains in the converter at the end of the blow only 3 tons of copper or 30 per cent of the original weight of matte.

3. There is comparatively little slag formed in iron converting, and usually the silicon and metals oxidized form a siliceous slag (in the acid process) which does not have a very severe corrosive action on the converter lining In matte converting, the initial blow produces large quantities of FeO which rapidly corrodes a siliceous refractory. Moreover, if silica is not available to fix iron as a ferrous silicate slag, the oxidation continues to form quantities of infusible Fe_3O_4.

The first successful application of the bessemer process to matte converting came in 1880, when Pierre Manhès of Éguilles, France, succeeded in producing blister copper from medium-grade matte on a commercial scale. Manhès' invention consisted mainly in placing the tuyères above the floor of the converter so that a space was provided for the liquid copper to collect. After this demonstration, the application of converting was immediate and it soon became the standard method for treating copper mattes.

The early converters were patterned after the bessemer (steel) converter and were all *acid lined* with silica or siliceous ore. Thus the lining served both as a refractory to protect the converter shell and as a flux for the oxidized iron. This resulted in rapid corrosion of the lining so that the converter shell had to be relined after every four to six blows.

Development of the *basic lined* converter was the next step, for it was realized that the slow and wasteful method of using the converter lining for flux left much to be desired. It was necessary to find a refractory lining which would resist the action of the basic FeO so that relining would not be required at such frequent intervals; the use of

such a basic lining would of course require the addition of siliceous flux to the converter to slag the iron oxide. The first successful use of a basic lining was made at the Garfield smelter about 1910; this operation was conducted in a Peirce-Smith horizontal converter lined with magnesite brick and using silica flux. The superiority of this over the acid lining was immediately evident, and soon it was adopted by other smelters. Today the basic lined converter is standard, and practically all converter linings are made of magnesia — either magnesite brick or a monolithic lining tamped in position.

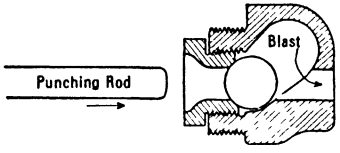


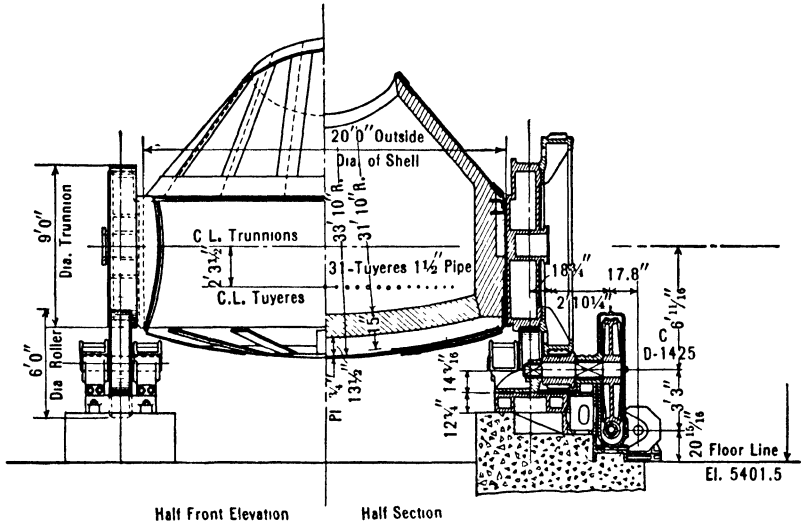
FIG. 1. Sketch Showing Principle of the Dyblie Tuyère Valve.

Another important invention made about this time was the Dibblie (or Dyblie) ball-valve arrangement for punching the tuyères. A converter tuyère will plug up and must be *punched* at intervals by thrusting a rod through it to open it up. The ball-valve is located back of the tuyère and a ball is seated in the valve so that it directs the air from the tuyère pipe into the tuyère proper. When the punching bar is thrust into the hole in back of the ball-valve (from the outside of the converter shell) it lifts up the ball and allows the bar to be thrust through the tuyère. As soon as the bar is withdrawn, the ball drops back into position and seals the hole to prevent escape of air. Before the use of this ball-valve, the punching holes were closed by wooden plugs or steel caps, which were wasteful of air and clumsy to operate.

CONVERTING OF COPPER MATTE

Upright Converter. Figure 2 is a diagram of a 20-foot Great Falls type converter. This furnace consists of a short cylindrical section surmounted by a tapering nose, or head. The converter is mounted and swung on two trunnions; one of these carries the ring gear by means of which the converter is turned about a horizontal axis, and the other is hollow and serves as a wind-box to feed air to the tuyères. The row of tuyères extends along the back of the converter shell as shown in the diagram. These tuyères are metal pipes extending through the shell and the refractory lining. On the outside each tuyère is equipped with punching hole and ball-valve and is connected to the air pipe leading from the wind-box. The converter can be turned through almost a complete circle about its horizontal axis; it is in blowing position as shown in the diagram, and when it is to be

charged or poured it is tilted forward — this raises the tuyère openings above the bath so that the air can be shut off. When the converter is tilted back again, the air is turned on just before the tuyère openings are submerged so that the matte cannot run down into the tuyère pipes. Figure 3 shows two Great Falls type converters. The



(Kelly and Laist, Am Inst Min & Met Eng Trans, Vol 106, p 128, 1933)

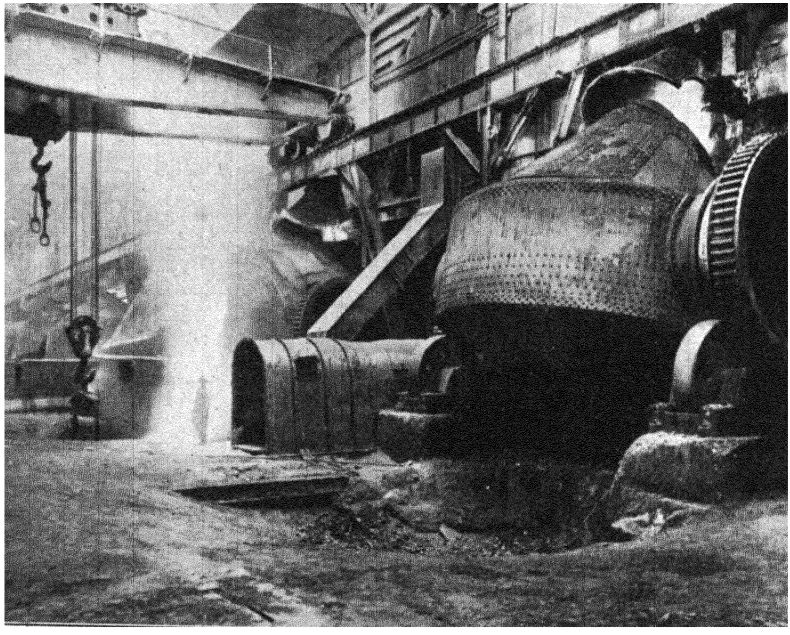
FIG. 2. Twenty-Foot Converter, Great Falls Type.

one in the foreground is in the blowing position and the one in the rear is tilted forward for pouring. Note that the shape of the nose is such that the converter must be tilted well over 90° from its blowing position before the liquid can pour out, and it must be tilted almost 180° before the converter can be completely emptied.

Upright converters have been made in different sizes, but probably the two most common are the 20-foot and 12-foot converters, outer diameter of shell (see Fig. 2). One disadvantage of the upright converter is the fact that the tuyères are not evenly submerged in the bath in all positions, and this results in an uneven distribution of the blast.

The Horizontal Converter. This type of converter is more widely used at present than the Great Falls, or upright, converter. Figures 4, 5, 6, and 7, show views of Peirce-Smith ("barrel") converters. These have cylindrical steel shells and two steel riding rings resting on sets of rollers; the weight of the converter is carried on these rollers and they permit the converter to be turned about its horizontal axis. Next to one of the riding rings is the ring gear which turns the converter.

Air enters through a flexible connection on one side (Fig. 4) of the converter, and the tuyères are connected to the air pipe by short lengths of flexible hose or steel pipe. Tuyères are equipped with Dyblie valves and punching holes.



(Courtesy Anaconda Copper Mining Company)

FIG. 3. **Great Falls Type Converters.**

The opening in the converter for charging and pouring is shown in Figure 7. The position of this in relation to the tuyères may be judged by noting that the air pipe which serves the tuyères is just visible at the top of the converter.

Size of Peirce-Smith converters is commonly given by the outer dimensions in feet — diameter and length. The two most common sizes are 13- by 30-foot and 10- by 26-foot converters. It is a feature of the Peirce-Smith converter that the tuyères are always evenly submerged regardless of the position of the converter.

Converter Linings. The old acid linings had a very short life because they served to flux the iron oxide, and in most operations a lining would only last long enough to produce about 10 tons of copper. Under these conditions it was impossible to use the relatively expensive silica brick for lining, and the lining was usually made from crushed

silica or siliceous ore with enough clay to serve as a binder. This mixture was rammed into place in the shell and carefully dried until the converter was ready for the first charge of matte. The thickness of the lining ranged from 12 inches to more than 60 inches (5 feet);

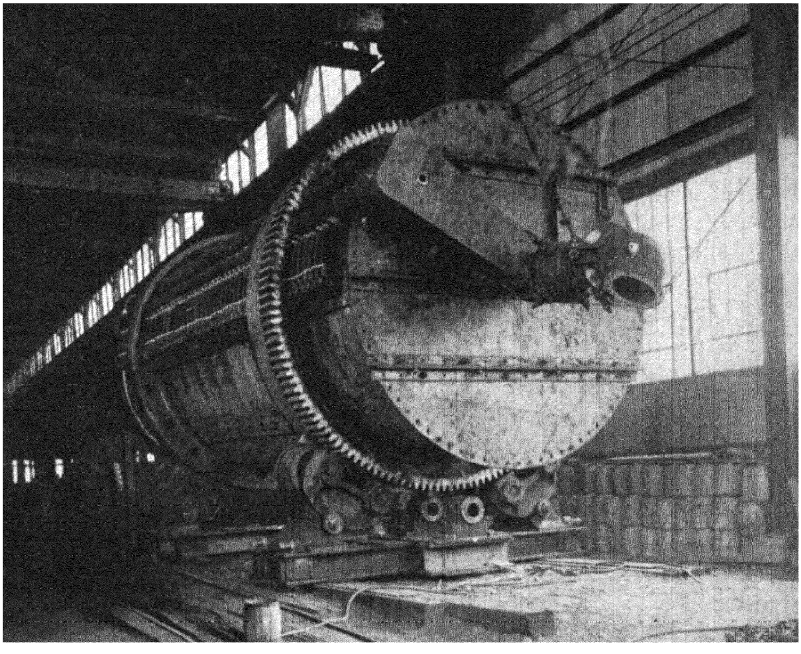


FIG. 4. 13′ × 35′ Peirce-Smith Converter.

obviously it was desirable to make the lining as thick as possible so that it would last longer. Some linings were so thick that the capacity of the converter near the end of a campaign was more than twice that of a freshly lined converter.

A well-designed basic lining will probably last from 200 to 300 times as long as an acid lining on matte of the same grade, and this means that the basic lining warrants greater care and expense in its construction. The most common type of converter lining consists of magnesite brick set in a single course and backed by grouting of ground magnesite and binder such as sodium silicate. The lining may range from 9 to 30 inches in thickness, and commonly the lining is made thicker in those parts of the converter where corrosion is most severe. A new lining is usually dried by warming it with a wood

fire in the converter and then treating it with a small amount of matte until all the cracks between the bricks have been filled and the lining has a smooth unbroken surface.

Some linings are coated with a " magnetite lining " by blowing some low-grade matte with little or no flux. This produces a large amount of magnetite and the slag formed coats the lining of the converter and protects the underlying brick. Such a slag is almost infusible because of its high content of magnetite, and when this coating wears away it can be replaced by repeating the same procedure.

The mouth of the converter must be of ample size to permit easy charging and pouring, to allow the gases to escape easily, and to minimize the formation of crusts which tend to accumulate around the converter mouth. On the other hand, the opening must not be larger than necessary because this would mean an excessive heat loss.

Monolithic magnesia linings have been employed at the United Verde smelter[1] with considerable success. The principal component of the lining mix is *periclase,* which is a grain magnesia made by burning high-grade magnesite at very high temperatures without fluxing impurities (such as are used in making magnesia brick to sinter the grains into a compact mass). This periclase will contain from 88 to 92 per cent MgO.

The periclase is mixed with water, clay, sulfuric acid and occasionally molasses to serve as a binder. The acid is used principally to control the pH of the mix, as this has a pronounced effect on the plasticity of the clay. The mix is tamped into position and carefully dried by means of a wood fire and an oil flame, and the converter is then ready for the first charge. Results have shown that the monolithic linings last longer than the 15-inch radial brick linings used previously and have brought about an over-all saving of about 30 per cent in lining costs.

One of the facts which led to the use of the monolithic linings was the patent litigation because of which the company had used acid linings during 1925 and 1926; in this period they had perfected mechanical methods for tamping linings and had crews trained in this work. Such a set of favorable conditions made the adoption of tamped basic linings a relatively simple task.

Converter Air. The air blast entering the converter must be under pressure greater than the static head of the matte column over the tuyères. Air pressure used is usually about 10 to 15 pounds per

[1] Parsons, F. H , Development of Monolithic Tamped Periclase Converter Linings at United Verde Copper Company Smelter: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 153, 1933.

square inch gage pressure. Quick-acting valves in the air line are used to turn the air on and off.

The amount of air entering the converter will depend upon the air pressure and the total tuyère area; we shall have more to say about this in the next section. The rate at which air enters the bath determines the rate of oxidation and hence the heat production and temperature rise in the converter. One factor which limits the blowing rate is the fact that with too rapid blowing the converter temperature may rise too high.

The amount of air theoretically required to convert FeS to FeO and SO_2 and Cu_2S to Cu and SO_2 can be calculated from the chemical equations. Actual practice shows that the air consumed by the converter will be about 50 to 60 per cent greater than this. The air loss is caused by leakage through the lining and by air lost through the tuyères when they are not submerged in the bath and the air is still on; also a certain amount of Fe_3O_4 may be formed which would call for more oxygen than that required to form FeO. Analyses of converter gases show that practically no free oxygen escapes from the bath during the slag-forming stage (while burning FeS). However, when burning Cu_2S during the blister-forming stage, as much as 20 per cent of the oxygen entering the bath may escape without combination.

Experiments have been made using oxygenated air for blowing converters, and although the results were promising, this method has not been adopted in practice.[2]

Converter Operation. The actual procedure used varies considerably, depending upon the grade of matte being treated, size of the converter used, etc. We shall give here a brief outline of the general procedure and later we shall consider in more detail the converter practice at several representative smelters.

The converter blow is divided into two stages — (1) the *slag-forming* stage and (2) the *blister-forming* stage. In the first stage the FeS is oxidized and slagged by means of the siliceous flux added, thus:

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2 + 223{,}980 \text{ Cal}$$

and

$$xFeO + ySiO_2 \rightarrow x(FeO)\cdot y(SiO_2)$$

The second stage begins when the FeS is all gone, and Cu_2S begins to oxidize:

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

[2] Tonakanov, S., Blowing with Oxygenated Air: Eng. and Min. Jour., Vol. 135, No. 12, p. 539, 1934.

or, by adding and then dividing by 3 we obtain the net reaction:

$$Cu_2S + O_2 \rightarrow 2Cu + SO_2 + 51{,}990 \text{ Cal}$$

A charge of matte is added to the empty converter while the converter is turned down, so that the tuyères are above the level of the liquid matte, flux is added, the air is turned on, and the converter turned to the blowing position. Blowing is continued long enough (usually about an hour or so) to use up the flux added, and then the converter is turned and the slag poured out. More matte and flux are added, and the blow continued. These partial blows are continued until all the iron has oxidized, and the converter contains *white metal*, which is essentially pure Cu_2S. On ordinary mattes several matte charges must be slagged before there is enough white metal in the converter to blow for blister copper.

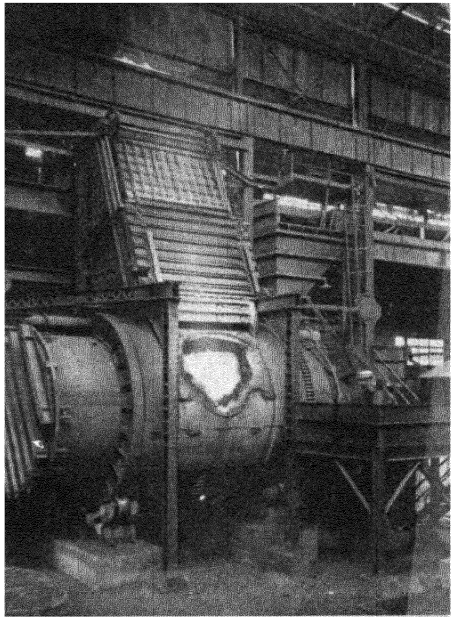


FIG. 5. Peirce-Smith Converter Turned out of Stack Ready for Charging.

During the second stage there is no slag formed, and as soon as the sulfur is all oxidized the metal is poured out and the converter is ready for another charge. In some plants the matte is partly blown in one converter and the resultant high-grade matte transferred to a second converter for finishing.

Note that the slag-forming reactions generate more heat than the blister-forming reaction. The heat generated during the blister-forming stage is not much more than sufficient to supply that lost by radiation and convection, and the temperature of the converter does not rise very much during the second stage. During the slag-forming stage, however, the temperature in the converter rises quite rapidly and it is necessary to add cold scrap copper, solid matte skulls, and other "dope" to cool the converter.

The capacity of a converter is rather hard to define and does not have much meaning except when applied to a given converter

handling matte of a definite grade. It may be expressed in terms of the amount of matte treated per day or the amount of copper produced per day.

Let us make a few approximate calculations to indicate what is involved in the question of converter capacity. Assuming that matte consists of FeS + Cu_2S, we can calculate the amount of air theoretically required to oxidize a unit weight of each.

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

For 1 ton of FeS we shall require $\frac{2000}{176} \times 3 \times 359 = 12{,}250$ cu ft of O_2 at standard conditions or $\frac{12{,}250}{0.21} = 58{,}300$ cu ft of air at standard conditions. For the blister-forming stage

$$Cu_2S + O_2 \rightarrow 2Cu + SO_2$$

we shall require per ton of Cu_2S

$$\frac{2000}{160} \times 359 = 4490 \text{ cu ft of } O_2$$

or

$$\frac{4490}{0.21} = 21{,}400 \text{ cu ft of air}$$

Since $\frac{58{,}300}{21{,}400} = 2.72$, if we assume that the blower delivers a constant amount of air and that the air loss is the same at all stages, we see that it takes 2.72 times as long to blow a unit weight of FeS as to blow a unit weight of white metal to blister.

If we know the volume of free air taken in by the blowers per unit of time and know the efficiency of air delivery to the converter, we can calculate the amount of oxidation in any given period — it is all based upon the rate at which oxygen is supplied to the molten matte. Mr. John S. Stewart[3] has worked out an analysis of this problem for the 13- by 30-foot Peirce-Smith converter. He assumes that, on an average, the air required for a given matte will be 165 per cent of that theoretically calculated for the oxidation of the contained iron and sulfur. He also points out the importance of taking into account the altitude of the plant; a blower might take in the same volume of free air per minute at sea level and at an altitude of 6000 feet, but the weight of oxygen delivered per minute would be less in the rarefied at-

[3] Stewart, J. S., An Inquiry into Converter Capacity: Eng and Min Jour., Vol. 137, No. 5, p. 224, 1936.

mosphere of the higher altitude, and consequently the converting capacity would be smaller. Table 1 is taken from Mr. Stewart's paper and illustrates the effect of the grade of matte and the altitude on the copper output of a 13- by 30-foot converter. These figures check quite closely with those found in practice and are based on the assumptions that the compressor takes in 20,000 cubic feet of free air per minute and that the converter requires 165 per cent of the theoretical air. Note how the capacity in tons of copper produced varies with the grade of the matte.

TABLE 1

METRIC TONS OF BLISTER COPPER PRODUCED DAILY FROM A 13- BY 30-FOOT PEIRCE-SMITH CONVERTER

Altitude (meters)	Grade of Matte, Per Cent Copper					
	10	20	30	40	50	60
0	21.8	53 0	88 6	129 8	178 3	235 8
300	21.4	52 0	87.0	127 5	175 3	231 7
600	20 9	51 0	85.3	125 1	172 1	227.7
900	20.5	50 0	83.6	122 8	169 0	223 9
1200	20 2	49 1	82.2	120 6	166 3	220.2
1500	19 8	48 2	80.7	118.5	163.4	216.7
1800	19.4	47.3	79 2	116.4	160.6	213.2
2100	19 0	46 4	77 7	114 3	157 8	209 4
2400	18 7	45 6	76 3	112 2	155 0	206 2
2700	18 4	44 8	75.0	110 4	152 4	202 6
3000	18 0	43 9	73.6	108.3	149.8	199.6

Liquid matte is poured into the converter mouth from ladles, and cold matte skulls, scrap, etc., are usually dumped into the converter mouth from " boats "; these ladles and boats are usually manipulated by an overhead crane. Flux may be charged by similar boats, by means of a hopper set above the converter, or it may be blown into the converter by means of a *Garr gun* set in the end wall of the converter (the last method applies only to Peirce-Smith, or horizontal, converters). The tuyères are punched at regular intervals while the converter is blowing — every half hour or so.

The temperature of the matte added to the converter will usually be about 1000° to 1100° C; i.e., from 100° to 300° C of superheat above its melting point. The rate of blowing and the addition of cold material (flux, scrap, etc.) is usually controlled so that the temperature in the converter never rises above 1250° to 1300° C. Another thing that governs the permissible blowing rate is the fact

that air pressures much greater than 14 or 15 pounds per square inch may cause too much spitting of liquid particles from the converter mouth.

Of course the bath must never be allowed to chill to the point where it freezes in the converter. In most plants some sort of auxiliary power is provided so that in the event of power failure (and stoppage of the air supply) the converter can be turned down and emptied, or at least turned down enough to bring the tuyère openings above the bath.

Converter Slag. The slag formed in a converter is essentially an iron silicate; while we often assume in calculations that converter slag is a ferrous silicate, a good part of the iron is always present as Fe_3O_4 (magnetite) rather than as FeO. This magnetite is partly dissolved in the slag and part of it is present as suspended crystals of magnetite.

Table 2 lists the analyses of three converter slags; note that these are high in copper and that the silica is lower than in reverberatory slags. The silica content is kept as low as possible to avoid corrosion of the basic converter lining; the iron is present as FeO and Fe_3O_4; slag from the Noranda converter, for example, contains about 17.2 per cent magnetite.

TABLE 2

ANALYSES OF CONVERTER SLAGS

Source	Per cent					
	Cu	SiO_2	Fe	Al_2O_3	CaO	MgO
Noranda[a]	4 40	25 0	47.7	4 8	0 5	0.3
Flin Flon[b]	1 50	30 0	39 8	4 4	1 7	1.0
Anaconda[c]	3 95	23 3	47 6	5 9	0 1	0.0

[a] Boggs, W B , and Anderson, J. N , op cit.

[b] Ambrose, J H., op. cit

[c] Laist, Frederick, and Maguire, H J., Reverberatory Furnace for Treating Converter Slag at Anaconda· Mining and Metallurgy (A. I. M. E.), No 157, Sec. 13, January 1920

Copper in Converter Slags.[4] The copper content of converter slags is so high (1 to 5 per cent) that the slags are not discarded but are treated to recover as much of this copper as possible. The contained copper is found as suspended prills of matte and metallic copper and as chemically combined copper silicate.

During a converter blow the bath is kept in agitation by the streams of air, and this tends to disperse a certain amount of copper and sulfides

[4] Wartman, F. S., and Boyer, W. T., The Form of Copper in Converter Slags: U. S. Bur. Mines, Rept. Inv 2985, January 1930.

in the slag — these are mechanically entrained in the slag and are carried out with it, as no opportunity is given for settling. The copper assay of the converter slag, therefore, depends somewhat on the grade of the matte. During the first stages of a blow there is less copper in the slags removed than in those slags which are formed from blowing enriched matte. Very little chemically combined copper is found in slags from the first steps of a blow, but as the matte approaches the white metal stage, more of this oxidized copper is slagged.

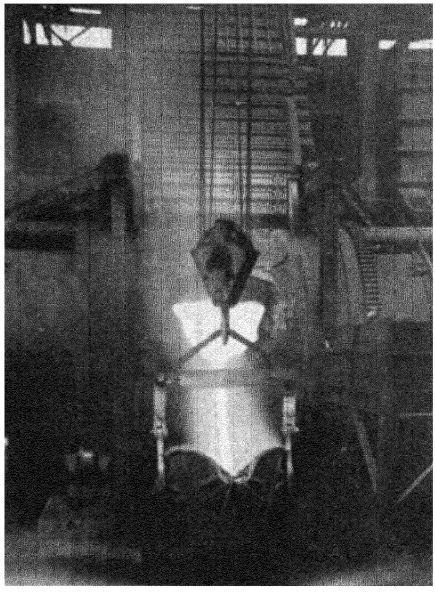


FIG. 6. Pouring Converter Slag.

Probably about 90 per cent of the copper in average converter slag is in the form of suspended prills of matte and copper; only about 10 per cent is in the oxidized form. However, this copper cannot be effectively removed by simply allowing the slag to stand; the magnetite dissolved and suspended in the slag tends to hold the copper in the slags, and it appears that high magnetite content in slags (reverberatory slags as well as converter slags) usually means high copper assays.

Generally the molten converter slags are poured back into the reverberatory furnace, and with low-grade matte the weight of slag charged may be as great as the weight of new solid material entering the reverberatory. With blast furnace smelting, the converter slag may be allowed to solidify so that it can be charged to the smelting furnace, or it may be poured directly into the forehearth of the furnace. In former days when smelting charges were more siliceous the converter slag constituted a valuable iron-bearing flux, but with the basic charges that are common at present the converter slag has lost its value as a flux — often additional siliceous flux must be added to the reverberatory to take care of the iron.

About 1915 research was undertaken at Anaconda to determine the feasibility of employing a special reverberatory furnace to treat converter slags. As a result of this investigation a large coal-fired re-

verberatory was constructed (23 ft 4 in. by 153 ft—probably the longest reverberatory ever built) to handle the converter slag This furnace was eventually abandoned, and the converter slag was charged in the regular smelting reverberatories. However, the practice adopted here serves as an excellent illustration of what must be done to converter slag to effectually recover the entrained copper.

It was found that in order to clean[5] these converter slags the following items were necessary:

1. The bulk of the Fe_3O_4 therein contained must be reduced to FeO.
2. More silica would have to be added to bring the waste slag up to at least 30 per cent SiO_2.
3. Iron sulfide would have to be supplied to form sufficient bulk of low-grade matte to collect the particles of metallic copper and sulfides.

The converter slag furnace at Anaconda attained these ends by smelting siliceous ores and calcines with the molten converter slag. In modern practice the converter slag is added to the smelting reverberatory, but it must be remembered that the same general treatment must

TABLE 3

QUANTITY OF MAGNETITE ENTERING AND LEAVING THE REVERBERATORIES AT NORANDA

Material	Weight (tons)	Fe_3O_4 content (%)	Fe_3O_4 (tons)	Fe_3O_4 (% of total input)	Fe_3O_4 reduced in reverberatories (%)
Calcine	64,703	10 4	6,729	47	
Converter slag	42,550	17 2	7,319	53	
Reverberatory slag	70,330	2 3	1,618	12	88

be given the converter slag to insure the saving of the bulk of the copper. There is a tendency for the liquid converter slag to simply spread out on the bath in the reverberatory, and for this reason the converter slag is usually poured in near the firing end of the reverberatory so that it will react with the piles of solid charge — the sulfides attack and reduce the Fe_3O_4 and the converter slag becomes diluted with more siliceous material. Table 3 shows the amount of magnetite[6] passing in and out of the Noranda reverberatories for 1 month. Note

[5] Laist, Frederick, and Magure, H J, op. cit.

[6] Boggs, W. B., and Anderson, J. N., The Noranda Smelter: Am. Inst. Min & Met. Eng. Trans., Vol. 106, p. 187, 1933.

that 53 per cent of the magnetite comes from the converter slag and that 88 per cent of the total magnetite is reduced to FeO in the reverberatory. The magnetite content of the reverberatory slag is much less than that of the converter slag.

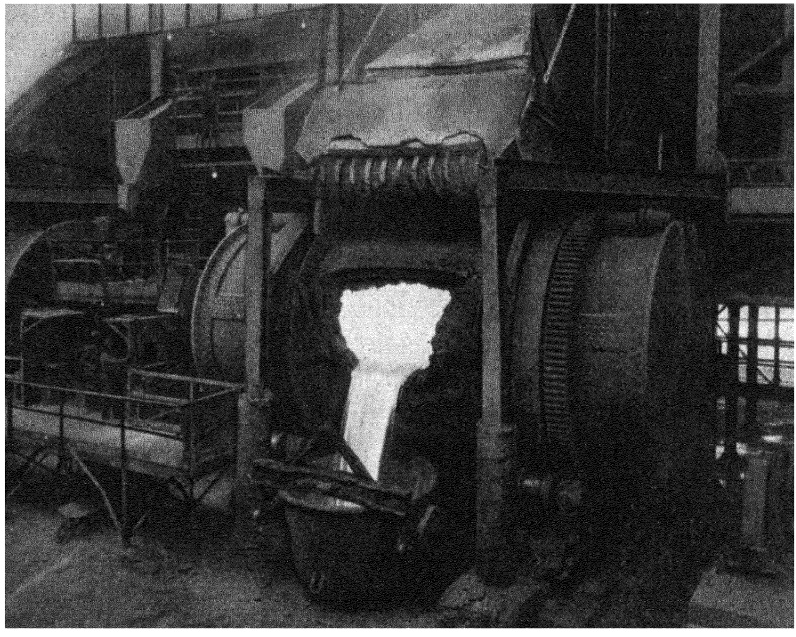


FIG. 7. Pouring Blister Copper.

Blister Copper. The metal produced in the converter will ordinarily contain 98 per cent or more metallic copper. The remainder consists of small amounts of base metal impurities — Ni, Co, Fe, Sn, Sb, As, Zn, and Pb. The exact amount of each of these depends upon the impurities in the matte and whether or not any of these metals are volatilized in the converter. If the copper is slightly underblown it will contain a small amount of sulfur; if overblown it will contain oxygen in the form of dissolved Cu_2O.

All the precious metals in the matte will pass into the blister copper, where they remain until separated by electrolytic refining. *Selective converting* is a method of blowing white metal to form a small amount of blister copper which is then separated from the white metal before the remainder is blown. This first fraction of the blister formed will contain most of the gold, just as did the copper bottoms in the

older Welsh process. This method, however, has not been used for many years.

Converter Practice. We shall now briefly summarize the details of converter practice at three copper smelters which treat low-, high-, and medium-grade matte respectively.

Noranda.[7] The Noranda smelter employs four Peirce-Smith converters — two are 12- by 26-foot converters with forty 1½-inch tuyères; the other two are 13 by 30 feet and have forty-four 1½-inch tuyères. The converters are served by overhead cranes, and the cranes and converter tilting motors are electrically operated. A storage battery set is connected to the converter motors so that in case of sudden failure of the converter air supply and the power supply to the motors, the converters are automatically turned until the tuyères are clear. About 12 pounds per square inch air pressure is used.

Three of these converters are usually operating at any one time, and they treat large quantities of low-grade matte (19.3 per cent Cu) with comparatively small production of blister copper. The converter slag contains about 25 per cent SiO_2. Molten blister copper is transferred to the anode furnace, where it is fire refined and cast into anodes.

Roan Antelope.[8] The Roan Antelope smelter is equipped with two 12- by 20-foot basic-lined Peirce-Smith converters, each with thirty 1½-inch tuyères spaced at 6-inch intervals. One converter has sufficient capacity to treat all the matte produced in the reverberatory, and the other converter is used as a spare.

The Roan Antelope matte is practically pure Cu_2S, so little or no converter slag is made, and the process corresponds to the blowing of white metal at other plants. It was believed at first that this would cause difficulties because most converting operations depend upon the FeS in the matte as the principal source of heat, and accordingly certain special features were incorporated in these converters. The mouth was made as small as practical (4 ft 6 in by 5 ft 4 in), and the magnesite brick lining was backed by an insulating layer of fireclay brick. A 14-inch burner port is situated in one end wall of each converter, and this is used to burn powdered coal to keep the vessel hot between blows. This port is sealed with clay-mud during the blow.

Actually, the heat generated during the blow is slightly greater than the corresponding heat lost by radiation, convection, and in the converter gases. Temperature readings show that with an empty converter at 2230° F (1220° C) and a matte charge at 2010° F (1100° C) the temperature at the end of the blow will rise to about 2370° F

[7] Boggs, W. B., and Anderson, J. N., op. cit., p. 171.

[8] Wraith, C. R., op. cit., p. 217.

(1300° C). This means an increase in temperature of about 2.3° F (1.3° C) per minute.

The converters are tilted by air motors, and there is always a sufficient supply of air at the proper pressure to revolve the converters to a safe position in case of failure of the air supply at the tuyères. Compressed air for converting is supplied by a single-stage compressor which is rated to deliver 15,000 cubic feet of free air per minute at 15 pounds per square inch pressure.

The average charge to a converter is 60 tons of matte, and this can be blown to blister copper in about 2 hours and 25 minutes; during the blow the tuyères must be punched almost continually. The appearance of the flame and the copper on the rod determines when the blow has been completed.

As no converter slag was available and it was not possible to provide a protective layer of magnetite over the converter lining, it was decided to charge some crushed hematite with the matte for this purpose. This experiment was a success as far as converter operations were concerned, but it had to be discontinued because the magnetite in the converter reverts formed a blanket in the reverberatory; neither the calcic-silicate slag nor the high-grade matte would take up the magnetite either chemically or mechanically; all the magnetite that entered the reverberatory furnace had to be removed eventually with rabbles.

Table 4 lists the converter data at Roan Antelope.

TABLE 4

CONVERTER DATA AT ROAN ANTELOPE

Charge, tons of matte	60
Air pressure	15 lb/sq in
Air consumed per ton of matte	30,590 cu ft
Free air consumed per minute	13,700 cu ft
Minutes per converter blow	134
Minutes per ton of matte treated	2 23
Minutes per ton of copper produced	2.83
Blister produced per blow	47.5 tons
Blister produced per converter hour	21.3 tons
Fuel consumed per day	5 9 tons
Blister copper, per cent Cu	99 6

The blister copper is transferred into a cylindrical casting furnace fired through a pulverized coal port at one end, and from this furnace it is cast into 350-pound cakes for shipping.

Andes.[9] Four Peirce-Smith converters lined with magnesite brick

[9] Callaway, L. A., and Koepel, F. N., op cit., p. 689.

are used; these are 12- by 26-foot vessels and have thirty-eight 1½-inch tuyères. Converter air at a pressure of 13 to 15 pounds pressure is used, and with matte containing 40 per cent copper each converter can make about 90 tons of copper per day. The flux used is regular mine-run sulfide ore from the fine crushing plant, and it contains about 70 per cent silica and 16 per cent alumina. Flux is charged from boats handled by the converter cranes. The converters have an emergency automatic tilting device operated by auxiliary storage batteries.

Blister copper is poured into two oil-fired cylindrical 8- by 18-foot receiving furnaces lined with 9 inches of magnesite brick. From these furnaces the copper is cast into blister cakes or anodes.

OTHER CONVERTING OPERATIONS

Converting of Lead Mattes. The copper which finds its way into lead smelters is usually recovered in the form of a lead-copper-iron matte, and this matte is generally treated in copper converters. Most of the lead, and also zinc, in these mattes is recovered as an oxide fume carried off in the converter gases, and recovered by filtering the gases in bag houses.

Lead and zinc in the metallic form are volatile enough so that they can be expelled from liquid slags or mattes at high temperature. Their boiling points are 1613° C for lead and 907° C for zinc, but there will be volatilization below these temperatures when the opposing metal vapor pressure is less than 1 atmosphere. Zinc and lead are removed from lead blast furnace slags by blowing powdered coal through the molten slag; this reduces the metals to the elemental state and they are volatilized and escape from the bath. As soon as the metal vapor strikes the air above the bath the metal oxidizes to form small particles of oxides which are carried out by the gas stream and recovered in bag houses. Zinc is more readily volatilized than lead because of its lower boiling point.

A similar process permits the recovery of lead and zinc in converters. The lead and zinc are reduced by means of the metallic copper or ferrous oxide formed in the converter, volatilized and reoxidized, and escape in the form of dense clouds of white fume in the converter gases. Unless the proper conditions are maintained, however, a high percentage of these metals may be oxidized and fixed in the slag.

The smelter at Tooele, Utah,[10] has had much experience in con-

[10] Kuchs, O. M., Lead-Matte Converting at Tooele Am. Inst. Min. & Met. Eng. Trans., Vol. 49, p. 579, 1915.

verting lead mattes. The composition of such a typical lead matte would be:

Pb	15.0 %	S	23.0%
Cu	9 05%	Fe	37.9%
Zn	5.4 %	Ag	20.3 oz/ton

The original method of treating this matte was to give it a preliminary blow without siliceous flux to eliminate almost completely the lead and zinc. In order to completely eliminate these volatile metals it was necessary to overblow the bath, and at the end of the blow the converter contained a heavy iron slag (FeO and Fe_3O_4), metallic copper, and cuprous oxide. This mixture was then transferred to another converter containing a regular charge of copper matte; here the iron slag was fluxed, copper oxide was reduced to copper by reaction with sulfides, and the blow was carried forward in the regular manner.

Practice at Tooele[11] has been changed since about 1927. Now the lead matte is blown with siliceous flux, and the resulting slag is skimmed. The matte is then blown to white metal, which is combined with white metal from copper matte and blown to blister copper. In this method most of the zinc goes into the converter slag instead of being volatilized as ZnO as was the earlier practice.

Converting of Nickel Matte. Nickel and nickel-copper mattes are obtained by smelting in the same way as copper mattes, and the converting of these mattes proceeds in the same way as copper converting in the same type of converters. There is one important difference, however, in the converting of nickel and nickel-copper mattes — the blowing can be continued only far enough to eliminate the iron sulfide, and the resulting nickel or nickel-copper sulfides must be poured from the converter and treated by some other method. Nickel oxidizes so readily that the matte cannot be blown down to the metal, and the end of the blow corresponds to the " white metal " stage in the converting of copper matte. The process is simply one of oxidizing and slagging the iron sulfide; the product of the converter is not a metal corresponding to blister copper, but a *bessemer matte* of copper and nickel sulfides corresponding to white metal.

The various methods used to separate the copper and nickel sulfides in bessemer matte are beyond the scope of this discussion.[12]

[11] Sackett, B. L., Converting Lead and Copper Matte at Tooele: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 132, 1933.

[12] See Canadian Min. Jour., Vol. 58, No. 11, 1937, for a discussion of the methods employed by the International Nickel Co.

Stationary Converter.[13] At the smelter of the Messina Development Company, Ltd., at Messina, Transvaal, South Africa, plans were made to treat a copper matte without using standard converter equipment; this was considered advisable because of the small production contemplated (about 20 tons of copper per day from high-grade matte containing 60 per cent copper). At first the Nicholls-James process was used, in which about two-thirds of the matte was roasted and then mixed with the unroasted matte in a reaction furnace; the oxide and sulfide copper then reacted according to the familiar roast-reduction equation to liberate metallic copper. This process did not work satisfactorily because the capacity of furnace and roaster was not great enough, and it was decided to employ the reverberatory reaction furnace as a stationary converter. After a number of experiments, the burner wall was removed and was replaced by a tuyère wall backed by a steel tuyère plate. Seven 1¼-inch tuyères pass through the tuyère wall 12 inches above the magnesite furnace bottom at the center. Quartz flux is added through a charge hole about 3 feet from the tuyère wall. Pulverized coal is burned to provide auxiliary heat, and about 7 or 8 pounds air pressure is employed. The maximum bath depth is 18 inches above the tuyère level.

Converting proceeds in much the same way as in an ordinary converter, except that the technique must be modified because the converter cannot be tilted to expose the tuyère openings before the air is cut off. Special oil-cooled tuyère plugs are used to seal the tuyères when not blowing, and this invention has been largely responsible for the success of the method. The stationary converter seems to be best adapted for small installations where available labor is cheap and not highly skillful.

DIRECT SMELTING IN CONVERTERS

Many of the copper concentrates produced today are heavy sulfide products containing very little gangue; chemically they resemble the artificial sulfide or matte from the reverberatory, and the principal difference is that the concentrates are solid, cold, and often moist, whereas the matte is tapped from the reverberatory in the form of a superheated liquid. The converter burns no extraneous fuel (except to keep it warm between blows in a few special cases; e.g., at Roan Antelope) and is not suited for the smelting of cold concentrates. If, however, the sulfide concentrates are added in small amounts to a con-

[13] Knickerbocker, R. G., The Messina Stationary Basic Copper Converter: Am. Inst. Min. & Met. Eng. Trans., Vol 106, p. 140, 1933.

verter containing hot liquid matte, the sulfides will melt and dissolve in the matte and will respond to the converting operation in the same way as the sulfides of the matte itself. Naturally the individual sulfide additions must be small enough to avoid freezing the matte in the converter.

Practice at Tennessee Copper Company. One of the outstanding examples of the use of the converter for smelting copper concentrates is the practice at the plant of the Tennessee Copper Company near Ducktown, Tennessee. All the copper concentrates treated at this plant are smelted directly in a converter. A blast furnace operating in 1937 on mine-run ore (Chapter IV) produces a 12 per cent copper matte and the concentrates are smelted[14] in conjunction with the converting of this low-grade matte.

The converter used is a 12- by 25-foot Peirce-Smith converter which is operated continuously during the year except for about two weeks, when it is shut down for relining. During this period a Great Falls converter, which is kept as a standby, is used. A blast pressure of 10 to 14 pounds per square inch is used, and a constant-volume regulator is used to hold the amount of air to a maximum of 12,000 cubic feet per minute — this is for the benefit of the acid plant which utilizes the converter gases.

The converter is lined with unburned magnesite brick; a strip 5 feet wide along the tuyères and running the full length of the converter is lined with 20-inch brick, and the rest of the lining is 13 inches thick. On starting after relining, a magnetite lining is blown on top of the brick by blowing matte until the magnetite layer freezes on the brick. The tuyère lining lasts approximately a year, the rest of the lining indefinitely.

Concentrates to be smelted in the converter have the following analysis: Cu, 20 per cent; Fe, 35 per cent; S, 35 per cent; SiO_2, 3.5 per cent; Zn, 2 per cent.

The cycle of operations is as follows: Each morning the copper made during the preceding 24 hours is poured, 20 tons of matte is added, and the converter is blown for about 20 minutes. Then four 4-ton charges of concentrates are added at 20-minute intervals, and before all the concentrates have melted, 5 tons of quartz flux is added. Blowing is now continued for about 2 hours, and at the end of this time the slag is removed. This operation is repeated six or seven times during the 24 hours of the day and night, and white metal steadily accumulates in the converter until the following morning, when it is

[14] Tennessee Copper Works toward Maximum Economy: Eng. and Min. Jour., Vol 138, No 10, p. 40, 1937.

blown to blister and poured. Flux is charged from a charging boat, and a Garr gun is used to charge the concentrates.

The first cycles call for a ratio of 16 tons of concentrate to 20 tons of matte, but after the white metal has built up in the converter, less concentrate is charged in each cycle. Normally the converter handles 120 tons of matte per day, 80 tons of concentrates, 20 tons of flue dust, and 19 tons of scrap. This means that 0.666 ton of concentrate is smelted for every ton of matte converted, under these particular conditions; as high as 1 ton of concentrate per ton of matte has been treated at this plant.[15]

The following tabulation[16] gives the data for a campaign in 1930–31; note that the copper assay of the concentrates was lower than that reported in 1937.

TABLE 5

TENNESSEE COPPER COMPANY, CONVERTER CAMPAIGN, JUNE 15, 1930, TO AUGUST 23, 1931

Blowing time (converter days)	349.90 days
Number of blows	427
Matte charged	38,335 tons
Concentrate charged	28,960 tons
Concentrate per ton of matte	0 76 ton
Flux used	11,845 tons
Copper assay of matte	13 67%
Copper assay of concentrate	17 13%
Flux per ton of matte	0 31 ton
Flux per ton of copper	1 28 tons
Flux per ton of iron	0 37 ton
Blister copper made	9,246 tons
Total charge per converter day	235 70 tons
Time to blow 1 ton of copper	54 50 minutes
Blast pressure	12 80 lb/sq ft
Air used per minute	12,500 cu ft
Air per ton copper	681,330 cu ft
Air per ton iron	199,040 cu ft
Converter slag per day	166 tons

Of the 166 tons of converter slag, 46.1 tons was in the form of slag skulls and was resmelted in the blast furnace. The remaining 119.9 tons of molten converter slag was poured into the blast furnace settler.

Entering the blast furnace settler was approximately 3 parts of converter slag assaying 1.34 per cent copper and 7 parts of furnace

[15] Beavers, G. E., Smelting Copper Concentrates in a Converter: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 149, 1933.

[16] Idem, p. 149.

slag containing 0.27 per cent copper. The combined slag overflowi the blast furnace settler assayed 0.35 per cent copper, which mea that about 60 per cent of the copper in the converter slag was recover by pouring the slag in the settler.

TABLE 6

TENNESSEE COPPER COMPANY, ANALYSIS OF CONVERTER SLAG, IN PER CENT

Cu	1.34	Al_2O_3	0.70
Fe	55.3	SiO_2	19 90
S	2.0	CaO	0 50

Smelting Copper-Zinc Ores.[17] Research at Clarkdale on the dire smelting of United Verde ore in converters has led to many interesti results. The ore in question is a heavy pyrite copper-zinc ore whi is microcrystalline and can not be dissected into copper and zinc co centrates by ore dressing methods, as in the case of Tennessee ar Flin Flon ores.

The experiments carried on at Clarkdale demonstrated that such a ore can be smelted in converters to recover copper as blister copper ar also to recover a good deal of the zinc and other volatiles (lead, ca mium, arsenic, and antimony) from the converter fumes. The invest gation involved the use of many techniques not commonly used wi converters, e.g., (1) blowing reducing gases through the tuyères to r duce cuprous oxide and magnetite, (2) use of a second row of tuyèr above the bath to burn excess reducing gases issuing from the bat and (3) use of preheated air for blowing. Using these various mod fications it has been found possible to treat heavy sulfide ores, wi the following possibilities as outlined by the authors.

1. It eliminates the necessity of roasters and reverberatory or bla furnaces and smelts coarse pyritic zinc-copper ore direct
2. No fuel is needed for the smelting and waste heat is available in su ficient supply to afford all necessary power for the process and to prehe the air blast
3. When no fuel is used and molten copper is not recirculated the zi vaporization is 50 to 60 per cent in the form of a high-grade zinc oxide fur containing most of the other volatile elements of the ore, but copper recove is likely to be low.
4. By using enough fuel to reduce magnetite to ferrous oxide, copper ca be separated with good efficiency.

[17] Ralston, O. C., Fowler, M. G., and Kuzell, C. R., Recovering Zinc fro Copper Smelter Products: Eng. and Min. Jour., Vol. 136, No. 4, p. 167, 1935.

5. No flux is necessary and a molten iron oxide product is made which may be further refined by gaseous or liquid reducing agents to give a product suitable for production of high-grade iron, and simultaneously all remaining zinc can be vaporized and recovered as an oxide fume.

6 Gases can be segregated containing no air and about 14 per cent SO_2 as raw material for the production of brimstone.

CHAPTER VI

FIRE REFINING

INTRODUCTION

Crude Copper. The copper produced by the pyrometallurgical methods we have discussed so far is usually too impure for direct use and must be *refined* to produce commercial grades of copper. The impurities in crude copper fall into two classes — (1) *base metals* and *nonmetals* which must be removed because of their harmful effect on the properties of the metal, and (2) *precious metals* which have sufficient value to pay for their separation As a rule the precious metals (principally silver and gold) have no deleterious effects on the properties of copper, and they may even be beneficial. They are usually present in small percentages — 100 ounces of silver per ton of crude copper represents only about $\frac{1}{3}$ of 1 per cent. Crude copper may be *blister copper* produced from matte, *black copper* from the reduction smelting of oxidized ores, or crude copper produced by smelting the native copper of the Lake Superior district — most of this last variety is fire refined to produce commercial *Lake copper.* Crude copper containing precious metals is often called *copper bullion.* Table 1 gives the analyses of some representative crude coppers.

These analyses show that crude copper will contain from 96.5 to more than 99 per cent copper and that the percentage of impurities varies quite widely. The gold and silver content, in particular, shows great variations — Noranda blister contains 3.10 ounces ($108 50) of gold per ton, Tennessee blister contains only 0.05 ounce ($1.75), and the crude Calumet and Hecla copper from the melting furnace contains practically none. Nkana copper contains 0.0068 per cent bismuth in addition to the impurities shown in the table. The amount and nature of the impurities determine the type of refining to be used.

Refinery Location. As crude copper contains approximately 99 per cent copper, the shipping weight which could be saved by refining it is negligible, and it is often desirable to ship crude copper from the smelter to refineries in more favorable localities. Most of the big copper smelters are located as close to the mines as possible, and the old practice of shipping ores, concentrates, and mattes to distant smelters has been discontinued except in a few special places. Many

TABLE 1

ANALYSES OF CRUDE COPPER

Source	Cu (%)	Ag (oz/ton)	Au (oz/ton)	As (%)	Sb (%)	Pb (%)	Ni + Co (%)	Zn (%)	Fe (%)	S (%)	Se + Te (%)
Katanga[a]	96 50	51 80	0 015	0 201	0 009	0.40	0 038	0 20	0 30	1 09	0 0002
Rio Tinto[a]	98 79	18 40	0 33	0.158	0 019	0 069	0 040	0 017	0 08	0 109	0 0065
Pyrite[a]	98 60	46 00	0 04	0 142	0 015	0 240	0 044	0 01	0 044	0 181	0 002
Phelps Dodge[a]	99 20	25 00	0 50	0 005	0 006	0 03	0 04	0 002	0 04	0 035	0 03
Tennessee[a]	99 20	8 50	0 05	0 005	0 006	0 013	0 025	0 002	0 044	0 023	0 025
Noranda[a]	99 20	14 00	3 10	0 004	0 004	0 005	0 025	0 002	0 025	0 151	0 20
Calumet and Hecla[b]	98 7	..	. .	0 04	.	. . .	.	.	1 0	0 2	.....
Nkana[c]	99 33	2 22	0 02		0 0006	0 0029	0 0383	trace	0 010	0 0265	0.0138

[a] Harloff, C. S., and Johnson, H F, The Nichols System of Electrolytic Copper Refining Am Inst Min & Met Eng Trans, Vol. 106, p 403, 1933.
[b] Lovell, E R, and Kenny, H C, Smelting Practice at Calumet and Hecla, Mining Cong Jour, p 68, October 1931
[c] Rhokana Refines Copper at Nkana Eng and Min Jour, Vol 140, No 1, p 42, 1939

ore deposits are in remote places where the problem of supplying the necessary power, fuel, and water is considerable; however, the mining operation itself requires considerable power, and all things considered it is better to locate the *reduction plant* (smelter) as close as possible to the ore deposit. This applies, of course, to deposits which are

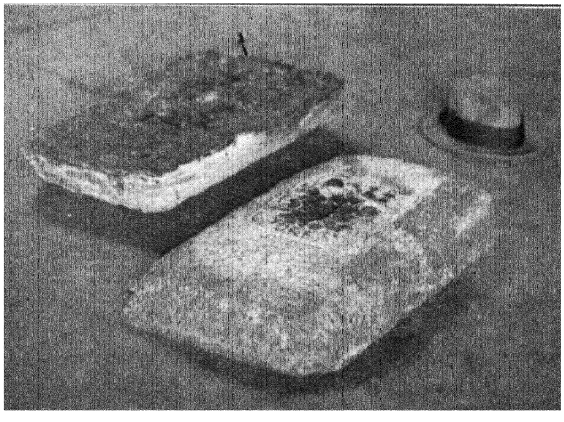


FIG. 1. Cakes of Blister Copper.

large enough to warrant the construction of a smelter; for smaller mines it is more expedient to install a concentrator and ship the concentrate to a large smelter.

Many refineries are located at a considerable distance from the source of the crude copper, and there are few smelters which are equipped to do a complete job of refining. In the United States, for example, there are several refineries located on the Eastern seaboard which treat crude copper from the Southwest, Africa, and South America. Belgium, France, and England also have large copper refineries for the treatment of crude copper from Africa and elsewhere. These locations are favorable because they are close to the large manufacturing centers which use the refined copper and also because they are accessible to cheap power.

Occasionally part of the refining is done at the smelter and part at a separate refinery. Anaconda, for example, fire refines its blister and casts it into anodes at its smelter in Anaconda, Montana. These anodes are then shipped to Great Falls, Montana, for electrolytic refining. The electrolytic refinery is located at Great Falls because this site is adjacent to a large hydroelectric plant on the Missouri River.

In recent years there has been a greater tendency to build refineries nearer to the smelters. Two recent additions are (1) The Montreal

East Plant in Quebec, Canada (1931), to refine Noranda and Flin Flon copper, and (2) the Nkana plant of the Rhokana Corporation in Northern Rhodesia (1935), which is the first electrolytic copper refinery to be erected on the African Continent.

Refining Methods. There are two methods for refining copper—*fire refining,* which we shall discuss in this chapter, and *electrolytic refining,* which will be taken up later. The two methods are closely connected, however, because much of the world's copper is treated by both. The normal sequence of operations in copper refining is (1) fire refining in an *anode furnace,* from which the copper is cast into *anodes,* (2) electrolytic refining of the anodes to produce *cathodes* of electrolytic copper, and (3) resmelting and further refining of the cathodes in a *cathode furnace,* from which the refined copper is cast into wirebars or other commercial shapes. The two fire refining steps are similar in principle; the crude blister copper is treated in the anode furnace to remove the bulk of the impurities and bring the copper to the proper *pitch* for casting into anodes; the cathodes are fire refined to remove sulfur and other impurities taken up by the copper in the melting operation, and again to bring the copper to the required pitch.

Fire refining is an oxidizing operation and is used to remove those impurities which are readily oxidized. Electrolytic refining serves to remove the impurities which cannot be oxidized ahead of the copper, notably (1) the precious metals, (2) bismuth, and (3) small amounts of several other elements — Ni, Co, Se, Te, As, and Pb. It is generally considered that copper should not be refined electrolytically unless it contains enough precious metals to pay for the refining or unless it contains bismuth, which is not removed in fire refining. This classification, however, includes much of the crude copper produced throughout the world; the notable exception in the United States is the Lake copper, which ordinarily is not electrolyzed.

REFINING FURNACES

Construction. Fire refining furnaces are called by different names depending either upon the nature of the charge or the nature of the material being cast — thus we have *refining furnaces, anode furnaces, cathode furnaces,* and *wirebar furnaces.*

All these are reverberatory furnaces, but they are small as compared with smelting reverberatories. In width they range from 11 to 14 feet and are from 26 to 43 feet long as a general average; refining furnaces will hold from 120 to 350 tons of molten copper.

The construction of these furnaces differs in some details from that of smelting reverberatories. Many furnaces are constructed prin-

cipally of siliceous refractories, but there is a tendency to use more magnesite and other basic material — especially in side walls and hearth, which are exposed to the corrosive metal oxides.

Acid bottoms are commonly made of silica brick, after the practice followed in the Michigan copper furnaces; these bottoms are more satisfactory than monolithic silica bottoms such as are used in matting furnaces. Bottoms may also be constructed of magnesite brick, and Noranda[1] has developed a successful basic monolithic bottom made by sintering on layers of "Magnafrit," a granular basic refractory consisting chiefly of magnesia and lime.

The construction of the bottom is of great importance in refining furnaces because of the danger of break-outs of the heavy charge of molten copper through the bottom and because the molten copper may penetrate cracks and float up parts of the refractory bottom. Brick bottoms are laid in the form of a shallow inverted arch, and the brickwork is tied in with the side walls. Monolithic bottoms are laid over a brick substructure and are sintered on in successive thin layers. All these bottoms must be carefully expanded as the furnace heats up to avoid cracking. Before using, a new bottom must be *seasoned* by melting a small amount of copper in the furnace and allowing the bottom to become saturated with copper. It is essential that refined copper be used for seasoning because impure copper would contaminate or "poison" subsequent charges.

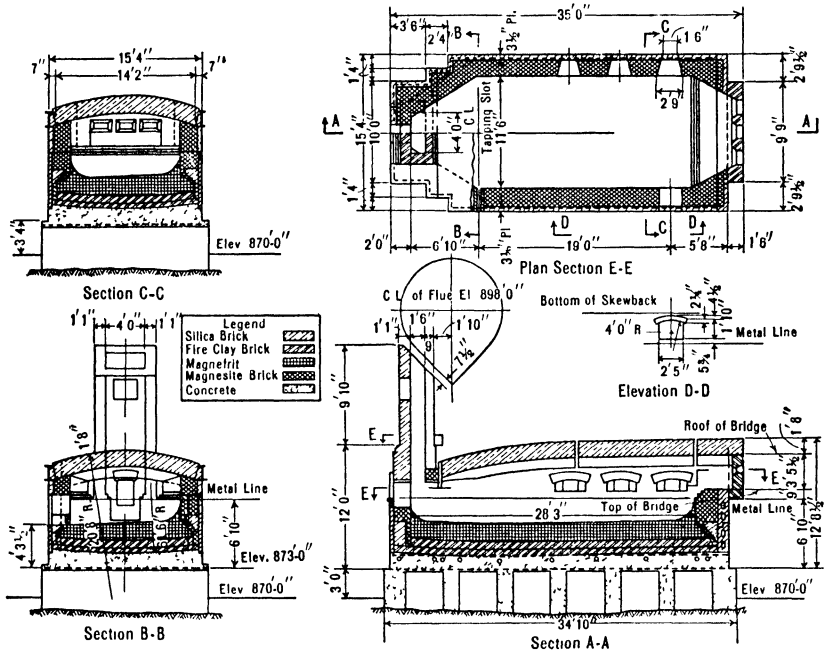
Many refinery furnaces have the foundation set on cast iron plates which in turn rest on brick pillars; others use some sort of vault under the foundation or have pipes embedded in the foundation through which air can be circulated. The purpose of these constructions is to keep the bottom cool and avoid the break-outs which might occur if the refractory bottom were to be softened by prolonged heating at high temperatures.

Refining furnaces are bound together with steel buckstaves and tierods, and some employ tension springs on the tierods to keep the tension constant as the furnace expands and shrinks on heating and cooling. Side walls are made of silica brick, lined with magnesite as a rule, and the roof is generally a sprung arch of silica brick.

These furnaces are provided with openings along the side for charging and skimming; these are closed by means of water-cooled metal doors (often copper), or by metal-backed refractory doors which can be luted in place with refractory clay. Molten copper is withdrawn from the furnace through a *tapping slot,* which is a slot in the side wall

[1] Boggs, W B and Anderson, J. N., The Anode Department of the Noranda Smelter: Am Inst. Min. & Met. Eng. Trans., Vol. 106, p. 329, 1933.

extending from the lowest point on the hearth to a point above the maximum depth of the molten charge. Before the furnace is charged, the tapping slot is filled with a stiff mixture of ground refractory and water and a number of *tapping bars* are set in place across the slot on the outside of the furnace. These are generally square iron bars placed horizontally across the tapping slot, one above another, and held in place by lugs on the outside of the furnace. These bars back up the refractory in the tapping slot and prevent it from being pushed out by the weight of molten copper behind it. The number of tapping



(*Boggs and Anderson, Am Inst. Min & Met Eng Trans, Vol 106, pp 335–337, 1933*)

FIG 2. Anode Furnace, Noranda.

bars used will vary from time to time, depending upon whether the charge fills the furnace completely or only partially. When tapping the furnace, these bars are removed, and the refractory material in the slot is broken out a little at a time so that the charge can be withdrawn slowly; when the slot has been cleaned out to the bottom, the hearth can be completely drained. Figure 2 shows the construction of the anode furnace at Noranda, and one view shows a section of the furnace through the tapping slot.

Fuels. Refining furnaces may be fired by pulverized coal, fuel oil, or gas, and in general the combustion, burners, etc., resemble those of

smelting reverberatories. A discussion of the advantages of various fuels used in refining furnaces is given in a paper by Bardwell,[2] of the Great Falls, Montana, reduction plant; lump coal on grates, pulverized coal, fuel oil, and natural gas have all been used at the Great Falls plant. The data in Table 2 are taken from Bardwell's paper.

TABLE 2

COMPARATIVE DATA ON USE OF PULVERIZED COAL, OIL, AND GAS AT GREAT FALLS, MONTANA

	Pulverized Coal	Oil	Natural Gas
Calorific value of fuel	12,590 Btu/lb 11,960 (as purchased)	19,224 Btu/lb	983 Btu/cu ft
Average production tons of copper per charge	235 tons	233 tons	233 tons
Average hourly rate of fuel consumption	2,663 lb	188 gal	32,983 cu ft
Fuel per ton of copper produced	272 lb	19 4 gal	3,397 cu ft
Btu per lb of copper produced	1,627	1,441	1,670
Average temperature of gases leaving furnace	1940° F (1060° C)	1940° F (1060° C)	1940° F (1060° C)
Stack temperature	600° F (315° C)	600° F (315° C)	800° F (427° C)
Heat distribution; per cent of Btu in fuel.			
Available in furnace	46 7	44 7	41.9
Absorbed in boilers	38 9	40 2	36 6
Stack loss	14 4	15 1	21.5

Refining furnaces are commonly equipped with waste-heat boilers to abstract heat from the waste gases. Note that Table 2 shows that about 35 to 40 per cent of the total heat in the fuel is absorbed in the boilers. Coal ash, which tends to form an insulating blanket on the charge, is partly responsible for the higher consumption of coal per ton of charge as compared with fuel oil; the higher consumption of gas may be accounted for by the fact that the non-luminous gas flame is a less efficient radiator than the luminous gas or coal flame. Bardwell, however, does not attribute much weight to this last reason and believes that the difference is caused by differences in furnace operation or in the placing of the burners. It is likely that under the best operating

[2] Bardwell, E S, A Comparison of the Use of Various Fuels in Copper-Refining Furnaces Am. Inst. Min. & Met. Eng. Trans., Vol 106, p. 449, 1933.

conditions for each fuel there would be little variation in thermal efficiency.

THE REFINING PROCESS

The operation of the fire refining process has changed very little since it was employed in the Welsh smelters in connection with the older smelting methods; furnaces have been improved and increased in size, better charging and casting methods have been developed, and the modern refinery has a purer copper to start with; but fundamentally the process has not changed. Refining is a batch operation, and one charge is refined and cast before more new material is added to the furnace. The steps involved in refining are listed below.

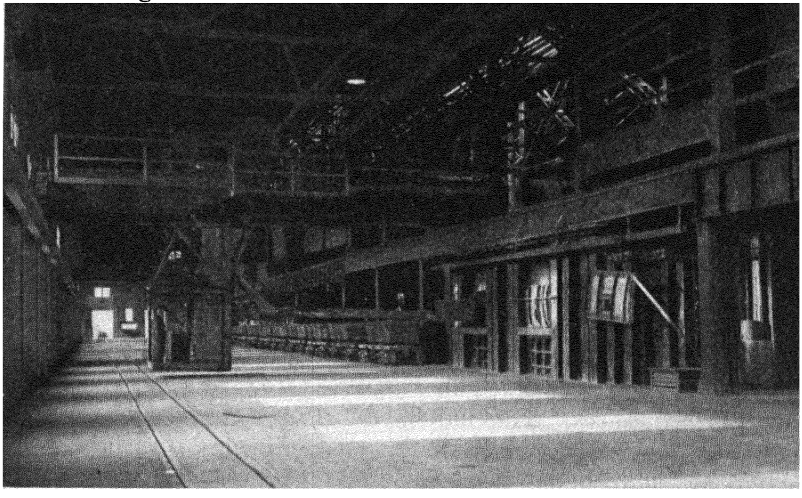
Charging. The manner in which the furnace is charged depends upon the form of the crude copper. If liquid blister is being treated it is charged by pouring it from ladles through a launder set in the side wall of the furnace. This form of charging is usually employed when the refining is done in the smelting plant, although the International Nickel Company[3] has designed a refractory-lined hot metal car to haul blister copper a distance of 1¼ miles from the smelter to the anode furnaces. This unit holds 70 tons of molten copper and consists of a cylindrical ladle mounted by means of trunnions on standard railroad trucks, the ladle is provided with burner ports for heating up a cold car or holding a charge under heat.

Crude copper which is shipped for any considerable distance arrives at the refinery in the form of solid cakes or slabs weighing perhaps 350 pounds each. Scrap charged to the furnace will usually be solid, and the cathodes (for cathode furnaces) are flat slabs which weigh about 150 pounds. These are placed in the furnace through the side doors by means of a charging machine. This machine employs a long arm with a flat paddle, or "peel," on the end; the operator of the machine can manipulate the arm in any direction and can turn the paddle over to dump its load in the furnace. The solid material is loaded on the paddle, and the operator then proceeds to stack it in the furnace in such a way as to load in the maximum amount. Figure 3 shows a picture of one type of charging machine.

Oxidizing; "Flapping." After the charge has melted down (melted "flat") the oxidation stage begins. Formerly the copper was "flapped" or struck with a rabble blade in such a way as to cause ripples to travel across the surface; this exposed a greater surface to

[3] Benard, Frederic, Transportation of Molten Blister Copper by Rail Am Inst. Min. & Met. Eng., Tech. Paper 909 (Metals Technology), February 1938

the oxidizing atmosphere in the furnace and aided in the oxidation of the impurities. The common method used today is to blow compressed air into the bath through iron pipes inserted through the side openings in the furnace. The oxygen in the air attacks the impurities and oxidizes them; the iron pipes gradually burn away and the iron oxide enters the slag or skim.



(*Courtesy Anaconda Copper Mining Company*)

FIG. 3. Charging Cathodes into Wirebar Furnace.

The operation of melting down solid copper slabs takes considerable time and makes a longer operation than the refining of liquid blister. This is not entirely a disadvantage, however, because the oxidation proceeds rather rapidly at the large surface exposed by the melting slabs, and a great deal of the oxidation will have already taken place by the time the charge has melted flat. This cuts down the time required for " flapping " or blowing. Oxidation during melting is more rapid than the oxidation caused by blowing air through the molten copper.

As the bath is exposed to oxidizing conditions, the base metal impurities are oxidized and escape from the metal bath. Sulfur and a little of the arsenic and antimony form volatile oxides and are carried out by the furnace gases. The other metal oxides together with a good deal of copper oxide rise to the surface of the metal bath as a viscous slag or " skim "; a little silica is sometimes thrown on the bath to slag the metal oxides. The appearance and amount of slag formed will depend upon the nature and quantity of the principal impurities

in the copper. The slag is skimmed continuously during the oxidizing period, and this continues until no more slag forms and liquid Cu_2O begins to form on the bath. This liquid has a characteristic oily appearance, and its presence indicates that the oxidation is complete and that the bath is completely saturated with oxygen in the form of Cu_2O. Toward the end of the *fining* (oxidizing) period, small ladle samples are taken and allowed to solidify, and the appearance of the surface and fracture of these serves to indicate the condition of the bath. As the amount of sulfur in the charge decreases, the bubbles (formed by SO_2) will disappear from the sample, and when the end of the fining period is reached the sample will be brick red, coarsely crystalline, lusterless, and brittle. This is *set copper* or copper completely saturated with oxygen.

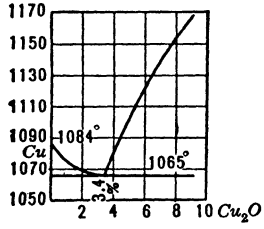
Cu_2O exhibits the rather remarkable property of being soluble in molten copper, and when the liquid is saturated with oxygen it contains from 6 to 10 per cent Cu_2O (0.60 to 0.90 per cent oxygen). The Cu-Cu_2O alloys freeze with the formation of a eutectic containing 3.45 per cent Cu_2O, so that solidified set copper consists of coarse crystals of Cu_2O in a matrix of the eutectic.

When the copper in the furnace has arrived at the set copper stage the sulfur and metallic impurities have been largely oxidized; the bath is now carefully skimmed and the metal is ready for the next stage, which involves the reduction of most of the Cu_2O back to metallic copper.

Poling. The reduction of the Cu_2O is accomplished by thrusting wooden poles into the bath. The heat of the bath causes destructive distillation of the wood, and the gases evolved (H_2O, CO, H_2, and hydrocarbons) stir the bath, and the reducing gases reduce the Cu_2O to metallic copper. As the poling proceeds, ladle samples of the copper are cast and examined, and the appearance of these samples indicates the degree of deoxidation of the bath. When the copper has been poled sufficiently the sample has a metallic luster and a rose color, as contrasted with the lusterless, brick-red set copper; the crystals are finely radiated and give the surface a silky appearance. Copper at this stage is known as *tough-pitch* copper.

The poles used are usually green tree trunks 6 to 10 inches in diameter; many varieties of wood have been used for this purpose. Green wood is preferable because it contains more moisture and gives off a greater volume of gas. About six or eight poles will usually suffice to treat 100 tons of copper, depending upon how much oxygen is present; the oxygen content of set copper depends upon the temperature, and the higher the temperature the more Cu_2O that can be

dissolved in the metal (Fig. 4). During the last stages of poling (often throughout the entire operation) the bath is covered with a layer of charcoal, wood, or low-sulfur coke to prevent reoxidation of the copper and to permit the operator to hold the copper at the proper *pitch* during casting.



(Reproduced by permission from Hofman and Hayward, Metallurgy of Copper, p. 16, McGraw-Hill Book Co., New York, 1924)

FIG. 4. The Cu-Cu_2O Equilibrium Diagram.

Tough-pitch copper is not completely deoxidized but contains about 0.05 per cent oxygen (0.45 per cent Cu_2O), and a microscopic examination of tough-pitch copper shows the Cu-Cu_2O eutectic at the boundaries of the large copper grains (Fig. 6). This copper has a flat *set;* i.e., when cast it will have a flat surface, it is tough and malleable and can be readily rolled, drawn into wire, etc. Most commercial metal is tough-pitch copper.

Overpoling means carrying the copper past the tough-pitch stage by removing too much of the oxygen, and this gives the copper undesirable properties. There are always some impurities remaining in refined copper because it is impossible to skim the slag perfectly; these will ordinarily be in the form of oxidized particles mechanically entrained in the copper, and as such are relatively harmless. If the reduction is carried too far, these impurities will be reduced to the metallic state and will alloy with the copper; in this form they may have a pronounced effect on electrical conductivity and other properties. Overpoled copper is porous and brittle and does not have the proper pitch for casting. This is probably due to the dissolution of reducing gases (CO, H_2) in the molten copper, for these gases are quite soluble if there is no oxygen in the bath to convert them to the relatively insoluble H_2O and CO_2.

The theoretical explanations of the phenomena encountered in fire refining of copper are still inadequate, and many factors are involved which are yet to be completely investigated — solubility of various gases in molten and solid copper; the exact reactions which take place and the equilibria involved; effect of "traces" of impurities; etc. A review of some of these investigations has been given by Ellis.[4] Some of the observed facts for which complete explanations are lacking are as follows:

1. Oxidation and poling will produce a tough, ductile copper containing in the neighborhood of 0.05 per cent oxygen. This *tough-pitch*

[4] Ellis, O. W., A Review of Work on Gases in Copper: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 487, 1933.

copper is the ordinary commercial " copper." By *pitch* is meant the physical properties of copper which regulate its casting and fabricating properties — thus a copper with the correct pitch can be cast in open



(*Courtesy United States Metals Refining Company*)

FIG. 5. Partly Oxidized Copper Showing Crystals of Copper in a Matrix of the Cu-Cu_2O Eutectic.

Taken from the " set " (oxidized) surface of a tough-pitch wirebar. The left side of the picture is the surface of the wirebar, and the oxygen content diminishes toward the interior. The region to the left of the arrow consists almost entirely of eutectic and will contain about 0.38 per cent oxygen. The region to the right of the arrow will average about 0.25 per cent oxygen.

molds to give a dense, sound bar or slab with a flat surface or *set*; the metal will be tough and can be readily rolled or drawn. If the pitch is not correct, however, the metal will be porous and brittle, and the surface will not be flat. Although the oxygen content of the copper may be the principal factor in determining its pitch, there is evidence that it is not the only factor.

2. Completely deoxidized copper can be produced which is as dense, tough, and ductile as tough-pitch copper or more so. The production of such copper requires a special technique, however, and it cannot be produced by overpoling in the refining furnace. Later we shall consider some of the methods used for making this oxygen-free copper.

3. Slight overpoling can be remedied by " flapping " the bath to

bring about slight reoxidation. If the overpoling is decided, however, the bath must be reoxidized to set copper and poled again, if the copper is to be held at the proper pitch during the casting.

4. The pitch and set of the copper are affected by the pouring temperature and the mold temperature.

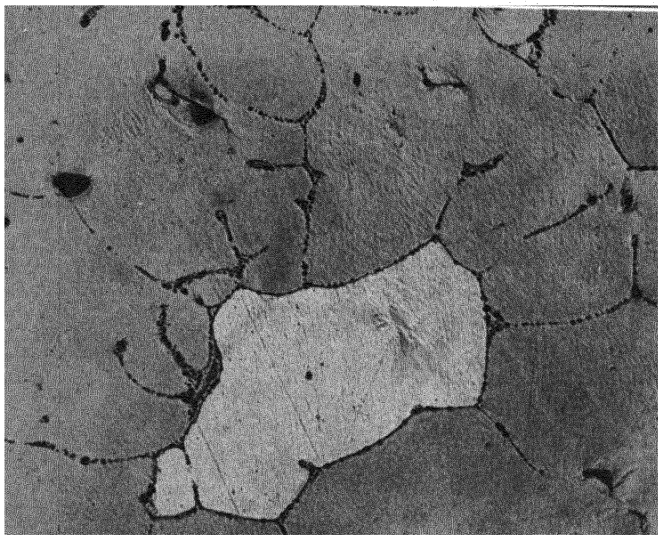


FIG. 6. Photomicrograph of Electrolytic Tough-Pitch Copper " As Cast."

Shows the Cu-Cu_2O eutectic at the grain boundaries of the copper crystals.

Composition of Fire-Refined Copper. Table 3 gives the analyses of a number of copper anodes — copper which has been fire refined but has not been electrolyzed. These can be compared with the analyses of crude copper as given in Table 1. The anode copper *a* in Table 3 represents the average limits of impurities in anodes produced at the Nichols refinery in treating a number of crude coppers — the analyses of some of these are those marked *a* in Table 1.

As a rule these fire-refined anodes will contain 99.2 to 99.6 per cent copper with not more than 0.4 to 0.8 per cent total impurities. The oxygen content of many anodes is higher than that of tough-pitch copper which is to be cast into wirebars or other finished products (such as would be produced from a cathode refining furnace). The gold and silver remain in these anodes as well as small percentages of most of the other impurities. Electrolytic refining of these anodes

TABLE 3

ANALYSES OF ANODE COPPER

Source	Cu (%)	Ag (oz/ton)	Au (oz/ton)	As (%)	Sb (%)	Pb (%)	Ni + Co (%)	Fe (%)	S (%)	Se + Te (%)	O (%)	Bi (%)
Nichols[a]	99.20	10	0 2	0 03	0 01	0 02	0 06	0 001	. .	0 02	0 10	.....
	99.60	48	2.4	0.144	0 06	0 12	0.27	0 0026	...	0 17	0 30	. ....
Noranda[b]	99.50	13 3	8 45	0 0004	trace	trace	0.0204	0 0160	0 0030	0 2900	0 094	0 0003
Montreal East[c]	99 49	31 40	4 577	0 0126	0 0073	0.0236	0 0143	0 0083	0 0155	0.183	.. ..	.....
Nkana[d]	99.40	2 22	0 02	.. . .	.....	. .	. .	. . ..	0 0030	.	0 003	.....
Raritan[e]	99 25	30 0	0.40	0 060	0 022	0.053	0 050	0.058	0.004	0 086	0.100	0.003
Great Falls[e]	99.3	67 0	0 30	0 085	0 04	. .	.....	....	. .	.....	.....	.....

[a] Harloff, C S , and Johnson, H. F , op cit , p. 403

[b] Boggs, W B , and Anderson, J. N , Anode Department of the Noranda Smelter Am Inst Min & Met Eng Trans , Vol. 106, p 344, 1933.

[c] McKnight, H S., Montreal East Plant of Canadian Copper Refiners Am Inst Min & Met. Eng Trans., Vol 106, p. 352, 1933.

[d] Rhokana Refines Copper at Nkana· Eng and Min Jour , Vol. 140, No 1, p 42, 1939

[e] Burns, W T , Refining Anaconda Copper at Raritan and Great Falls: Eng and Min Jour., Vol. 128, No 8, p 306, 1929.

will produce copper containing less than 0.06 per cent total impurities as a rule.

" Refined " and " pure " copper are relative terms; there is no such thing as absolutely pure copper, and the object of the various refining methods is to produce a commercial metal which meets certain specifications and tolerances set up by the trade. In another chapter we shall consider some of these standards, but for the present we shall be mainly concerned with the technique and practice of refinery operations.

REFINERY PRACTICE

In order to illustrate the application of fire refining methods we shall give brief descriptions of some representative fire refining operations; the first two operations (Calumet and Hecla, and British Copper Refiners Ltd.) produce commercial copper directly from crude copper; the third is an example of blister refining to produce anodes (anode furnaces) and the fire refining of cathodes (cathode furnaces).

Calumet and Hecla.[5, 6] The furnaces used in refining copper at the Calumet and Hecla plant resemble those used for melting of the native copper concentrate (Chapter IV) except that jackets are used instead of tierods for binding the ends of the refining furnaces. These furnaces will hold from 250 to 450 tons of molten copper depending on whether the sides and bottom are new or very much worn.

The charge consists principally of molten copper from the melting furnace, and it flows directly from the melting furnace to the refining furnace through a launder. Copper oxide precipitate from the leaching plant is treated in the refining furnace also. A blanket of rich concentrates is spread over the furnace bottom to protect the acid refractory, and the copper oxide is charged on top of this; after this solid material has been partly melted the molten copper from the melting furnace is added.

As soon as the molten copper is in the furnace, air pipes are inserted in the bath and oxidation begins; and the charge is completely oxidized by the time the solid material is completely molten. The copper oxide in the precipitate aids in this oxidation. The principal function of the oxidation is to remove iron and sulfur, and silica is thrown on top of the bath to slag the iron oxide as fast as it forms.

[5] Lovell, E. R., and Kenny, H. C., Present Smelting Practice at Calumet and Hecla: Mining Cong. Jour., p. 67, October 1931; Eddy, C. T., Arsenic Elimination in the Reverberatory Refining of Native Copper: Am. Inst. Min. & Met. Eng. Trans., Vol. 96, p. 104, 1931.

[6] Hillenbrand, W. J., Poull, R. K., and Kenny, H. C., Removal of Arsenic and Antimony from Copper by Furnace-Refining Methods: Idem, Vol. 106, p. 483, 1933.

After the oxidation is complete and the iron slag has been skimmed, green hardwood poles are inserted and the bath poled to about 0.04 to 0.05 per cent oxygen — this tough-pitch copper is then ready for casting. The slag is skimmed, granulated in water, and then dried and mixed with coal screenings to be charged back into the melting furnace.

The native copper in the Lake deposits is extremely pure, and hand-picked pieces of the metallic copper display electrical properties and purity superior to the best electrolytic copper. In addition to the copper, however, the deposits contain heavy arsenic minerals and occasionally native silver. These follow the copper into the concentrate and become alloyed with it in the melting furnace. To remove the arsenic a special treatment is used.

After the iron slag has been skimmed, powdered soda ash is blown into the bath while the copper is still oxidized but before poling begins. Most of the arsenic reacts with the soda ash thus:

$$2As + 5Cu_2O \rightarrow 10Cu + As_2O_5$$

$$As_2O_5 + 3Na_2CO_3 \rightarrow 2Na_3AsO_4 + 3CO_2$$

The sodium carbonate melts at the furnace temperature and forms a liquid slag on the surface of the bath; the sodium arsenate is soluble in this slag and is thus removed. Any antimony present is removed by a similar set of reactions. The soda ash slag is very fluid and extremely corrosive to the furnace brickwork so it must be skimmed as soon as possible. After this slag is removed the poling and casting proceed in their normal order — often the poling is started even before the soda ash slag is skimmed.

Copper treated by the soda ash process is sold as " Prime C. and H." copper and meets all the specifications required of electrolytic copper. For some architectural and other uses, arsenic is a desirable constituent because it imparts greater resistance to corrosion; so two other brands, " Natural C. and H." and " CL " brands, are made in which the soda ash treatment is not used Typical analyses of the three grades are given in Table 4.

In addition to these brands, some metal is sold on the basis of silver content. High-silver Calumet and Hecla copper is used for special purposes which require the metal to maintain its strength at high temperatures.

British Copper Refiners, Ltd.[7] The refinery of British Copper Refiners, Ltd., is located at the city of Prescot, about 8 miles northeast

[7] Aldrich, C. H , The Fire Refinery of British Copper Refiners, Ltd.: Am. Inst. Min. & Met. Eng. Trans , Vol. 106, p. 467, 1933.

TABLE 4

ANALYSES OF LAKE COPPER

	Prime C. and H.	Natural C. and H	CL
Copper + silver	99 9500	99 9100	99 6545
Arsenic	0 0025	0 0445[a]	0 2000[b]
Iron	0.0025	0 0025	0.0025
Nickel	0.0015	0.0015	0.0015
Sulfur	0 0015	0 0015	0 0015
Oxygen	0 0420	0 0400	0.0400

[a] Arsenic content ranges from 0 02 to 0 06 per cent
[b] Arsenic content ranges from 0 06 to 0 50 per cent.

of Liverpool, England. The refinery treats Roan Antelope blister from Africa.

The refining furnace has a capacity of 200 tons of copper and is fired with pulverized coal. The furnace is set on 4-foot concrete piers to permit cooling of the hearth; these piers are capped with ¼-inch steel plates spread with a thin layer of graphite. On top of the piers rest the 2-inch thick ribbed cast iron plates which carry the furnace bottom. These plates are separated by 1-inch spaces to provide for expansion, and the graphite prevents binding to the metal caps on the piers.

The furnace bottom is shaped by a layer of concrete composed of ganister and cement tamped in place; sheets of 1/16-inch steel are laid over this concrete and the silica-brick bottom laid on top of these steel sheets. The working bottom consists of two 12-inch inverted arches of silica brick laid dry with broken joints, and any cracks are filled with hot pulverized silica. The brick in these arches is keyed in such a way that if any of the brick in the upper layer wears thin and floats up, the bottom layer can be depended on to hold the charge. Side walls are made of magnesite brick to about 6 inches above the metal line. The roof is a sprung arch of 15-inch silica brick laid dry and with broken joints.

In charging the furnace, four or five wheelbarrows of sand are first thrown on the hearth, and then a thin layer of wire scrap is added to serve as a cushion. The cakes of blister copper are then stacked in the furnace with the charging machine, and melting is started. When the charge is melted (" off bottom ") the slag is skimmed, and the air pipes inserted. Blowing is continued and the slag is skimmed at intervals until the " say ladle " sample indicates an oxygen content of 0.90 per cent; then the slag is skimmed clean and a fairly thick

layer of low-sulfur coke is spread over the bath. Any rejected wirebars or refined scrap which is to be remelted are added at this point.

Poling is carried out in the usual manner, using a good grade of green hardwood poles. When the oxygen content has reached 0.03 to 0.04 per cent the poling is stopped and the charge cast into wirebars. The bars produced are equal in appearance to the best electrolytic wirebars and show an appreciable margin over the requirements of standard specifications for electrolytic copper.

The slag produced amounts to 2 or 3 per cent of the weight of the charge. This is skimmed into steel boxes, and after solidification it is crushed and shipped to an associated plant for further treatment.

Ontario Refining Company.[8,9,10] The Ontario Refining Company treats principally the blister copper from the Copper Cliff smelter of the International Nickel Company; it maintains both anode and cathode furnaces.

Anode Furnace Practice. The plant has three anode furnaces with space provided for a fourth. These are rated at 300 tons capacity, but charges up to 350 tons are handled regularly. The inverted arch of the furnace bottom is made of concrete, which rests on cast iron plates supported on 4-foot concrete piers; the working bottom consists of two layers of 12-inch silica brick. The walls below the metal line are 15-inch magnesite brick, and above the metal line they are 15-inch fireclay brick. The roof is a sprung arch of 20-inch silica brick; the skewbacks are of water-cooled steel. The verb is made of chrome brick, and chrome brick dividers are used throughout the furnace between magnesite and acid brick. There are four charging bays in each furnace; two of these are closed by water-cooled doors and the other two have doors of clay brick in a steel frame. Doors are operated by hydraulic lifts. The life of the various refractories in the furnace is approximately as follows: roof, 100 to 125 charges; magnesite side walls, 200 charges; clay-brick side walls, 100 charges; and bottoms, 3 to 5 years, by patching the top layer when needed.

Prior to 1936 all the incoming blister reached the refinery in the form of 460-pound cakes. These were cast from two 150-ton holding

[8] Benard, Frederic, Electrolytic Copper Refinery of Ontario Refining Company: Am. Inst. Min. & Met. Eng. Trans., Vol 106, p 369, 1933

[9] Benard, Frederic, Transportation of Molten Blister Copper by Rail from Smelter to Refinery: Am. Inst Min. & Met. Eng., Tech Paper 909 (Metals Technology), February 1938.

[10] Benard, Frederic, An Investigation into Anode-Furnace Refining of High-Nickel Blister Copper: Am. Inst. Min. & Met. Eng., Tech. Paper 910 (Metals Technology), February 1938.

furnaces at the smelter and hauled to the refinery. The practice employed when charging solid blister is outlined below.

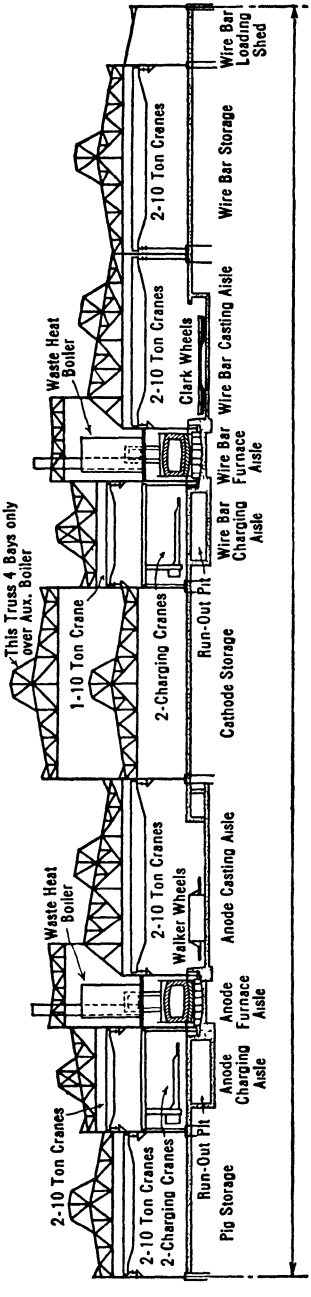


FIG. 7. Section Through Casting Building, Ontario Refining Company. (*Benard, Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 376, 1933*)

The first charge to the furnace was a layer of anode scrap spread over the floor to protect it from the impact of the copper pigs. The blister cakes or pigs were then charged by means of a crane-operated casting machine. Other miscellaneous feed to the anode furnace included more anode scrap, silver-refinery slag, tank-house and storage-building sweeps, bosh scale, metallics from slags, etc. About 325 tons could be charged in 2 hours.

After charging, the charge was melted, and oxidized to about 0.60 per cent oxygen; then the slag was skimmed, the bath covered with a layer of coke and the charge poled until the oxygen content was low enough to give a flat set. Green poles of white and yellow birch were used, and 5 to 6 tons of poles would be required per charge. The anodes cast from the furnace contained about 99 per cent copper with varying amounts of gold and silver; the chief base-metal impurity was nickel, which would average about 0.45 per cent. The slag produced averaged about 2 per cent of the weight of the charge, and this was crushed and returned to the smelter. Pulverized coal was used for firing, and the coal burned amounted to 11 to 12 per cent of the weight of the charge.

Practice since 1936 has been essentially the same as that outlined above except that the blister copper reaches the refinery furnace in the liquid form. In 1936 a specially

designed car was developed to haul molten blister from the smelter 1¼ miles away. A standard-gage track was laid in the anode-charging aisle so that the car could be spotted directly along the side of the furnace and its contents poured into the furnace through a launder. The car holds about 70 tons of metal, which means that 4 to 5 carloads are required to provide a furnace charge (300 to 350 tons).

Table 5 shows the time required for a complete furnace cycle, using solid blister and liquid metal.

TABLE 5

COMPARISON OF FURNACE CYCLE FOR BLISTER CAKE AND HOT METAL, ONTARIO REFINING COMPANY

Process (300-ton charge)	Time (hours)	
	Blister Cake	Liquid Metal
Charging	2	15
Melting and skimming	14	5
Flapping	1½	0
Poling	2½	3
Casting	3½	7
Complete cycle	23½	30
Percentage of slag	2%	5%

The holding furnaces previously used at the smelter were coal-fired reverberatories; blister from the converters was charged directly into these furnaces, slag was skimmed, and the charge was poled sufficiently to give a flat set to the blister cakes. Under the new system the blister copper goes directly from the converters to the transfer car and from there to the anode furnace. The entrained converter slag which was formerly removed in the holding furnaces now enters the anode furnace, and this accounts for the fact that the slag production is more than doubled. About one-third of the blister copper coming from the smelter is *Orford process copper* (copper obtained from the working of copper-nickel *bessemer matte*), and this metal is so highly oxidized that ordinarily no "flapping" or oxidizing is necessary — by the time the copper is charged and skimmed it will contain about 0.9 per cent oxygen and is ready for poling.

The total time for a furnace cycle has been increased by about 6½ hours over the old practice; this is because each anode furnace actually serves as a holding furnace for about 15 hours while enough blister copper is being produced to fill it. During the filling period

sufficient coal is burned to keep the charge at approximately 2250° F (1232° C), and slag skimming begins as soon as the charge level is high enough. As there must always be furnace room available for the molten blister, the furnaces are operated on a staggered schedule so that there is always one furnace being filled. These refining furnaces are equipped with two tapholes, and under the old practice both were used for casting; the new schedule makes it more desirable to use only one taphole, and accordingly the time required for casting a charge has been doubled.

Blister copper reaching the refinery will contain from 0.50 to 1.50 per cent nickel, and the anode furnace treatment removes about 15 to 20 per cent of this. The rest of the nickel is removed in the electrolytic tanks, and it appears that the oxygen content of the anodes (as regulated by poling) has its effect on the dissolution of nickel from the anodes. Low-oxygen anodes (0.03 to 0 04 per cent oxygen) seem to give the best results because most of the nickel dissolves in the electrolyte (which is desirable from the refinery standpoint). When the oxygen content of the anode is higher (0.10 to 0 30 per cent) less of the nickel dissolves, and more of it is found in the electrolytic slimes. The reason for this behavior is not clear, and this is one more example of the interrelation of the oxygen content, impurity content, "set," and "pitch" of copper for which a complete explanation is lacking.

Cathode, or Wirebar Furnaces. The furnaces, charging aisle, waste heat boilers, casting equipment, etc, in the wirebar furnace building practically duplicate the anode furnace equipment. The cathode furnaces are also rated at 300 tons capacity, but the normal charge is about 320 tons. This is less than the anode furnace charge because a part of the refined copper produced is sold as sheared cathodes and hence is not remelted in the cathode furnace.

The cathodes from the electrolytic tanks are slabs of highly purified metallic copper about 3 feet square and ½ inch thick; each cathode weighs about 240 pounds. These may be sheared into smaller sections for remelting in the brass trade, to be used as anodes for copper plating, etc., but most of them are remelted in the cathode furnace to be cast into wirebars to be rolled and drawn into wire; the rough surface of cathodes makes them unsuited for direct mechanical fabrication. When these cathodes are melted down in a fuel-fired furnace the copper absorbs small amounts of impurities (principally sulfur), and to remove these and bring the copper to the proper pitch the metal must be carried through the complete cycle of melting, flapping, and poling.

At Ontario the cathodes are stacked in the furnace by means of a

crane-operated charging machine. The bath is oxidized by blowing compressed air through the metal until the oxygen content is about 0.90 per cent; slag is then skimmed and the bath poled down to 0.028 per cent oxygen to give tough-pitch copper. Coal consumption is about 12 to 13 per cent of the total charge, and the slag formed amounts to 1.75 per cent. A complete cycle requires about 24 hours, broken down as follows:

Charging,	$1\frac{1}{2}$ to 2 hours	
Melting period,	10 to 11 hours	Flat, $6\frac{1}{2}$ hours Afloat, 4 hours
Oxidizing, poling, and casting,	11 to 12 hours	Flapping, 4 hours Poling, 3 hours Casting, 5 hours

The temperature of the copper at various stages is given as follows:

	°F	°C
"Off bottom" or afloat	2150	(1177)
Flapping, early stages	2140	(1171)
Flapping, before coking	2175	(1191)
Poling, 1 hour after coking	2125	(1163)
Poling, 2 hours after coking	2100	(1149)
Ready to cast, about 3 hours after coking	2070	(1132)
Casting	2060	(1127)

The cast copper (wirebars and other shapes) will contain 99.96 per cent copper, 0 03 per cent oxygen, and a total of about 0 01 per cent of all other impurities. Complete analyses of this and other electrolytic coppers will be given in Chapter VIII.

Summary. The examples quoted above illustrate the application of fire refining methods although, of course, they do not illustrate all the different modifications of furnace practice. The following general observations may be made.

1. Fire refining may be used alone to produce a marketable grade of copper, and when it is so used the product is often equal to the best grade of electrolytically refined metal.

2. Copper containing precious metals in any quantity will be refined electrolytically, as this is the only practical method for their separation. The electrolytic process also removes the base metal impurities associated with the copper.

3. Bismuth is one metal which cannot be removed satisfactorily by fire methods. The Nkana refinery, for example, was built to treat copper which contains too much bismuth to make a satisfactory fire-

refined product; the Nkana blister does not carry sufficient gold and silver to warrant electrolytic treatment for their recovery alone.

4. Blister copper is generally fire-refined before casting into anodes; this removes some of the impurities and thus makes the electrolytic refining easier. In some cases, e.g., Mount Lyell, Tasmania,[11] a high-grade blister may be cast directly into anodes. Fire-refined anodes will usually contain about 99.2 per cent copper; these will be produced from crude copper which may contain as little as 96.0 per cent copper.

5. Copper for anodes is usually poled only enough to give a flat set, and the oxygen content may be as high as 0.30 per cent. Finished shapes such as wirebars and cakes for mechanical fabrication must be poled to the tough-pitch stage with an oxygen content of about 0.03 per cent; this applies whether the treatment is all fire refining or the melting of electrolytic cathodes.

CASTING OF COPPER

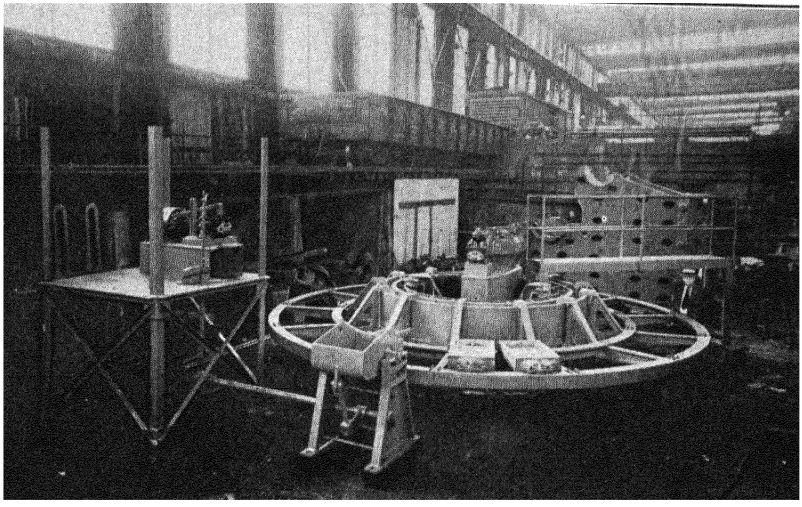
The casting of copper into suitable shapes involves a number of considerations — temperature of the metal, " pitch " and " set " of the metal, and the type of casting equipment used. The old method of casting copper was to dip the copper from the furnace with hand ladles and pour it into molds; modern furnaces are too large for this method of casting, and today practically all copper is cast by mechanical methods.

The care which must be exercised in making copper castings depends upon the purpose for which the finished object is intended. In casting blister copper, for example, it is only necessary that the cakes be flat enough to stack properly, and irregularities and blow-holes on the surface are not of great importance. Wirebars and cakes for rolling, on the other hand, must have smoothly finished surfaces so that when rolled there will not be any defects in the wire or sheet.

Molten copper has a strong tendency to absorb oxygen from the atmosphere, and therefore it must flow from the furnace to the mold through the shortest possible distance. The flow of metal from the furnace is usually a steady stream, and this flows into a tilting spoon or ladle from which it flows into the mold. The interruption of the flow which is necessary when replacing a filled mold by an empty one is brought about by raising the lip of the pouring ladle for a short time. Meanwhile, of course, the copper continues to flow from the furnace into the pouring ladle. The lip of the pouring ladle should be as close to the mold as possible.

[11] Murray, R. M , Electrolytic Copper Refining at Mount Lyell, Tasmania: Am. Inst. Min. & Met. Eng. Trans , Vol 106, p. 408, 1933.

Casting Blister Copper. Blister copper (and other forms of crude copper) is usually cast in the form of large cakes (Fig. 1) which will weigh from 350 to 450 pounds. The blister is usually stored in a holding furnace as it comes from the converters and is cast from this



(Courtesy Traylor Engineering and Manufacturing Company)

FIG. 8. Twenty-Two-Foot Casting Wheel.

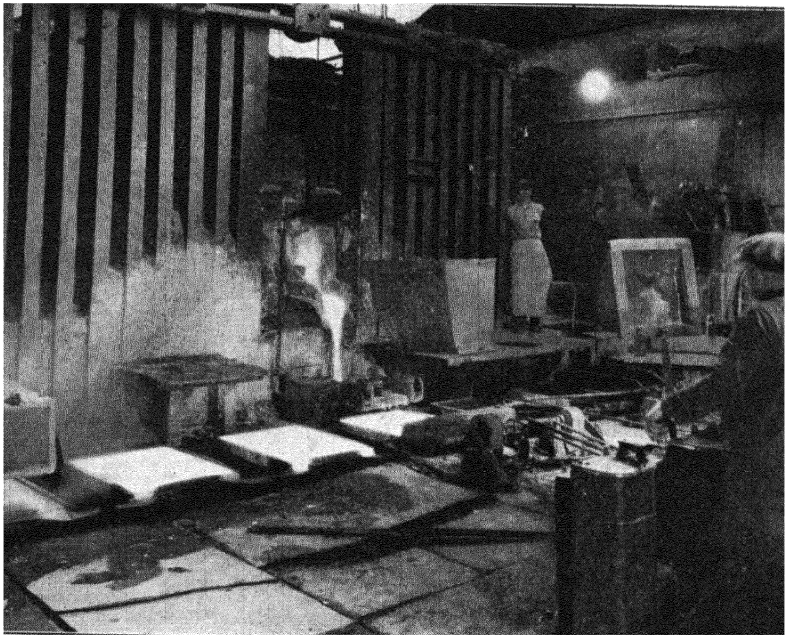
Two molds are in place on the wheel. The pouring ladle and its control mechanism can be seen in the foreground.

furnaces resembling refining furnaces; others are cylindrical furnaces which are nothing more than Peirce-Smith converters without the tuyères and equipped with burners to keep the charge hot. The cylindrical furnaces are convenient for casting because they can be tilted easily for pouring.

When blister is to be cast it is often taken from the converter while slightly underblown and still contains about 0.1 per cent sulfur — this gives a sounder casting. If the blister copper is overblown it may be necessary to pole the blister copper enough to bring the oxygen content down and give the copper a flat set. Some slag may be skimmed from the holding furnace if necessary.

The blister copper molds are carried on a mechanically driven horizontal wheel or on a " straight-line " casting machine by means of which the molds are successively brought under the pouring lip of the casting ladle. The molds are usually made of copper and are

cast as needed by means of a master mold. When cylindrical holding furnaces are used the blister may be poured directly into the molds without the use of a pouring spoon or ladle. After the filled molds pass under the pouring lip the copper begins to solidify; and as soon as it is frozen, sprays of water are played on the cakes to cool them.



(Courtesy Anaconda Copper Mining Company)

FIG. 9. Casting Copper Anodes in a Straight-Line Casting Machine.

Casting Anodes. The liquid copper from which anodes are cast is usually furnace-refined copper although blister may be cast directly. Anode molds are commonly made of refined copper and may be made from a cast iron master mold or cast in sand. The molds are carried on casting wheels or on straight-line machines (Fig. 9), and the copper enters the mold from a pouring spoon into which it flows from the furnace. Flow of the copper from the refining furnace is regulated by gradually cutting the burned clay out of the tapping notch as the level of the metal drops.

It is essential that the pouring spout be controlled by a mechanism which gives a smooth motion so that there is no sudden surge of metal into the mold to cause splashing. The casting machine must be driven so that it accelerates and decelerates smoothly, because any

sudden jerks of the molds would mar the surface of the solidifying metal.

Figure 9 shows the casting of anodes in a straight-line machine, and Figure 10 shows some finished anodes. All anodes have the same general shape — a flat rectangular slab with supporting lugs at the top — but they may vary somewhat in size and weight. Anodes such as those

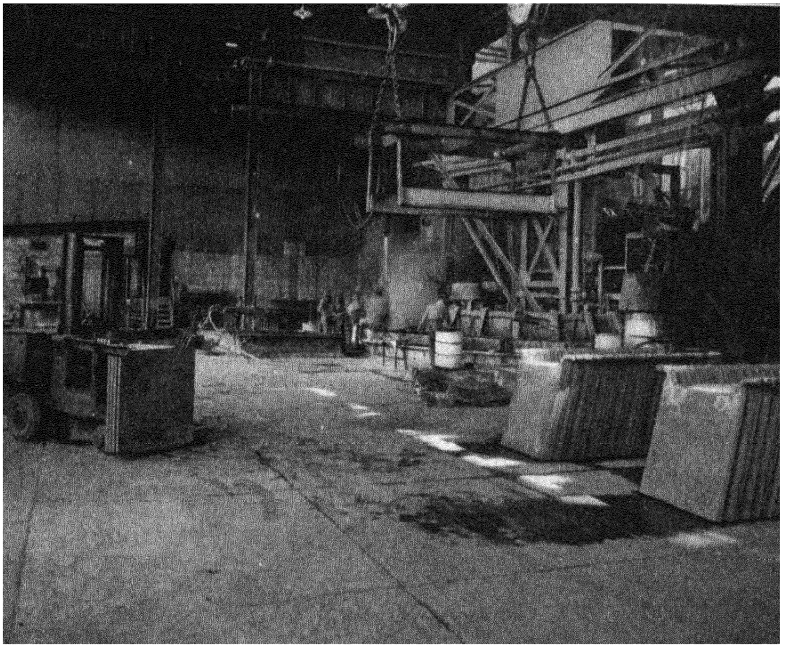


FIG. 10. Copper Anodes.

shown (for multiple refining) will be approximately 3 feet square and about 2 inches thick; smaller anodes will weigh about 500 pounds and larger ones up to 750 pounds. The cast lugs serve to support the anode in the electrolytic tank and one of them makes contact with the *busbar* which carries the electric current. Some anodes are cast with a "Baltimore groove" in one lug — a special notch which gives a better contact between anode and cathode bar.

The following description applies to casting of anodes on a casting wheel; the procedure with a straight-line machine would be essentially the same except that the molds would move in a straight line instead of a circle.

For the first round or two of the machine only about ½ inch of copper may be poured in each mold to dry and warm the molds; these cast "warmers" are scrapped and remelted. After this each mold

is filled to the proper depth; then the pouring ladle is tilted back and the wheel turned until the next mold is under the pouring lip. After a filled mold has moved through ⅕ to ¼ of the circumference, the surface will have frozen over, and from here on water sprays are played on the surface to aid the cooling. After the mold has moved far enough so that the anode is completely solidified it is lifted from the mold by an automatic device and transferred to a water *bosh* or tank through which a large volume of cold water is circulating. This quickly chills the anodes down to room temperature, and then they are taken from the bosh for inspection. Defective anodes are scrapped, and the good anodes are racked for transport to the tank house.

The empty mold is sprayed with a wash (usually a slurry of powdered silica or bone ash in water) to prevent the copper sticking to the mold and continues on its journey around the wheel until it again comes under the pouring lip.

Casting of Refined Copper. Refined copper for the market is usually cast on a casting wheel. In many respects the process resembles that used in casting anodes. These are large horizontal wheels carrying the molds on the circumference. The central wheel or turntable rests on rollers running in a circular track and is driven by an electric motor. The two principal types of casting wheels are the Walker and Clark machines. On the Walker wheel the molds are placed with their long axes along the circumference of the wheel; on the Clark machine the molds are set parallel to the radial arms of the machine. Figure 8 shows a casting machine set up in the manufacturer's plant; two of the molds are in place, and in the foreground can be seen the pouring ladle and the control platform from which the ladle is tilted.

In general the casting procedure follows that used in casting anodes —" warmers " are made in the cold molds, the molds are sprayed with a wash (which dries immediately on the hot mold) to prevent sticking, sprays are used for cooling, and the final cooling takes place in a water bosh. Usually the molds are turned over automatically to discharge the piece into the bosh.

Great care is taken to insure a finished shape having no defects; the temperature of both mold and liquid metal must be controlled, and of course, the copper must have the correct " pitch." Finished shapes are carefully inspected before being shipped.

Where a variety of shapes are made on the same wheel, a large supply of molds must be kept on hand; each type of mold may require a different type of pouring ladle. Figure 11, for example, shows a pouring ladle with five spouts pouring wirebars into a five-bar mold.



FIG. 11. Pouring Wirebars.

Vertical Casting of Copper.[12] The top or "set" surface of copper cast in an open mold is somewhat wrinkled, and it often has a high oxygen content and some porosity. Copper cast in "flat" molds (Fig. 9) with a short vertical dimension will have this "set" surface on its largest face; the faces in contact with the mold are comparatively smooth. When copper wirebars or cakes are rolled down into rods or

[12] Strom, B. H., Vertical Casting of Copper at Carteret: Eng. and Min. Jour., Vol. 136, No. 2, p. 59, 1936.

sheets, the set surface may result in surface imperfections on the finished object.

In order to diminish the amount of this set surface, the copper refinery of the United States Metals Refining Company at Carteret, New Jersey, has developed a method of " vertical " casting in which the mold for cakes is placed with its long dimension vertical, and the set surface then appears on the end rather than on the face of the cake. Vertical casting has been used even for the relatively long, thin wirebars. Other refineries throughout the world have been licensed to use the vertical casting method, and it is used in casting shapes for certain particular specifications.

It is often necessary to " scalp " or machine the set surface off wirebars or cakes when these are to be used to produce wire or sheet with carefully finished surfaces; the use of vertically cast shapes obviates the waste and expense of the scalping operation.

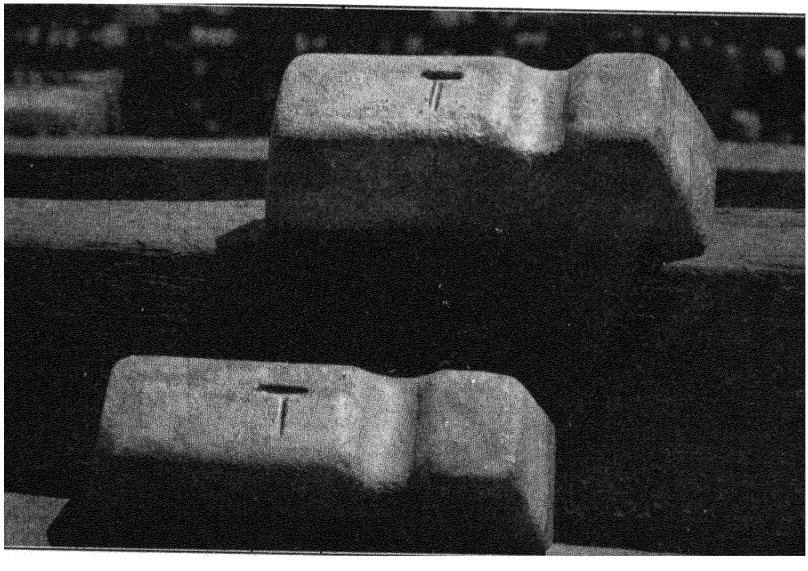


FIG. 12. Copper Ingots.

Commercial Shapes of Copper. Following are the shapes in which most refined copper appears on the market. These are castings, or refinery products; of course much copper is sold in semi-fabricated forms such as rods, bars, tubes, plates, and sheets, but these are all originally made from refinery shapes such as are listed below.

Shapes for Remelting. Copper for remelting or alloying is commonly sold as *ingots* (Fig. 12), cathodes, and " warmer bars." Ingots weigh

about 20 pounds apiece, and *ingot bars* (essentially two or three ingots cast together) weigh about 50 pounds. These ingot bars are notched so that they can be easily broken into smaller pieces. Cathodes may be sold just as they come from the electrolytic tanks, but usually they are first sheared into smaller pieces.

Copper sold for melting and alloying must meet certain required chemical and electrical specifications, but physical defects such as imperfect bars, shrink holes, and concave tops are of no consequence. The shapes listed below, however, are used primarily for direct fabrica-

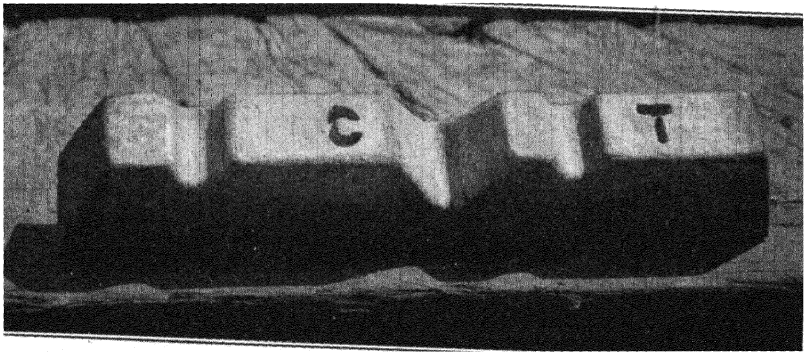


FIG. 13. Copper Ingot Bar.

tion, and in addition to chemical and electrical specifications, these shapes must meet rigid requirements as to freedom from surface defects in set and casting, and they must not show more than a certain specified variation from standard weight.

Wirebars. Because of the large amount of copper used for rod and wire, the *wirebar* is one of the most common shapes for refined copper — some refineries cast their entire output in the form of wirebars. These shapes are used for rolling to rod, which may then be drawn into wire. They are long rectangular rods (Fig. 14) about 3½ to 4 inches square and tapered at both ends to facilitate rolling; they range in length from 38 to 54 inches and in weight from 135 to 300 pounds. The cross-section is not perfectly square because the molds are slightly tapered so that the bar can be readily removed. Ordinary wirebars have a set surface on the largest flat face; when desired, "scalped" wirebars or vertically cast bars can be supplied which do not have this set surface.

Cakes and slabs are used principally for rolling to sheet; these are approximately rectangular in section and of various sizes and shapes, depending upon the product to be rolled. Vertically cast cakes

(" wedge cakes ") have the set surface on the end where it is relatively harmless.

Billets are round bars cast on end, and they are principally for piercing in the manufacture of seamless tubing; often they are

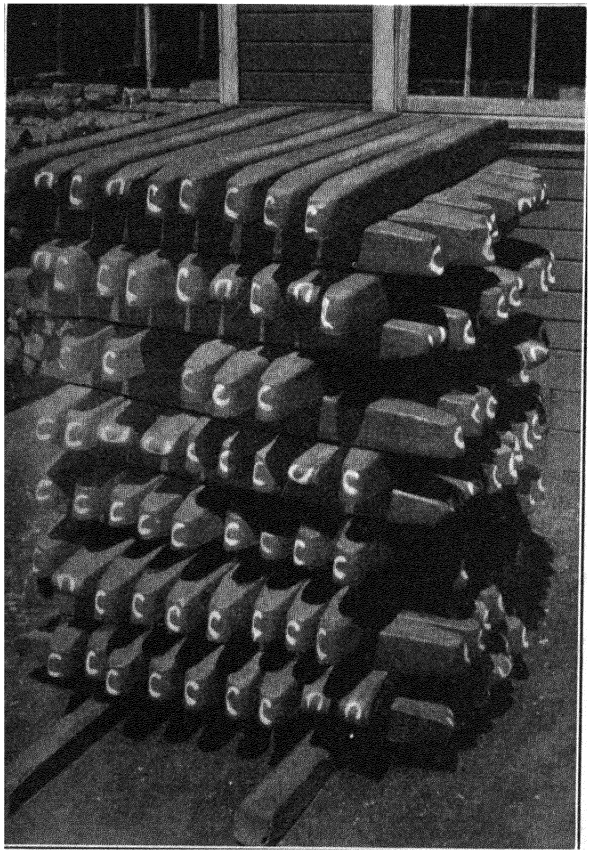


FIG. 14. Copper Wirebars.

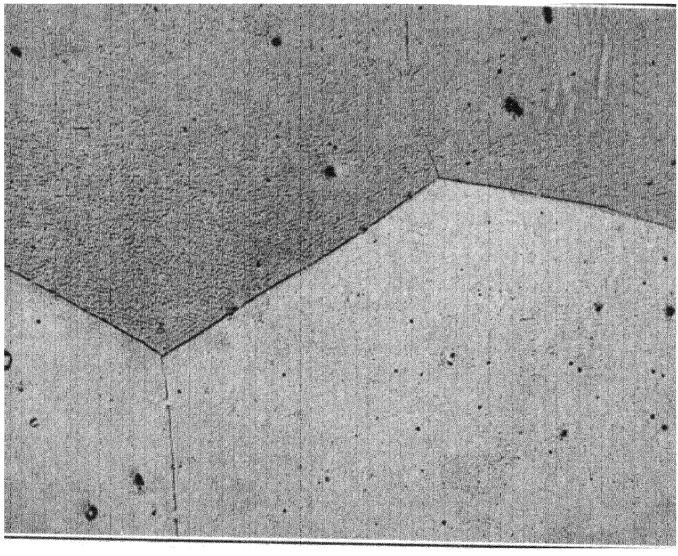
made of deoxidized copper. Some billets are also used for rods and other shapes made by the extrusion method. Billets range from 2 to 10 inches in diameter and from 75 to 750 pounds in weight.

DEOXIDIZED COPPER AND OXYGEN-FREE COPPER

Table 6 gives some typical analyses of commercial copper; note that some of these types (tough-pitch coppers) contain about 0.03 to 0.04 per cent oxygen whereas others, including the cathode copper, contain no oxygen. As we have already noted, the presence of this small

amount of oxygen is essential to get sound castings from the ordinary refining furnace. Tough-pitch copper yields castings with a slightly crowned, almost flat set, and it freezes without the formation of cavities or *pipes*.

The removal of this small amount of oxygen produces some important changes in the properties of the metal. Oxygen-free copper is exceptionally ductile, is easily welded, and can be used where it must



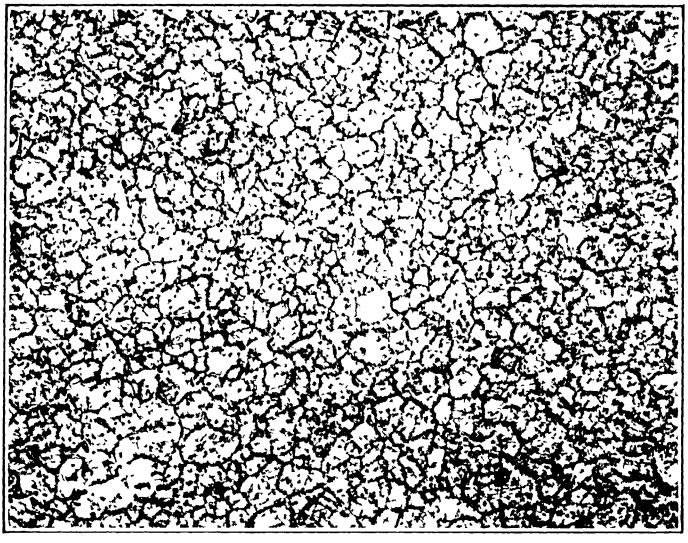
(*Courtesy United States Metals Refining Company*)

FIG. 15. O F H C Copper "As Cast."

Compare with Fig. 6.

be heated in a reducing atmosphere. If ordinary tough-pitch copper is heated in a reducing atmosphere above 400° C the reducing gases react with the oxide particles at the grain boundaries (see Fig. 16) and thus form cracks which cause the section to become brittle. Thus there are certain uses for which copper must be completely free of oxygen, and we shall now consider some of the methods of making such copper. Copper free from oxygen forms a deep pipe or shrinkage cavity on freezing, and this portion must be cropped and discarded or eliminated by feeding with molten metal during the solidification period.

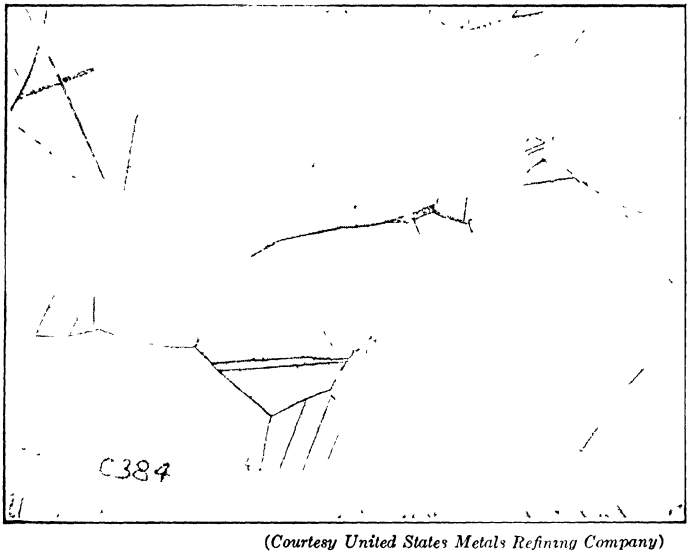
The difference between *deoxidized* and *oxygen-free* copper lies in the method of manufacture; deoxidized copper is tough-pitch copper that has been treated with a deoxidizing agent, and oxygen-free copper



(Courtesy United States Metals Refining Company)

FIG. 16. Tough-Pitch Copper, 12-Gage Wire Heated in Hydrogen Atmosphere for ½ Hour at 850° C.

Note the " attack " on the grain boundaries.



(Courtesy United States Metals Refining Company)

FIG. 17. O F H C 12-Gage Wire Heated in Hydrogen Atmosphere for ½ Hour at 850° C.

Compare with Fig. 16.

TABLE 6[a]

TYPICAL ANALYSES OF COMMERCIAL COPPER

Type of Copper	Impurities (per cent)											Electrical Conductivity (per cent)
	Ag	O	S	Fe	As	Sb	Pb	Ni	Se + Te	P	Si	
Cathode copper	0 0001	0 0000	0.0032	0 0010	0 0002	0 0005	0 0003	0 0013	0 0000	0.0000	0 0000	102 0
Electrolytic wirebar, United States	0 0007	0.0350	0.0021	0.0026	0 0009	0 0009	0 0014	0.0021	0.0002	0 0000	0.0000	100.5
Electrolytic wirebar, Chile	0 0001	0 032	0.0023	0 0037	0 0005	0 0004	0.0002	0 0005	0.0006	0 0000	0.0000	101.0
High conductivity, Lake	0 03	0.0420	0.0015	0 0025	0.0025	0.0005	0 0006	0 0015	0.0000	0 0000	0.0000	100.0
Arsenical, Lake	0.0000	0.0400	0.0015	0 0025	0.04	0.0000	0 0000	0 0015	0.0000	0 0000	0.0000	88.0
Phosphorized copper	0.0000	0.0000	0.0016	0.0013	0 0005	0.0010	0 0003	0 0016	0.0032	0.020	0.0000	80.0
Oxygen free copper[b]	0.002	0.0000	0 0025	0.0015	0.0008	0 0028	0 0004	0.0016	0.0031	0.0000	0.0015	100.5

[a] Metals Handbook, 1936 ed., p 1068, American Society for Metals, Cleveland.

[b] The oxygen-free copper contains a trace of bismuth.

is made by treating cathodes under such conditions that no oxygen is allowed to enter the copper. Note that the cathodes (Table 6) are free from oxygen.

Deoxidized Copper. Deoxidized copper is made by adding a strong reducing agent to molten copper. The copper is usually in the tough-pitch stage (0.03 to 0.05 per cent oxygen), and it may be taken directly from the refining furnace, or it may be obtained by remelting solid copper. The deoxidizing agent is added to the ladle or crucible containing the liquid metal, and it combines with the residual oxygen. The resultant oxide is insoluble in the melt, and it rises to the top; some will remain in the metal as mechanically included particles.

Phosphorus in small amounts is commonly used where the copper is not to be used for electrical purposes; it is necessary to add a small excess of phosphorus to insure removal of the oxygen, and this excess phosphorus alloys with the copper and greatly decreases its electrical conductivity (Table 6). Other deoxidizing agents are silicon, calcium, lithium, and calcium boride — the last three do not have much effect on the electrical conductivity.

Deoxidized copper forms a deep pipe when it freezes, so usually the upper part of the cast billet is cropped and scrapped.

Oxygen-Free Copper. Oxygen-free copper is made by special methods, of which we shall describe two.

O F H C Copper.[13] Commercial copper known as "O F H C" (oxygen-free, high-conductivity) copper is made by a patented process developed by the United States Metals Refining Company at Carteret, New Jersey. The plant contains a 75-ton, oil-fired reverberatory melting furnace (Fig. 18) which operates continuously; cathodes are fed in as fast as the copper is tapped out. The bath is poled continuously at the end opposite the burners to keep the oxygen content between 0.03 and 0.05 per cent. A constant stream of metal flows from the taphole of the furnace at a temperature of 1150° C.

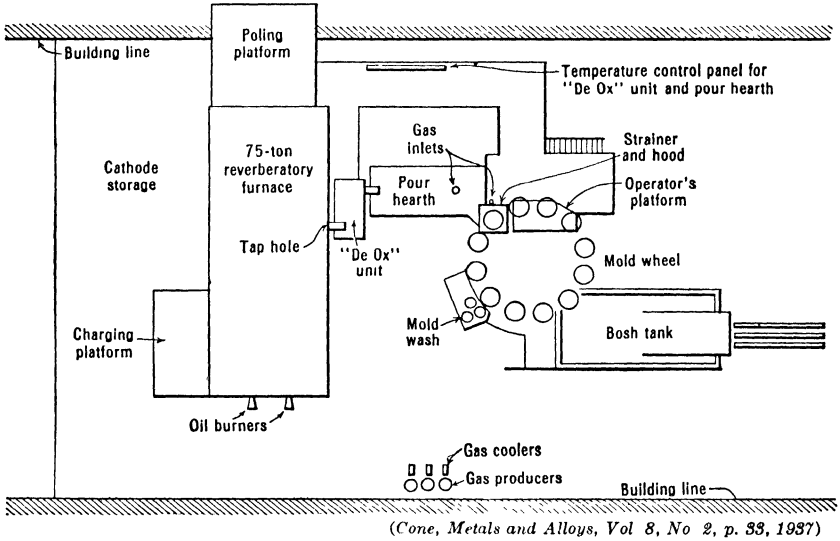
The molten copper flows through a refractory lined trough under a cover of charcoal and enters the deoxidizing unit. This is a specially designed refractory-lined vessel filled with high-grade wood charcoal over which the stream of molten copper trickles. The residual oxygen is reduced thus:

$$C + Cu_2O \rightarrow 2Cu + CO$$
$$CO + Cu_2O \rightarrow 2Cu + CO_2$$
$$C + CO_2 \rightarrow 2CO$$

The copper leaving the unit is completely deoxidized.

[13] Cone, E. F., Oxygen-Free High-Conductivity Copper: Metals and Alloys, Vol. 8, No. 2, p. 33, 1937.

The deoxidized copper passes through a special spout and into a closed launder which conducts it to the pouring hearth. The entire atmosphere in the spout, launder, and pour hearth consists of a special charcoal producer gas which contains about 27 per cent CO, 0.50 per cent CO_2, and the balance N_2; this gas should be free of H_2, H_2O, and hydrocarbons.



(*Cone, Metals and Alloys, Vol 8, No 2, p. 33, 1937*)

FIG. 18. Equipment Used in the Production of O F H C Copper.

The pouring hearth is an elongated cylindrical hearth in which a large bath of metal is constantly maintained; its purposes are (1) to regulate the temperature, and (2) to control the stream of metal during pouring. This hearth contains two low-frequency induction heaters, and by means of these the temperature is held within a 10° C variation. The pouring hearth is rocked mechanically to control the pouring, and the copper enters the molds through a spout enclosed in a special hood. This hood and the pouring hearth are kept filled with a controlled atmosphere of charcoal producer gas, and the bath of metal in the pouring hearth is covered with a layer of charcoal. These methods illustrate the difficulty of keeping molten copper from absorbing oxygen — deoxidized copper will pick up as much as 0.01 per cent oxygen in flowing from the furnace to the mold in an atmosphere of air.

The oxygen-free copper is cast into wirebars, billets, and cakes, all of which are cast vertically. These shapes all contain the shrink hole or pipe near the top which is characteristic of oxygen-free copper; the upper portion of each casting is cropped and scrapped.

One of the routine tests which is regularly made on samples of the finished shapes demonstrates some of the qualities of O F H C copper as compared with tough-pitch copper. The sample is forged and drawn into 0.08-inch wire, and the wire is annealed in a hydrogen atmosphere at 850° C for 30 minutes and then quenched. The wire is then subjected to a reverse bend test through a 90° angle. O F H C copper must stand 10 reversals without breaking, and as many as 12 or 15 are common. Tough-pitch copper subjected to the same treatment usually breaks after one reversal.

Coalesced Cathode Copper.[14] A recent process takes advantage of the fact that cathode copper is essentially oxygen-free copper and that the oxygen content of tough-pitch copper is caused by the exigencies of melting and casting. In the new process the absorption of oxygen is avoided because the copper is fabricated without ever becoming molten.

Small particles of cathode copper are first *briquetted* by compressing them at a pressure of 20,000 pounds per square inch. This is performed at room temperature and yields a coherent briquette which has a density of 80 to 86 per cent that of solid copper. The briquette is then heated in a reducing atmosphere — consisting of such gases as propane gas, nitrogen, steam, and hydrogen — at 1600° to 1670° F (871° to 910° C). The briquette then passes directly to the extrusion press through a controlled-atmosphere chamber which prevents oxidation.

In the extrusion press the copper is forced through a die at pressures of 30,000 to 53,000 pounds per square inch and emerges as a rod (or other shape, depending on the die used) of solid metallic copper. Under the high pressures in the extrusion chamber, the copper particles coalesce and develop a complete new grain structure; for this it is essential that the particle surfaces be clean and unoxidized, and this is the reason for the treatment in the deoxidizing atmosphere. The copper produced exhibits the same general properties that are characteristic of oxygen-free copper prepared by other methods.

One of the necessary requirements for this process is a suitable method for obtaining electrolytic copper in the form of small pieces, and research has solved this problem by developing methods for producing *brittle cathodes*. We shall describe these when we discuss the electrolysis of copper.

[14] Tyssowski, John, The Coalescence Process for Producing Semifabricated Oxygen-Free Copper: Am. Inst. Min. & Met. Eng., Tech. Paper 1217 (Metals Technology), June 1940.

Electrical Melting of Cathodes. Another method for the melting of cathode copper is the use of electric furnaces. The following quotation is taken from The Mineral Industry.[15]

> An interesting innovation of possible far reaching importance is the introduction of a new method of converting cathode copper into finished shapes. The International Nickel Co. has installed an electric arc furnace which is fed continuously with cathodes and delivers finished copper to vertical billet molds without going through the usual blowing and poling operations. Details of the operation are not available for publication, but it may well be that this will prove to be the forerunner of many similar operations. It has always seemed incongruous that material with the purity of cathode copper should require such a cumbersome treatment as that usually accorded it just to put it in a form suitable for use.
>
> It should be remembered that the real pioneer in the use of an electric furnace on a large scale was the United States Metals Refining Co. in their early work on O F.H.C. copper. They used an induction furnace rather than an arc furnace and the relative merits of the two must still be settled. It may even be possible that the same results obtained at the International Nickel plant may be reached in a reverberatory furnace provided special precautions are taken to keep a reducing atmosphere. The important thing is that it has been fully demonstrated that first class wire bars can be produced without oxidizing and poling in the accepted way.

[15] The Mineral Industry During 1937, Vol. 46, p. 196, McGraw-Hill Book Co., New York.

CHAPTER VII

SMOKE AND GASES

INTRODUCTION

In the previous chapters we have considered roasting, smelting, converting, and fire refining, and although we have discussed the solid and liquid products of the various furnaces, we have only casually mentioned the gaseous products. Perhaps this has been an unconscious holdover from early metallurgical practices, when roasting was done in heaps and stalls and smelting furnaces were equipped with short individual stacks which discharged the waste gases directly into the atmosphere. The damage to surrounding vegetation and the "stack losses," both in heat and in metallic values, caused by this wasteful practice soon led to the development of methods for better handling of waste gases. At this point we shall briefly consider the general problem of smelter smoke and the methods used in handling smoke and gases.

The importance of this question may be seen from a single example A reverberatory smelting furnace treating 800 tons of charge per day and burning 112 tons of coal would require about 38 million cubic feet of air (1500 tons) and would produce about 40 million cubic feet of waste gases (1650 tons). The heat carried by these waste gases would represent the equivalent of 50 to 60 tons of coal, and in addition these gases would carry off in suspension perhaps 80 tons of the charge in the form of dust and fume. The copper loss in the dust might easily amount to 5 or 10 tons a day, and in addition there might be considerable quantities of gold, silver, arsenic, etc. contained in the dust and fume.

The methods used for handling smoke and gases vary considerably, and the practice used at any given smelter will depend upon local conditions. In general there are four important facts to be considered about any particular smoke:

1. The amount produced per day.
2. The nature of the gaseous constituents.
3. The temperature of the smoke, and its sensible heat content.
4. The nature and amount of suspended matter carried by the smoke.

The terms *waste gases, flue gases,* and *smoke* are used rather loosely

and somewhat indiscriminately. Strictly speaking, the term *gas* or *gases* should be restricted to material which carries no solid or liquid matter in suspension; a *smoke* is gas carrying a certain amount of suspended matter, and it is this that renders it visible; all true gases are transparent, and the common gases found in metallurgical smokes are also colorless.

Gases produced in pyrometallurgical operations are discharged into the atmosphere, but before this is done, it is necessary to

1. Remove the suspended matter.
2. Abstract as much of the sensible heat as is practicable.
3. Remove the SO_2 or dilute with other gases to cut down the concentration of SO_2. Where it is not possible to remove all the SO_2, the smoke should be discharged into the upper atmosphere by means of a tall chimney.

COMPOSITION OF SMOKES

Gases. The principal gases found in the smokes from copper smelting operations are nitrogen, water vapor, carbon dioxide, carbon monoxide, oxygen, and sulfur dioxide. None of these gases have any commercial value except SO_2; when this is present in sufficiently high concentration the gases can be used for the manufacture of sulfuric acid or sulfur compounds.

Sulfur dioxide is also the only one of the true gases which is harmful to vegetation, and as it may also yield valuable byproducts, it is the most important from the standpoint of treatment and disposal of waste gases.

In all the pyrometallurgical operations that we have considered (except electric smelting), air has been used to burn either carbonaceous fuel or sulfides, or both, and as air contains 79.0 per cent by volume of nitrogen (including about 1.0 per cent argon and other inactive gases) which passes unchanged through the reactions, it follows that nitrogen will make up a large percentage of all smokes. Copper smelter smokes will contain from 73 to 77 per cent nitrogen as a rule. Carbon dioxide will be present if carbonaceous fuel is used; carbon monoxide is seldom found except in very small amounts. Water vapor will always be present, and the amount depends upon the moisture (if any) in the furnace charge, and the amount of hydrogen and moisture in the fuel. Let us briefly consider the approximate analyses of the gases produced in different operations.

Reverberatory Matte Smelting. Reverberatory furnaces usually operate with a draft of about 0.1 inch water gage, and the combustion

is usually regulated so that a slight excess of air is used. The analyses of reverberatory flue gases will be:

	Per Cent		Per Cent
N_2	72 to 76	O_2	0 5 to 6 0
CO_2	10 to 17	H_2O	4.0 to 10 0
CO	0 0 to 0.1	SO_2	1.0 to 2.0

The amounts of CO_2 and H_2O will depend upon the fuel used, and the amount of moisture on the charge; the SO_2 content will depend upon the sulfur elimination from the charge. A large part of the free oxygen found in these flue gases may be due to leakage of air through charging holes and other openings in the furnace. These gases will leave the furnace at a temperature of 1800° to 2300° F (980° to 1260° C).

Refining. The gases from reverberatory refining furnaces are essentially the products of combustion of the fuel used; firing conditions resemble those of smelting reverberatories, but the amount of gas evolved from the bath is comparatively small. Following are some typical gas analyses:

	Per Cent		Per Cent
N_2	73 to 77	O_2	2 0 to 4 0
CO_2	8 to 15	H_2O	5 0 to 16 0
CO	0 0	SO_2	0.1

The exit gases from refining furnaces will have a temperature of 1900° to 2000° F (1040° to 1090° C).

As a general thing, two facts are characteristic of the gases from reverberatory furnaces (both smelting and refining furnaces) — (1) the high temperature of the gases makes it possible to use waste-heat boilers and other devices to recover much of their sensible heat content, and (2) the SO_2 content is too low to make suitable raw material for acid manufacture.

Converters. The gases from converters consist principally of N_2, SO_2, and O_2. The oxygen which passes through the bath is largely consumed, but some air is drawn into the flue around the converter mouth. Converters are blown into *hoods* (Fig. 4) and there is enough space between the converter and hood to permit the ingress of cold outside air. This dilution, together with the intermittent operation of the converters, makes it difficult to satisfactorily recover the sensible heat from converter gases. The SO_2 content of converter gases will range from 3.0 to 13.0 per cent.

Roasters. Roaster gases contain principally nitrogen, oxygen, and sulfur dioxide, the amount of SO_2 ranging from 4.0 to 9.0 per cent. The

amount of SO_2 in the gases depends upon the amount of sulfur in the charge; in copper roasting the conditions may vary from simple drying of high-copper concentrates (with the use of auxiliary fuel) to the autogenous roasting of heavy pyritic concentrate, and the SO_2 content of the gases will vary accordingly. The gases from blast roasting will resemble hearth-roaster gases in composition. Roaster gases are not as hot as the gases from smelting and refining furnaces; they will generally leave the roaster at a temperature of 1000° F (540° C) as compared with 2000° F (1093° C) for the reverberatory flue gases.

Blast Furnaces. Gases from blast furnaces smelting heavy pyrite ores and concentrates contain N_2, CO_2, H_2O, and SO_2; the amount of CO_2 will range from 2.5 to 4.0 per cent, depending on the amount of fuel used, and the SO_2 content will usually be about 6.0 to 7.0 per cent. Blast furnace gases are cooled by passing upward through a column of charge which abstracts much of the sensible heat. The gases from furnaces smelting oxide ores or concentrates (either blast furnaces or reverberatories) will be practically free of SO_2.

Electric Furnaces. The gases evolved from electric smelting furnaces (Chapter IV) are different from all the other gases considered in that no blast of air is required for the furnace, and consequently the waste gases are not diluted with such a large volume of nitrogen. If the electric furnace is sealed to prevent air leakage, the bulk of the waste gases comes from the charge itself, and the furnace gases will contain from 10 to 20 per cent SO_2. This is a decided advantage when it is desired to recover the sulfur. There is a possibility that gases much richer in SO_2 might also be made in roasting and converting if the practice of using oxygen or oxygen-enriched air were to be adopted.

Dust. The amount of dust carried out in stack gases will depend upon the fineness of the particles on the charge, the type of furnace, the method of charging, etc. The dust itself may include anything in the furnace charge which is fine enough to be carried by the gas current.

Fume. *Fume,* as differentiated from dust, refers to material which has been volatilized or sublimed, and then condenses when the gases become cooler. The most important constituents found as fume in copper smelters are

1. The lower, volatile oxides of arsenic and antimony As_2O_3 and Sb_2O_3.
2. Oxides of other volatile metals — e.g. PbO and ZnO.
3. Condensed water vapor.
4. Sulfuric acid and sulfates. A certain amount of SO_3 gas is formed from the further oxidation of SO_2, and the higher the SO_2 content the greater will be the amount of SO_3. The SO_3 combines with

water vapor to form droplets of sulfuric acid (H_2SO_4 + water), or it may combine with certain basic oxides, notably ZnO, to form $ZnSO_4$. Smokes which contain free acid are known as *acid smokes; basic smokes* contain an excess of basic oxides, and any free acid is neutralized.

In practice the dust and fume are often mixed together and collected as a single product; usually the collected product is called a dust — e.g. flue dust, Cottrell dust — even though the bulk of the material may be a true fume.

Table 1 gives the chemical analyses of a few smelter dusts taken at random. Note the extreme variation in composition and that the copper content is usually rather high.

WASTE-HEAT RECOVERY

Of the various methods which have been employed for recovering waste heat from furnace gases, by far the most important is the use of waste-heat boilers on reverberatory smelting furnaces

Waste-Heat Boilers.[1-7] Most of the discussion and illustrative examples given in this section are taken from a symposium on waste-heat boiler practice in the United States as published in the Transactions of the American Institute of Mining and Metallurgical Engineers.

Waste-heat boilers are standard equipment on practically all reverberatory furnaces. These boilers are usually set directly in front of the furnaces so that the furnace gases strike the boiler tubes as soon as they leave the furnace laboratory. The boilers themselves are usually of the vertical water-tube type, and the Stirling boiler (Figs. 1 and 2) is the most widely used Boilers may be arranged in different ways — each furnace may have a single boiler, or the furnace may have two boilers arranged in parallel or in tandem (Figs. 1 and 2).

Boiler practice does not greatly differ from that of direct-fired boilers in most respects, and we shall not consider such questions as boiler-feed

[1] Bardwell, E. S., Copper-Refinery Waste-Heat Boilers at Great Falls: Am. Inst. Min & Met. Eng Trans., Vol 106, p 225, 1933

[2] Barnard, E A., and Tryon, George, Waste-Heat Boiler Practice at Anaconda Idem, p. 230.

[3] Sager, N. W., and Mossman, H. W , Waste-Heat Boiler Practice at Nevada Consolidated Copper Corporation: Idem, p 237.

[4] Marston, J. R , Waste-Heat Boiler Practice at United Verde: Idem, p. 246.

[5] Honeyman, P. D. I , and Faust, P. A , Waste-Heat Boiler Practice at Miami Idem, p. 251.

[6] Rose, J. H., Waste-Heat Boiler Practice at the Magna Copper Company Smelter· Idem, p. 255.

[7] Marriott. R. A , Waste-Heat Boiler Practice at the Garfield Smelter: Idem, p. 257.

TABLE 1

ANALYSES OF SOME DUSTS, IN PER CENT

Type of dust, and location	Cu	As	Sb	Zn	Pb	Bi	S	SiO_2	Fe	Ca	Al_2O_3
Anaconda: Reverberatory furnace dust; collected under waste-heat boilers. Sample No. 1.[a]	22 0	11 6	12 0	9 2	3.4	1 4	0 7	9.0	14.2	0.4	1.5
Anaconda: Reverberatory furnace dust; collected under waste-heat boilers. Sample No. 2.[a]	19 7	22 0	0 3	3 5	2 3	1 5	0.1	5.7	10.7	0.6	2.7
Roan Antelope: Reverberatory furnace dust.[b]	31 22	. .	.		. .	..	5 7	19 82	3 9	2.2	11.37
Flin Flon: Roaster flue dust.[c]	7 43	.		4 2	. .	..	..	18 3	28 5	...	.....
Flin Flon: Roaster Cottrell dust.[c]	6 86	.	.	4 2	.	.	....	20.0	23 6	...	.....
Noranda: Roaster Cottrell dust.[d]	7 41	.			.		7.2	15 8	36 8	..	.....
Roan Antelope: Converter dust[b]	73 29				.	..	11 41	0.88	0.54	0.22	1.32
Noranda: Converter balloon dust.[d]	47 94		.	.	...	.	16 2	8 0	20 0	...	.....
Noranda: Converter Cottrell dust[d]	27 94			.		.	9 2	24 8	16 6	..	.....

[a] Barnard, E A , and Tryon, George, Waste-Heat Boiler Practice at the Anaconda Reverberatory Plant Am Inst Min & Met. Eng. Trans., Vol. 106, p. 230, 1933.
[b] Wraith, C. R , Smelting Operations at Roan Antelope, Idem, p 218
[c] Ambrose, J H , The Flin Flon Copper Smelter Canadian Inst Min Metallurgy, Bull 281, September 1935
[d] Boggs, W. B , and Anderson, J N , The Noranda Smelter. Am Inst Min. & Met Eng Trans , Vol 106, p. 184, 1933.

water and removing scale from the interior of the water tubes, which apply to all boiler operations. The operation of waste-heat boilers involves some additional factors which are discussed below.

The steam generated in these boilers may be used for many purposes around the plant — heating, generation of power, etc. It must be remembered, however, that these are essentially *waste-heat* boilers and that the smelting or refining furnace is not primarily a steam-producing unit; in refining furnaces, for example, the firing conditions vary considerably during the different stages of the refining cycle, and consequently the steam production is not constant. Waste-heat steam should not be relied upon to produce a steady and uninterrupted supply of steam power, as it would not be practical to operate the furnaces in such a way as to develop the maximum power of the boiler at all times. This fact applies to refining furnace boilers in particular because of the intermittent nature of the refining operation.

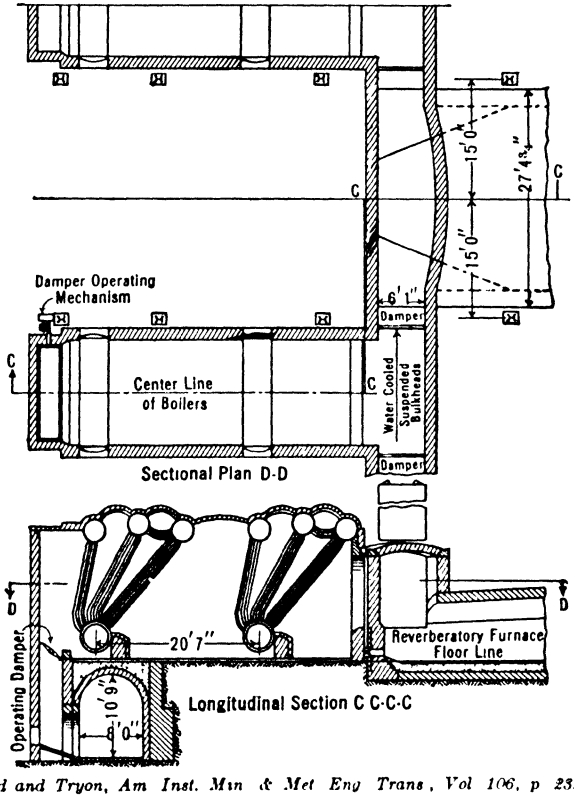
The gases from reverberatory furnaces are laden with dust and fume, which tend to deposit on the boiler tubes. Consequently the boiler and its setting must be arranged to permit frequent cleaning of the tube surfaces, and the removal of the dust which accumulates under the boiler. Fumes such as As_2O_3 and Sb_2O_3 tend to condense on the cool boiler tubes, and if the resulting deposit of dust and fume is not removed at frequent intervals it insulates the boiler and cuts down its efficiency. The tubes are generally cleaned by means of *soot blowers* supplemented by hand-operated lances of high-pressure air or steam. The dust which collects beneath the boiler is removed through clean-out doors. The first two entries in Table 1 give the analyses of waste-heat boiler dust at Anaconda; note the large amount of arsenic and antimony in these products, caused by the condensation of the volatile oxides on the cold boiler tubes.

The waste-heat boilers installed on the reverberatory furnaces at the Douglas smelter[8] are located directly over the skimming end of the furnace; the boiler tubes are exposed directly to the molten bath in the furnace, and there is no damper between the furnace and boiler. Waste-heat recovery has been greater than was ever attained with the conventional system of boilers and furnace separated by flues — largely because of the heat which reaches the boiler tubes by direct radiation from the incandescent bath of slag. Side skimming of slag is necessary in these furnaces because of the chilling effect of the boiler directly over the slag bath at the end of the furnace, and also to avoid fouling

[8] McDaniel, L. L., New Reverberatory Waste-Heater Boiler and Power Plant at Douglas Smelter: Am. Inst. Min. & Met. Tech. Paper 996 (Metals Technology), February 1939.

of the slag by the high-grade sintered dust dislodged during hand lancing to clean the boiler tubes.

Figures 1, 2, and 3 illustrate the waste-heat boiler installations on the smelting furnaces at Anaconda and United Verde (Clarkdale) and on the refining furnace at Great Falls, Montana. A brief summary of the practice at each plant is given below.



(*Barnard and Tryon, Am Inst. Min & Met Eng Trans., Vol 106, p 232, 1933*)

FIG. 1. Arrangement of Waste-Heat Boilers on Reverberatory Furnace, Anaconda

Anaconda. The use of boilers in tandem at Anaconda has been necessitated by limitations in building space; these tandem boilers are smaller than would be the case if single boilers were used. The boilers are located between the reverberatories (Fig. 1) and a pair of boilers may take the gases from the furnace on either side. About 80 per cent of the steam is generated in the first boiler in this tandem arrangement. The small boilers in tandem do not require the use of baffles to slow down the passage of the hot gases. These baffles are used in some cases on waste-heat boilers to permit more efficient ab-

straction of the heat in the gases; their principal disadvantages are (1) the increased resistance to passage of the gases and resulting loss of draft, and (2) the increased accumulation of accretions on the boiler tubes.

The accretions on the boiler tubes result from the mixing of fine dust with arsenic trioxide and other volatile compounds which condense on the relatively cool boiler surfaces, and the deposit formed is rather sticky and can be removed satisfactorily only by use of a compressed air lance. Lancing is necessary about six times during an 8-hour shift.

TABLE 2

WASTE-HEAT BOILER DATA AT ANACONDA

Amount of fuel (natural gas) per 24 hours	2,742,000 cu ft
Calorific power of fuel (gross)	1021 Btu/cu ft
Make of boiler	Stirling
Average boiler rating	600 hp
Type of boiler installation	Tandem
Equivalent evaporation from and at 212° F per 24 hours	749,267 lb
Average steam-gage pressure	124 5 lb sq in.
Average feed-water temperature	72 7° F
Horsepower developed	904 9 hp
Horsepower, per cent of rating	150 8
Equivalent evaporation from and at 212° F per 1000 cu ft of gas burned	303 10 lb
Percentage of total heat absorbed by boiler (based on gross Btu)	28 81%
Average gas temperature at boiler inlet	2050° F
Average gas temperature at boiler exit	810° F
Solid material smelted per furnace day	612 27 tons

United Verde. Two M-26 Stirling type boilers serve each reverberatory furnace (Fig. 2), each is rated at 713 boiler horsepower. These boilers are set at the same elevation as the tapping floor of the furnace so that the waste-heat gases enter at the top of the front bank of tubes, necessitating the inversion of the usual baffling arrangements

The boilers are equipped with valve-in-head soot blowers which keep most of the dust blown off the surface of the tubes, but it is necessary to supplement the soot blowers by high-pressure air lances inserted by an attendant through side doors in the boiler setting Pulverized coal is used for firing, and the coal ash and dust which accumulate in the flues between the furnaces and the boiler must be cleaned out by hand — an operation which requires the greater part of an 8-hour shift during each 24 hours.

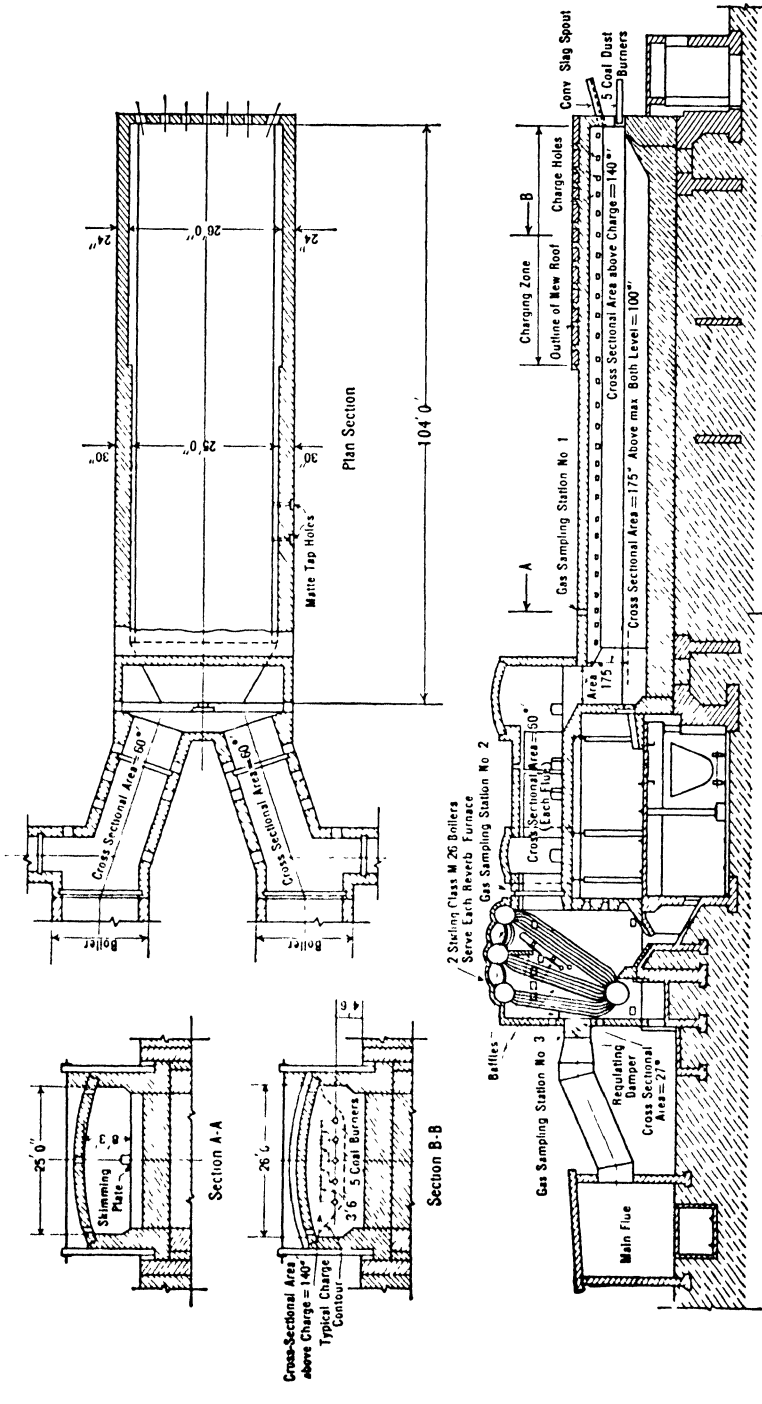


FIG. 2. Section Through Furnace, Waste-Heat Boiler, and Flues, United Verde Smelter

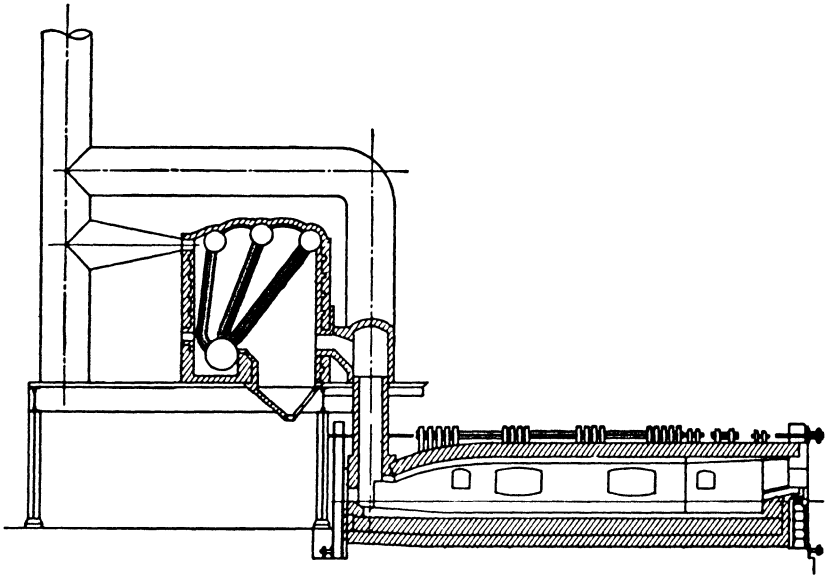
(*Marston, Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 247, 1933*)

TABLE 3

WASTE-HEAT BOILER DATA AT UNITED VERDE

Amount of coal burned per day	112.58 tons
Calorific power of coal as purchased (gross)	10,790 Btu/lb
Calorific power of coal as burned (gross)	11,520 Btu/lb
Feed-water temperature	113° F
Temperature of steam	528° F
Steam-gage pressure	178 lb/sq in
Distribution of heat in coal as burned:	
To smelting, conduction, convection, and radiation losses, etc.	43 0%
Transferred to steam	43 6%
Leaving in stack gases	13.4%

Great Falls. Figure 3 shows a waste-heat boiler installation on a refinery furnace at Great Falls, Montana. This plant has three refining furnaces and each is provided with a boiler; two of the boilers



(*Bardwell, Am Inst Min & Met Eng Trans, Vol 106, p 226, 1933*)

FIG. 3. Waste-Heat Boiler on Refining Furnace, Great Falls.

are Stirling class A-30, rated at 400 horsepower, and the third is a class A-21 Stirling boiler at 300 horsepower. The boilers are not baffled.

Each furnace has a 125-foot steel stack which takes the gases as they leave the boilers and a bypass flue so that the gases can be diverted around the boiler if necessary (Fig. 3). The boilers are

ordinarily operated at 75 pounds steam pressure with feed water at 60° F; from 36 to 40 per cent of the calorific power of the fuel is absorbed by the boilers.

Table 4 shows the rate of steam production at different stages of the refining cycle for three separate furnace tests. Note the considerable variation in steam production during the different stages.

TABLE 4

RATE OF STEAM PRODUCTION, IN BOILER HORSEPOWER AT GREAT FALLS REFINERY

	Oil Fuel, 400-hp Boiler	Gas Fuel, 400-hp Boiler	Gas Fuel, 300-hp Boiler
Charging	295	178	146
Melting	395	290	306
Skimming	...	310	283
Rabbling	[a]288	298	134
Poling	368	573	630
Casting	260	441	282
Average	337	322	312

[a] Includes skimming

Other Methods of Heat Recovery. Attempts have been made to abstract more heat from waste gases by the use of *economizers* or *recuperators* which preheat the cold air used for combustion; these devices have been used on reverberatory gases after passing through the boilers and also on roaster gases. Although these economizers have been used successfully in some places, they have not been universally adopted as have the waste-heat boilers.

RECOVERY OF DUST AND FUME

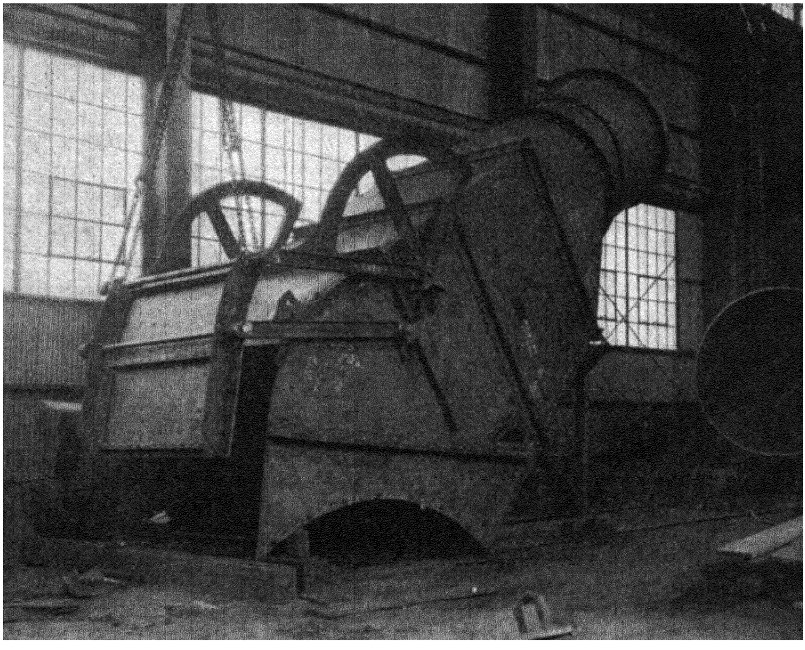
The common methods employed at copper smelters for removing suspended material from smokes are:

1. Collection of dust beneath flues, expansion chambers, balloon flues, and boiler settings.
2. Filtration through cloth bags in " bag houses."
3. Electrostatic precipitation in Cottrell treaters.

Flues, Expansion Chambers, Etc. The principle involved in the recovery of dust and fume is simply that as the smoke is cooled by expansion in large chambers and by radiation and convection losses, its velocity and carrying power diminish. The cooling permits condensation of fume, and particles of fume and dust settle to the bottom

of the chamber by the action of gravity. Only the larger particles will settle out in this manner, and the finer particles of dust and fume remain in the smoke stream from which they must be removed by other methods.

All boiler settings, flues, etc., through which dust-laden gases are passing are equipped with clean-out doors or hoppers to permit removal of the accumulated dust; and the dust is cleaned out at intervals which depend upon the rate at which it collects.



(Courtesy Traylor Engineering and Manufacturing Company)

FIG. 4. Converter Hood.

Bag Houses. A bag house is a filtering chamber containing a number of cotton or woolen bags made of specially woven cloth. The bags are about 18 inches in diameter and 30 feet long; they are suspended vertically by means of a thimble at the top of each bag. The lower ends are connected to the gas intake, and the dust-laden gases are forced to enter the bags at the bottom and escape through the meshes of the cloth. Dust and fume are caught and held inside the bag, and the cleaned gases pass through.

Woolen bags have longer life than cotton bags but are more expensive. Hot gas cannot be cleaned in bag houses because the heat destroys

the fabric — gases should not be hotter than about 270° F (132° C) as a maximum and in many cases the limit would be 200° to 215° F. Acid smokes cannot be treated in bag houses because the sulfuric acid attacks the fabric and soon destroys it.

The deposit which collects in the bags is removed by cutting off the gas entering the bag and shaking the bag vigorously — a reverse current of gas may be drawn through the bag while it is being shaken to

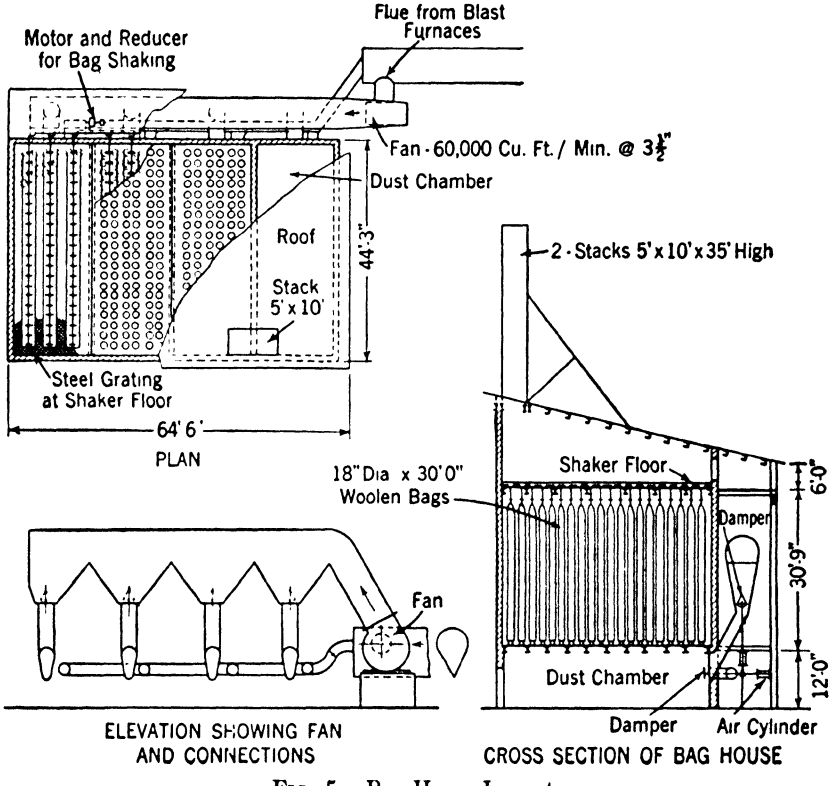


FIG. 5. Bag House Layout.

aid in loosening the cake. The collected dust and fume drop into hoppers beneath the bags. In most bag houses the bags are enclosed in steel compartments each of which holds about 12 bags, and the bags are shaken by means of an automatic hammer which raps the steel members supporting the bags.

Bag houses offer considerable resistance to the flow of gas, and the draft loss will usually be from 3 to 6 inches of water gage. Auxiliary "booster" fans are generally used to handle gases passing through bag houses.

Basic smokes are most commonly filtered in bag houses, and they are widely used to recover lead and zinc oxide fumes. The smokes produced in copper smelting are generally quite acid, so the use of bag houses in copper smelters is not as prevalent as their use in lead and zinc metallurgical works. When it is desired to filter acid smoke in a bag house it is possible to neutralize the smoke by introducing pulverized lime into the smoke stream (*Sprague process*). This does not neutralize all the acid in the smoke, but the lime does collect on the bags and neutralizes the free acid which would otherwise destroy the fabric. At Tooele, Utah,[9] where bag houses were used to catch the fumes produced in converting leady matte, there was originally enough ZnO in the fume to neutralize the acid, but when the converting process was altered so that the zinc no longer entered the fume, it became necessary to add dehydrated lime to the gases just before they entered the bag house.

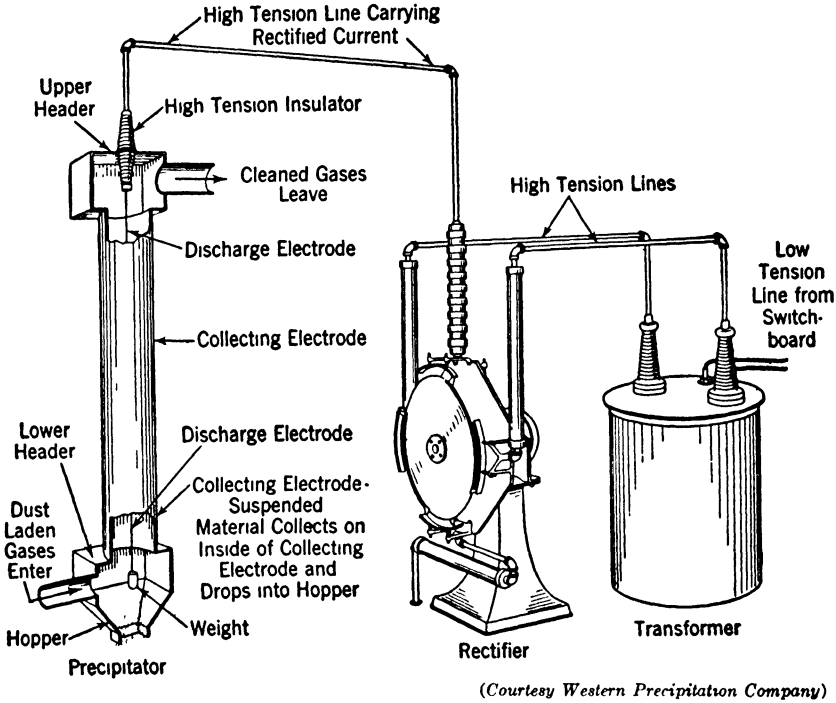
Cottrell Treaters. The Cottrell process for removing suspended particles from smoke utilizes the fact that if an electrostatic charge can be placed on these particles, they can then be attracted to an electrode carrying the opposite charge. Commercial Cottrell treaters are large chambers containing positive and negative electrodes; the positive electrodes have a large surface area and small radius of curvature as compared with the negative electrodes, and the dust and fume are collected on the positive electrodes. The positive electrodes are usually pipes or plates; the negative electrodes are wires or chains. The positive electrodes are grounded and the potential difference between positive and negative electrodes will be from 25,000 to 65,000 volts.

Electrostatic precipitation requires two definite electrical considerations — (1) there must be a unidirectional flow of ionizing current from one electrode, and (2) a high-potential static field must be maintained between the two electrodes. The *discharge electrode* (wire or chain) has a small radius of curvature and a small surface area, and hence it is possible to maintain a high density of charge on its surface. The potential gradient at its surface is sufficient to disrupt the neutral electrical state of the neighboring gas molecules and convert them into *charged* or *ionized* molecules with a charge of the same sign as that of the discharge electrode. As soon as a molecule becomes charged, it is subjected to the electrical stress of the static field and it moves away from the discharge electrode and toward the *collecting electrode* (pipe or plate), carrying with it other uncharged gas molecules. This gives rise to the "electric wind" and amounts to a very

[9] Sackett, B. L., Converting Lead and Copper Matte at Tooele: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 132, 1933.

low amperage electric current passing through the gas; the current is carried on gas molecules which are charged at one electrode and discharged at the other.

If the gas between the electrodes contains suspended particles of dust or fume, these collide with the gaseous ions, become charged, and are attracted to the collecting electrode, where they are discharged; these particles form an adherent deposit on the collecting electrode.



(*Courtesy Western Precipitation Company*)

FIG. 6. Diagram of a Pipe-Type Cottrell Treater Unit.

The discharge electrode may be either positive or negative, but practically it has been found that precipitation is more effective if the discharge electrode is negatively charged; and this system is used in all commercial Cottrell treaters.

Practically any type of suspended material can be removed from a gas stream by Cottrell treaters, and the method has wide applications. It will remove all dust and fume found in copper smelter smokes and is the only method that will satisfactorily remove free H_2SO_4 (or SO_3). There is no important copper smelter in the United States or Canada which does not employ Cottrell treaters.

The accumulated deposit which adheres to the pipes or plates is dis-

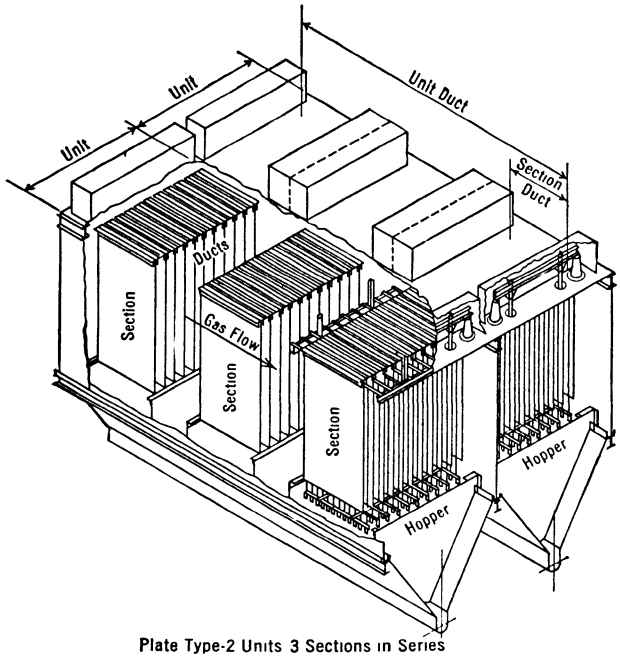
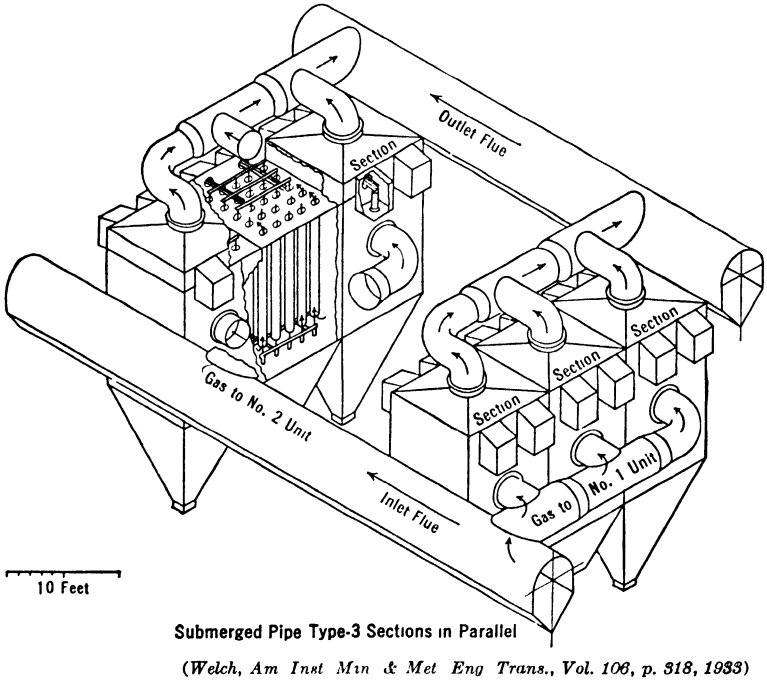


Plate Type-2 Units 3 Sections in Series



Submerged Pipe Type-3 Sections in Parallel

(Welch, Am Inst Min & Met Eng Trans., Vol. 106, p. 318, 1933)

FIG. 7. Sketch Illustrating Nomenclature in Gas-Treating Parts of an Electrical Precipitation Installation.

lodged by rapping the electrodes at intervals with automatic hammers; the deposit falls into hoppers at the bottom of the treater chamber, from which it is removed at intervals.

Smokes are classed as *conducting* or *non-conducting* according to the nature of the deposit formed on the collecting electrode; con-

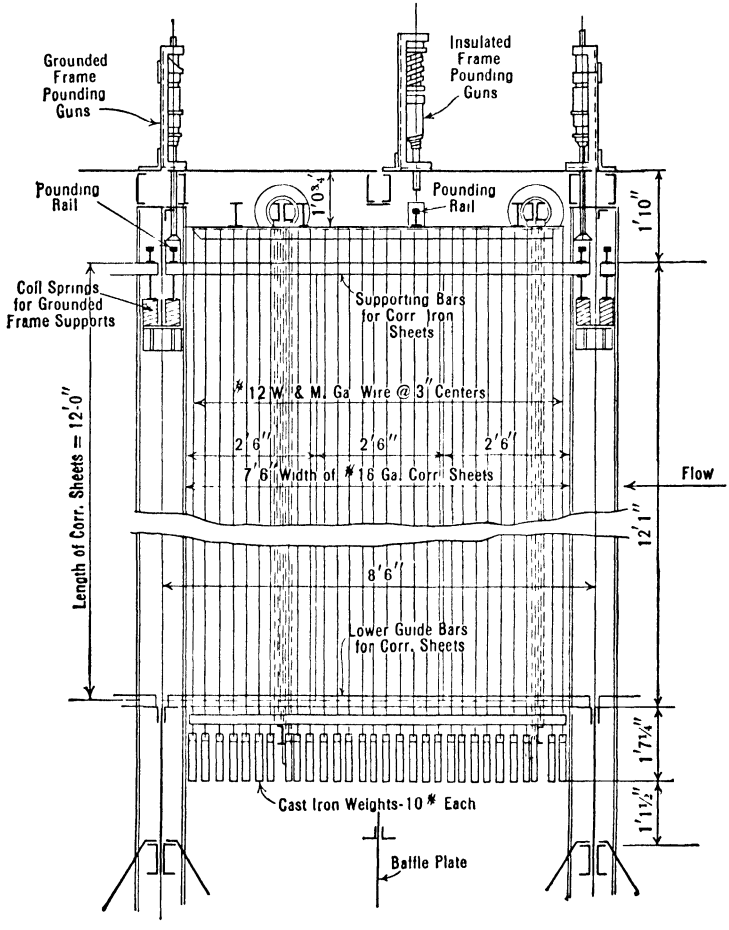


FIG. 8 Section of a Plate-Type Cottrell Treater.

ducting smokes may be treated directly by the Cottrell process, but non-conducting smokes must first be *conditioned.* The non-conducting smokes are usually basic smokes, and common examples are smokes containing fumes of lead or zinc oxides; these substances form an insulating blanket on the collecting electrode and prevent the rapid discharge of the positively charged particles. This means that a

positive charge accumulates on the electrode and does not leak off to the ground; this diminishes the static potential between the electrodes and cuts down the efficiency of the operation.

Conducting smokes contain suspended matter (SO_3, H_2SO_4, H_2O, and others) which renders the deposit conducting and permits rapid discharge of the particles to the ground. Acid smokes are conducting because only a small amount of H_2SO_4 is needed to make the deposit a conductor. Non-conducting smokes are made conducting by adding a suitable conducting medium, and the most common method is *humidifying* or treating the smoke with a water spray — the water droplets collect in the deposit and make it a conductor. A non-conducting dust can usually be made satisfactorily conducting if the collected dust contains from 2.5 to 4.0 per cent moisture.

Most copper smelter smokes are conducting because many of them are acid, and many contain considerable moisture from the roasting or smelting of wet concentrates. Cottrell treaters are generally more suitable for treating copper smelter smokes than are bag houses, although bag houses are used for certain special purposes.

Table 5 gives the essential data on the Cottrell installations at several representative copper smelters.[10] In operation, the gas passes through the treater between the collecting electrodes, and the dust is collected on them. The efficiency of collection depends upon the rate at which gas is passed through the treater — with adequate time, practically all of the suspended matter can be removed. Commercial units usually show better than 90 per cent recovery. Capacities and efficiencies for several copper smelter installations are given in Table 5.

TREATMENT OF RECOVERED DUST AND FUME

Treatment given to the dust and fume collected in copper smelters will depend upon the composition of the dust, but usually the dust is simply charged back into the smelting circuit. Most dust is fed into the reverberatories, but some is also charged into roasters or converters.

The principal byproduct from smelter fume is "white arsenic," As_2O_3; practically all the world's supply of arsenic is a byproduct of copper and lead smelting. Where arsenic is present in any quantity in the smelter feed it tends to accumulate in the flue system because the lower oxide, As_2O_3 is relatively volatile and is driven off in both the roasters and reverberatories.

Crude arsenic-bearing dusts are subjected to repeated distillations

[10] Welch, H. V., Recovery of Suspended Solids from Furnace Gases: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 296, 1933.

TABLE 5

DATA ON COTTRELL TREATERS

Plant	Nature of Smoke	Nature of Dust and Fume	Size and Type of Installation	Electrical Equipment	Voltage	Amount of Dust Collected	Efficiency of Collection
Garfield, Utah	Reverberatory smoke; 700,000 cu ft/min at 150° C		7 units in parallel, each containing 66 plates and 496 vertical weighted wires. Plates are 11 ft by 9 ft 5 in. made of corrugated iron and spaced 6 in. apart.		20,000		90%
Cerro de Pasco Copper Corporation, Peru	Roaster gases; 300,000 cu ft/min at 120° C	Crude arsenic fume.	3 units of "rod curtain" type. "Rods" are $\frac{1}{8}$-in. standard pipe hung in a "curtain," 8 ft wide and 24 ft long. Pipes are spaced on $1\frac{1}{4}$-in. centers; curtains are 8 in. apart. Discharge electrodes are square twisted $\frac{1}{8}$-in. bar.	10 sets of 25-kva capacity; one used as a spare	35,000	10 tons/day	97%
Noranda	Roaster gases; 450,000 cu ft/min at 900° F		Similar to "rod curtain" installations at Cerro de Pasco. Six units, each containing 48 curtains each 18 ft high and 7 ft 4 in. wide.	12 sets of 25-kva. Synchronous motor sets.			95% on contained copper.
Anaconda	Mixed gases; treater located at base of main stack. 2,225,000 cu ft/min at 150° C	Dust contains considerable arsenic fume.	20 units in parallel; each unit contains 21 corrugated iron plates, 24 ft high and 20 ft wide, spaced on 12-in. centers. Discharge electrodes are No. 14 wire tensioned by weights.	12 750-kva motor-generator rectifier sets, each connected to 75 kva maximum 100,000 volt transformer.	65,000	120 tons/day	90% on total dust. 95% on copper, gold, and silver. 86% on arsenic trioxide. 84% on lead.

and condensations until a commercially pure white arsenic is produced, and the residue is then sent back to the reverberatory furnace.

The ore deposits at Butte contain the copper-arsenic mineral enargite, and as a result, a large amount of arsenic is recovered at the Anaconda smelter; we shall present a brief description of this plant to illustrate the methods used.

Arsenic Recovery at Anaconda.[11] The principal feed to the arsenic plant consists of dust from the main flue leading to the stack and Cottrell dust from the treaters at the base of the stack. The flue dust is mixed with coal or flotation concentrates which reduce As_2O_5 and arsenates to As_2O_3, and the mixture is treated in 6-hearth McDougall multiple-hearth roasters fired with gas burners on the third and fifth hearths. The gases from these furnaces pass into condensers, and the residue is either shipped back to the reverberatories or stock-piled and sold for its lead and bismuth content. The fumes from these furnaces pass into three condensers in series; these condensers are McDougall furnaces from which the interior hearths have been removed and baffles hung down the center. The rakes on the sixth hearth operate to discharge the condensed arsenic (together with some dust), and the spent gases pass on to the main flue system.

Cottrell dust mixed with coal or concentrate yields a crude arsenic containing 93 to 95 per cent As_2O_3, which is pure enough to go to the refinery. The low-grade flue dust, however, yields a more impure product, and this is usually mixed with flue dust to give a composition of 55 to 60 per cent As_2O_3 and re-treated in the roasters; this gives a crude of about 94 per cent As_2O_3.

Crude arsenic is treated in small batch reverberatories. The high-grade crude (93 to 95 per cent As_2O_3) is heated on the hearth and the firing is regulated to give a temperature of 950° F. Arsenic-laden gases pass into brick chambers or *arsenic kitchens,* where the arsenic trioxide condenses to form commercial " white arsenic." About 1½ to 2 tons of crude arsenic is treated at a time in the refining furnace, and at the end of each day the residue remaining is worked to the end of the furnace, where it drops into cars to be taken to the copper reverberatories.

Other Byproducts. Arsenic trioxide is the only important byproduct removed from the fume and dust in copper smelters; small amounts of lead and bismuth may be separated in the arsenic plant (as noted above). Unless these dusts contain enough arsenic to warrant special treatment, however, they are usually returned to the smelting circuit,

[11] Bender, L. V., and Goe, H. H., Production of Arsenic Trioxide at Anaconda: Am. Inst. Min. & Met. Eng. Trans, Vol. 106, p. 324, 1933.

and the contained impurities find their way out of the plant either in the slag or in the crude copper.

In the treatment of the slimes produced in electrolytic refining, furnace operations produce dusts and fumes which contain valuable by-products. We shall discuss these in the next chapter.

REMOVAL OF SO_2 FROM GASES

A great deal of work has been done on the subject of removal of SO_2 from gases in the last several years, and many methods have been developed for the recovery of SO_2 from gases by fixing it in the form of a non-volatile sulfur compound. One of the principal reasons for this is the fact that SO_2 discharged into the atmosphere in sufficient quantity is harmful to surrounding vegetation; the sulfur-bearing compounds formed by its removal will have some commercial value, but usually this itself is not a sufficient reason to warrant an elaborate treatment plant to recover sulfur dioxide — especially from lean gases carrying up to 2 5 per cent SO_2.

Sulfur dioxide is a gas which is non-condensable at ordinary temperatures and pressures (its normal boiling point is $-10°C$) so that it passes freely through bag houses, Cottrell treaters, etc., and it has only a limited solubility in water. Commercial methods for extracting SO_2 usually depend upon converting the SO_2 into a compound which can be dissolved in water in relatively high concentrations. A summary of the various methods which have been used for this purpose is given in a recent publication of the United States Bureau of Mines;[12] but we shall mention only one method here — the production of sulfuric acid — as that is the only treatment that has been applied to any extent to copper smelter smokes.

Production of Sulfuric Acid.[13] Sulfuric acid may be prepared from smelter gases containing SO_2 by the standard methods of manufacture, in which the gas is oxidized to SO_3 and dissolved in water to form H_2SO_4. We shall not enter into a discussion of sulfuric acid manufacture but shall simply point out the relation of this method to the general problem of removing SO_2 from smelter smoke.

In the first place, the SO_2 content of gas should be about 5 per cent by volume, or more, for acid manufacture. This means that the gases from converters, and some roasters and blast furnaces can be used for this purpose; reverberatory smoke, however, is too low in SO_2.

[12] Roberson, A. H., and Marks, G. W., Fixation of Sulfur from Smelter Smoke: U. S. Bur. Mines Rept Inv. 3415, October 1938.

[13] Fairlie, A. M., Sulfuric Acid Manufacture: Reinhold Publishing Corporation, New York, 1936.

Secondly, sulfuric acid is a fairly cheap commodity, and it does not pay to manufacture it in quantity when it must be shipped a great distance.

Because of these two reasons we find that copper smelters ordinarily maintain sulfuric acid plants only when the sulfuric acid can be used directly in the plant; and only a part of the smelter smoke is used for acid manufacture. Thus Anaconda manufactures sulfuric acid from a portion of the roaster gases and utilizes the acid in making phosphate fertilizer. Andes Copper Mining Company maintains a smelter for sulfide concentrates and a leaching plant for oxidized ore; part of the roaster gases are used to make the sulfuric acid needed by the leaching plant. The plant of the Tennessee Copper Corporation illustrates a special case (Chapter IV); here most of the gas produced — from roasters, converter, and blast furnace — goes to a sulfuric acid plant, and the sulfuric acid formed is one of the most important products of the low-copper, heavy sulfide ore.

DISPOSAL OF WASTE GASES

In modern copper smelters the gases are satisfactorily cleaned of suspended matter, and part of the SO_2 may have been removed. In order to render the waste gases as harmless as possible they are then discharged high in the atmosphere so that they may be highly diluted before they can diffuse back to earth.

The question of damage caused by smelter smoke is still highly controversial, and it is very difficult to make positive statements about it; the amount of research being done on methods to remove SO_2 indicates that the "smelter smoke" problem is still of considerable importance. In most smelters, all the sulfur-bearing waste gases are led into a common flue and discharged through a high stack; shorter stacks may be employed for the direct disposal of gases which are free of SO_2 and suspended matter, such as those from cathode furnaces (Fig. 3). Some of the tallest stacks in the world are found at copper smelters.

Unless part of the sulfur is fixed in the form of sulfuric acid or other compound, all the sulfur that enters the smelter in ore or concentrates must pass out in the waste gases. The amount of sulfur in the final stack gases at copper smelters will usually be about 2 or 3 per cent by volume, although this may vary considerably.

TABLE 6[a]

HEIGHTS OF SOME COPPER AND COPPER-NICKEL SMELTER STACKS

Plant (copper)	Height of Stack (feet)
Anaconda, Montana	588
Chinnampu, Korea	600
Clarkdale, Arizona	430
Copper Cliff, Ontario (copper-nickel)	510 and 554
Tacoma, Washington	571
Hurley, New Mexico	500

[a] U S Bur Mines Rept Inv 3415, p 42, 1938.

TABLE 7[a]

RELATION OF ODOR INTENSITY AND PHYSIOLOGICAL EFFECT TO CONCENTRATION OF SO_2 IN AIR

Concentration of SO_2 by volume		
Parts per Million	Per Cent	Physiological Effect
3 to 5	0 0003 to 0 0005	Faintly detectable by smell or taste.
8 to 12	0.0008 to 0 0012	Slight throat irritation and tendency to cough.
20	0 002	Very distinct throat irritation, coughing, constriction of chest, and smarting of eyes
50	0 005	More pronounced irritation of eyes, throat, and chest, but possible to breathe several minutes.
150	0 015	Extremely disagreeable, but may be endured for several minutes
500	0 050	Causes sensation of suffocation even with first breath

[a] U. S. Bur Mines Rept Inv 3415, p 45

CHAPTER VIII

ELECTROLYTIC REFINING

INTRODUCTION

The practice of refining copper electrolytically started late in the nineteenth century and has since assumed great importance in the metallurgy of copper. Of a total of 1,644,505,129 pounds of copper produced in the United States in 1937,[1] 1,548,857,307 (94%) was electrolytic copper. In Chapter VI we have already had occasion to refer to electrolytic refining in connection with the casting of anodes and the refining of electrolytic cathodes.

As a brief introduction to the subject of electrolytic refining we shall quote a few excerpts from a paper by Walker[2] dealing with the history of its development.

> At the beginning of 1893 there were 11 electrolytic refineries in the United States, most of them using the multiple system. * * *
>
> The total production of these 11 plants in 1892 was very small; I have not been able to discover reliable figures of production. There were about thirty electrolytic copper refineries in the world that year, according to Titus Ulke, and the entire production of these refineries was 64,000,000 pounds annually, as much as could be produced in the United States at the present time, 1931, in 6½ days This shows conclusively what enormous strides have been made in the industry. * * *
>
> In the early nineties the electrolytic copper refiners found it practically impossible to produce copper of a standard quality regularly. We had a lot to learn. Sometimes the cathodes were tough, crystalline and pure; at others the product was distinctly inferior. I have seen cathodes in the tank room of the Baltimore Electric Refining Company covered with wide streaks of a brittle black deposit of copper containing impurities. It used to be said that when the cathodes were removed from the tank we might expect to take them out in sheets or with a shovel, which, of course, was an exaggeration. Still, at best the product was far from uniform, and on this account electrolytic copper did not command so high a price as the product from the Lake Superior mines, a standard brand of copper of excel-

[1] Minerals Yearbook, U. S. Bur. Mines, p. 90, 1937.

[2] Walker, A. L., Learning How to Refine and Cast Copper; Choice of Methods in Mining and Metallurgy: Am. Inst. Min. & Met. Eng., New York, 1932 (Seeley W. Mudd Series).

lent quality. The difference in price then was from ⅛ to ¼ cent per pound, in favor of the latter. Electrolytic copper producers had a serious problem to solve. * * *

It required years to convince the purchasers of copper that electrolytic copper of a high standard could always be regularly and uniformly produced, but the consumers finally were willing to concede that this class of copper was fully equal to the product coming from the Lake Superior district and, in fact, superior for electrical purposes on account of its higher electrical conductivity. From 1914 electrolytic copper has been used as the basis for official price quotations, Lake copper being sold at the same price to large consumers. * * *

THEORY OF ELECTROLYTIC REFINING

The theory involved in the electrolytic refining of copper is quite simple, and the principal obstacles that had to be overcome in developing the process were the many details of practical operation. Let us begin by describing the *copper coulometer,* an instrument which operates exactly the same as an electrolytic refining cell and comes about as close to " perfect " electrolysis as is humanly possible. With this as a background we shall be better able to appreciate the less perfect cell used in electrolytic refining.

The Copper Coulometer.[3] The copper coulometer is an instrument for measuring small quantities of direct current electricity, and it is similar in construction and operation to the even more accurate *silver coulometer,* by means of which the value of the standard ampere is defined — the international ampere is the current strength which deposits 1.11800 milligrams of silver or 0.3294 milligram of copper from suitable solutions of salts of these metals in 1 second.

The coulometer is simply a glass beaker containing an electrolyte into which dip two electrodes of pure copper. These electrodes are connected to the electrical terminals so that the current passes through the cell, and copper dissolves from the anode and deposits on the cathode (negative terminal). After the current has passed for a definite time, the cathode is removed, washed, and weighed, and for every 0.0003294 gram increase in weight, 1 *coulomb* (*ampere-second*) of electricity has passed through the cell.

This last statement depends on *Faraday's laws,* which state:

1. *The quantities of substances set free at the electrodes are directly proportional to the quantity of electricity which passes through the solution.*

[3] Creighton, H. J., and Koehler, W. A., Electrochemistry: 3d ed., Vol. 1, p. 22, John Wiley and Sons, Inc., New York, 1935.

2. *The same quantity of electricity sets free the same number of equivalents of substances at the electrodes.*

From the second law we derive an electrical unit, the *faraday,* which is the quantity of electricity required to liberate 1 gram-equivalent of a substance; 1 faraday = 96,500 coulombs.

Faraday's laws are among the few generalizations in physical science which are exact and to which there are no exceptions. This fact follows naturally from our conception of ionization and the nature of the flow of current through a *second-class conductor* (an electrolyte). An electric current is a directed flow of electrons, and such a current passes through a *first-class conductor* (such as a metallic wire) by the movement of the cloud of free electrons in the metal. There is no such flow of electrons in an electrolyte, but the " current " is carried by the free-moving ions found in the solution. For example, in the copper coulometer, the negative electrode gives up its excess electrons to neighboring copper ions, which become neutral copper atoms; at the positive electrode (anode) electrons are removed from the surface atoms of copper, which then become ions (Cu^{++}) and enter the solution as $CuSO_4$. With the same number of electrons entering at the cathode as passing out at the anode, the *anodic and cathodic reactions must be chemically equivalent;* which in this case means that exactly the same weight of copper dissolves from the anode as plates out on the cathode.

In other examples there will be different reactions at both anode and cathode, but regardless of the nature of the reactions the principle of equivalent reactions will hold. Electrolytic action is best regarded as two equivalent chemical reactions taking place at the electrodes; at the cathode, electrons enter the solution, and some substance is *reduced;* at the anode, electrons leave the solution and some substance is *oxidized* (has its valence increased). In the coulometer, copper ions are reduced at the cathode and metallic copper is oxidized at the anode.

The anodic and cathodic reactions are therefore

$$Cu - 2\,(e) \rightarrow Cu^{++}$$

and

$$Cu^{++} + 2\,(e) \rightarrow Cu$$

where (e) represents an electron.

Equivalent amounts of copper are involved, so there is no change in the composition of the electrolyte. If instead of a copper anode we had used an *insoluble anode,* such as a strip of platinum, the metal would not corrode and the oxidation reaction at the anode might be represented thus:

$$SO_4^{--} - 2\,(e) \rightarrow SO_4$$
$$H_2O + SO_4 \rightarrow H_2SO_4 + \tfrac{1}{2}O_2$$

This may not represent the exact sequence of reactions, because there probably is no such thing as a neutral SO_4 group; however, it does indicate the end products of the reaction. The cathodic reaction would remain the same as before. The use of an insoluble anode would lead to the following effects.

1. For every equivalent of copper plated on the cathode, one equivalent of H_2SO_4 would be formed in the electrolyte, and ½ equivalent of O_2 gas would be liberated at the anode. Hence as the electrolysis proceeded, the solution would become depleted in copper and enriched in free sulfuric acid.

2. The *net* chemical reaction in the cell would be

$$CuSO_4 + H_2O \rightarrow Cu + H_2SO_4 + \tfrac{1}{2}O_2$$

When we had a soluble anode, however, there was no net cell reaction and consequently no change in the composition of the electrolyte nor evolution of gas (O_2).

Soluble anodes are used in copper refining, and we shall be concerned only with them in this chapter; insoluble anodes are used in the *electrolytic extraction* of copper from leach solutions, and we shall consider them in more detail in the next chapter.

Let us now return to the description of the coulometer. The electrolyte should be made as follows:

150 grams of crystallized copper sulfate
50 grams of sulfuric acid (sp gr 1.84)
50 cc ethyl alcohol
1000 cc distilled water

The current density should be between 0.002 and 0.02 ampere per square centimeter of surface. The alcohol is used to minimize oxidation of copper by air at the surface of the liquid — the alcohol concentrates in the surface layer and is itself slowly oxidized to acetone and acetic acid. The electrolyte is agitated by bubbling a stream of CO_2 gas through it.

When the instrument is set up as described, the *current efficiency* is practically 100 per cent; i.e., all of the current passing is utilized in depositing copper and none is consumed by other reactions. The cathode deposit adheres tightly, and there is no chemical dissolution of the deposited copper in the electrolyte. Thus the weight of copper deposited can be taken as an accurate measure of the current. Let us now express the electrolyte composition and current density in the units commonly used in practice so that we can later compare these with the conditions which obtain in practice. Of course, alcohol is not used in commercial electrolytes, and we shall figure this as an

equal volume of water; neglecting changes in volume due to solution, we find that the electrolyte contains approximately

Copper, 33 grams per liter
Free sulfuric acid, 44 grams per liter

The current density will be from 18.6 to 186.0 amperes per square foot of cathode surface.

Finally let us consider a list of the characteristics in which commercial electrolytic cells differ from the simple coulometer.

1. Arrangement of electrodes.
2. Construction of tanks.
3. Composition of electrolyte.
4. Composition of the anodes.
5. Disposition of the impurities in the anode.
6. Nature of the cathode deposit.
7. Circulation of electrolyte.
8. Current density and cell voltage.
9. Purification of the electrolyte.
10. Electrical equipment and conductors.

REFINING METHODS

There are two principal methods of copper refining — the *multiple* or *parallel* system and the *series* system. In the multiple system separate anodes and cathodes are used and the cathode deposit is built up on a *starting sheet* made of refined copper. The series system employs no starting sheets, and the electrodes of impure copper serve as both anode and cathode — the copper dissolving from one side of each electrode and the purified copper depositing on the opposite side of the adjacent electrode. All anodes and cathodes in a given cell have a *multiple* or *parallel* electrical connection in the first system; in the second system the electrodes in any one cell are in *series* electrically.

The multiple system is more widely used than the series system. A brief comparison of the advantages and disadvantages of the two systems are given by Walker,[4] as follows (the *Hayden* and *Nichols* systems are both series systems):

Advantages of Multiple System:

1. Ability to treat copper of any quality, no matter how impure or how rich in precious metal.

2. Less loss in precious metals in the cathodes produced — about 0.35 per cent of the gold and silver in the anodes of the multiple system;

[4] Walker, A. L., op. cit., p. 73.

1 per cent in the Hayden system and 2 per cent in the Nichols process, due to the very long cathodes.

3. Ability to handle electrodes and scrap in larger units and with less cost for labor.

4. Requires less care in maintaining the purity of the electrolyte, as it is possible to effect a much better circulation.

5. Cost of casting and preparing anodes much less, especially when compared with the Hayden system, where the plates must be rolled.

Advantages of Series System:

1. For a given amount of power more copper can be deposited. Although the leakage of current around the electrodes in this system is large, the voltage between plates is much less. The production in the Hayden system is about 140 per cent and in the Nichols cast anode system about 170 per cent of that in the multiple system per unit of power.

2. Less carry of metals in process; electrodes are much thinner.

3. Less scrap produced; about 6.7 per cent in the Hayden system, 10 to 15 per cent in the Nichols, and 14 to 18 per cent in the multiple.

4. Less tank room space required for a given output. Tanks can be placed closer together, and there are many more electrodes in each.

5. Much less copper is required for busbars and conductors.

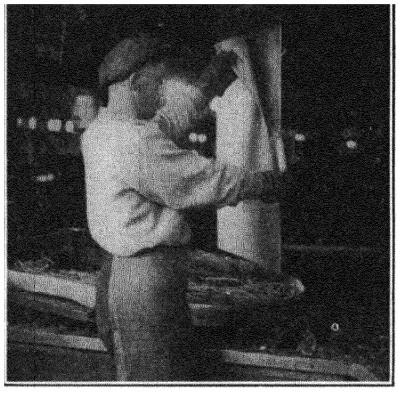
The significance of these remarks will be brought out as we discuss the two methods.

THE MULTIPLE SYSTEM

Anodes. The anodes used in multiple refining are flat rectangular slabs of impure copper with two cast lugs at the top of each anode to support it as it hangs in the tank. Typical analyses of anodes are given in Table 5. Anodes are from 1½ to 2 inches thick, 35 to 40 inches long, 28 to 36 inches wide, and weigh 500 to 700 pounds apiece. The anodes are usually transported to the tank house by means of a rack on which they are spaced just as they will be in the electrolytic cell; thus an entire load of anodes can be picked up by a crane and placed in the tank in a single operation.

Cathodes. Cathodes are built up on *starting sheets* which are thin sheets of electrodeposited copper made in special electrolytic tanks known as *stripper tanks*. These operate with regular anodes, but the cathode deposit is formed on plates of rolled copper. A current density of about 17 amperes per square foot is used, and it takes about 24 hours to deposit a $\frac{1}{16}$-inch layer on each side of the blank. These starting sheets are then stripped off the blanks (which had been oiled to make the sheets strip off more readily), straightened, and fitted with a sup-

porting bar of copper. The starting sheet is usually fitted with one or two loops of sheet copper through which the supporting cathode bar extends (Fig. 2).



(Courtesy Anaconda Copper Mining Company)

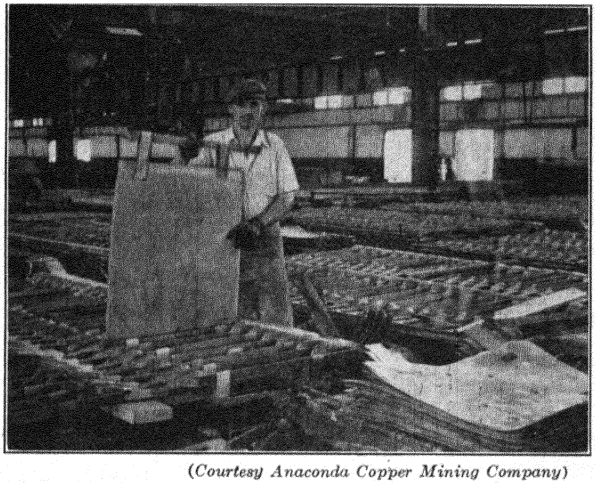
FIG. 1. Stripping Starting Sheets from Blanks.

New starting sheets are usually placed in a tank one at a time, inserted between the anodes which are already in position. While the sheets are still thin they have a tendency to curl and buckle, so that for the first day or so they must be inspected at intervals and removed and straightened if necessary. After 6 to 15 days the cathodes will have grown to the required size, and then they are removed, washed, and sent to the cathode furnace or sheared into smaller pieces for the market. Finished cathodes are about ½ inch thick, and their lengths and widths usually correspond to the anode dimensions; they weigh from 130 to 300 pounds each. From two to four crops of cathodes are commonly made from each set of anodes.

Electrical Connections. Figure 4 illustrates the earliest and simplest form of multiple connections. If we think of the current as flowing from + to − (the conventional picture, but actually opposite to the flow of electrons), the current enters the first tank through the + *busbar*. This is a heavy copper conductor of rectangular cross-section (about 2 by 4 inches) running along one side of the tank; the anodes are hung in the tank so that one lug of each anode rests on this busbar and the lug on the opposite side rests on an insulator. The cathodes are hung so that the cathode bars rest on the bus on the opposite side, and they are insulated from the anode bus. Thus the current enters on the anode bus, splits, and passes through the anodes, through the electrolyte, on to the cathodes, and out through the cathode busbar. The extension of the cathode bus becomes the anode bus in the next tank.

Anodes and cathodes in each tank are electrically in parallel or multiple, as the incoming current is evenly divided among the electrodes, and, except for minor differences, the voltage drop across the entire tank is the same as the voltage drop between any pair of anodes and cathodes. The tanks are electrically in series with one another.

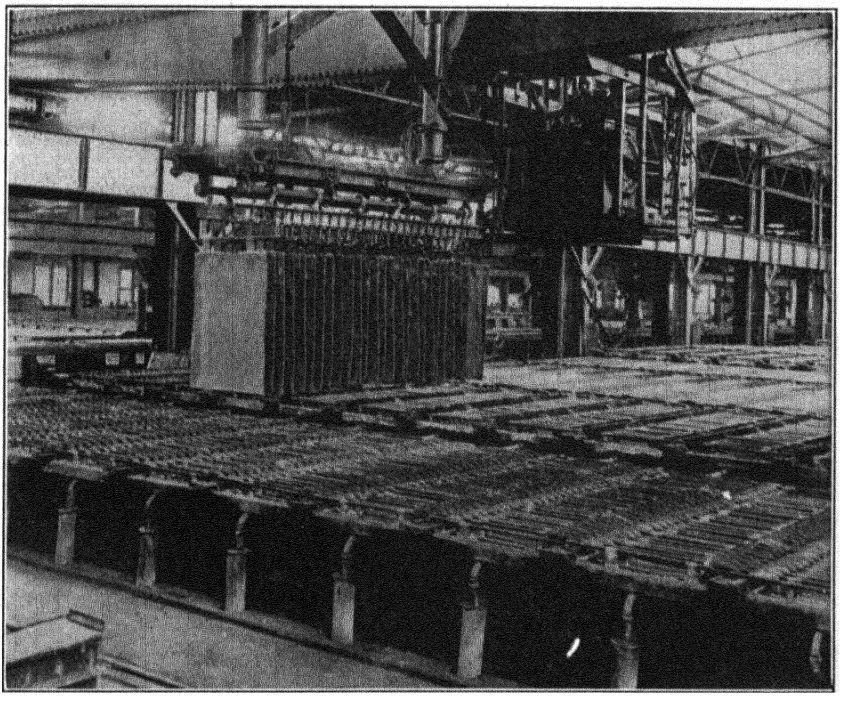
The current entering a tank may amount to several thousand amperes,



(*Courtesy Anaconda Copper Mining Company*)

FIG. 2. Inserting Starting Sheets in Tank.

Note the method of attaching the cathode bar.



(*Courtesy Anaconda Copper Mining Company*)

FIG. 3. Lifting Cathodes out of an Electrolytic Refining Tank.

and a large bus is required to carry this current without undue heating. In the system illustrated in Figure 4 two full-length busbars are required for each tank plus the extensions connecting the tanks, and this means that a large amount of copper is tied up as busbars. Several modifications of the original system have been developed to cut down the amount of copper required for conductors.

Only one end of a busbar carries the total current entering the tank; for example the plus busbar of the first tank in Figure 4 brings in the entire current, but as the current passes down the bus, a certain amount is drawn off by each anode; near the opposite end of the tank the bus is carrying only a small fraction of the original current. Thus it is

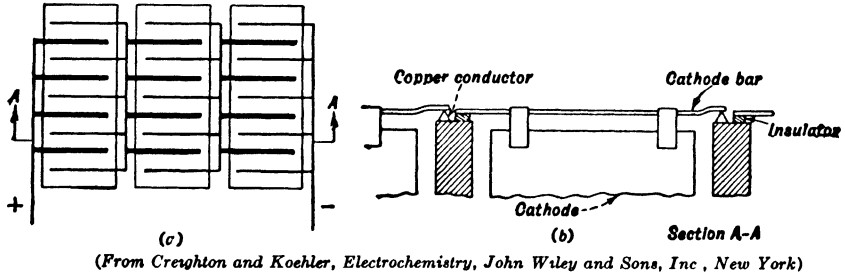


(*From Creighton and Koehler, Electrochemistry, John Wiley and Sons, Inc., New York*)

FIG. 4. Simple Form of Multiple Connection.

possible to use a *tapered* bus (Fig. 7) which contains less copper than a bar of uniform cross-section but is just as effective. Note that in the system illustrated in Figure 4 the cathode bus on the first tank would be tapered in the opposite direction to that of the anode bus.

The *Whitehead* and *Walker* systems were devised to avoid the practice of collecting the entire current from each tank on a heavy bus and then splitting it up again in the next tank. Figure 5 illustrates the Walker system, in which the tanks are placed side by side and the

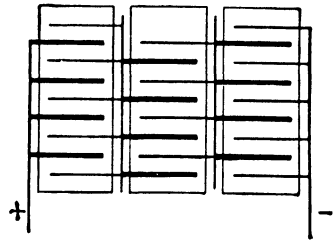


(*From Creighton and Koehler, Electrochemistry, John Wiley and Sons, Inc., New York*)

FIG. 5. The Walker System of Multiple Connection.

cathode bars of tank No. 1, and the anode lugs of tank No. 2 rest on a common conductor set between the tanks; originally this conductor was a flat bar, but later a bar of triangular cross-section was used to obtain better contact. This conductor has a small cross-section as compared with a busbar because any given section carries only a small part of the total current.

The Whitehead " single contact " system (Fig. 6) does away with the conductor required by the Walker system, and the cathode bar in No. 1 tank rests directly on the lug of an anode in tank No. 2. In the original Whitehead system the anodes are cast with a triangle on top of one lug, and the cathode bar rests on this triangle; another development by P. K. Aubel utilizes a groove cast in the top of one lug (" Baltimore groove ") in which fits a wedge-shaped cathode bar.



(From Creighton and Koehler, Electrochemistry, John Wiley and Sons, Inc., New York)

FIG. 6. The Whitehead Single Contact System.

These modifications do not change the essential nature of the electrical connections — electrodes in parallel in each tank and tanks connected in series.

Current and Voltage. The current density commonly used in copper refining is 18 to 20 amperes per square foot of cathode surface, and the voltage drop per cell about 0.2 to 0.4 volt. The anodic and cathodic reactions balance each other almost exactly, so there is no " decomposition " or " chemical " potential and the voltage is simply that required to overcome the ohmic resistance of the electrolyte and the resistance of the contacts.

Let us make a few calculations to illustrate the amount of current passing through an electrolytic tank, the rate of growth of the cathode deposit, and the reason for connecting the tanks in series. We shall assume that the current density is 20 amperes per square foot, that the cathodes have a submerged area 37 by 30 inches, and that each tank contains 28 anodes and 29 cathodes. This is the usual arrangement — one extra cathode is used, and each cathode receives a deposit on both sides except the two end cathodes, which receive a heavy deposit only on the inner sides. In calculating the total cathode surface per tank, it is necessary to count both sides of all the inner cathodes, and one side of each end cathode. The total cathode area in this instance would be:

$$\frac{37 \times 30}{144} \times 28 \times 2 = 432 \text{ square feet}$$

and the total current per tank

$$432 \times 20 = 8640 \text{ amperes}$$

Now if the voltage drop per tank is 0.3 volt, each tank will require $8.64 \times 0.3 = 2.59$ kilowatts of power, but commercial generators do

not develop currents of such heavy amperage at such low voltages, and therefore it is necessary to connect a number of tanks in series. If the generator could produce 8640 amperes at 190 volts, then $\frac{190}{0.3} = 633$ tanks would be connected in series and served by the generator. Electrolytic plants require direct current, of course, and usually employ motor-generator sets to convert alternating current into direct current for the tanks.

At 20 amperes per square foot and 100 per cent current efficiency, the weight of copper deposited per day per square foot would be

$$\frac{63.57}{2} \times \frac{20}{96{,}500} \times 86{,}400 = 570 \text{ grams}$$

and this would mean a thickness (on one side) of:

$$\frac{570}{8.92} \times \frac{1}{929} \times \frac{1}{2.54} = 0.0271 \text{ inch}$$

But the deposit forms on both sides, so the thickness will increase at the rate of 0.054 inch per day, thus requiring about 9 days to give a thickness of ½ inch.

Current Efficiency. Although there are no exceptions to Faraday's law in the electrolysis of aqueous solutions such as these electrolytes, there may be several reasons why the deposit of metal actually formed is less than that calculated theoretically from the current flowing. The principal cause in copper refining is the fact that the solution picks up some oxygen from the air, and copper is slightly soluble in sulfuric acid solutions containing oxygen. As a result some of the copper deposited on the cathode is chemically dissolved by the electrolyte.

The *current efficiency* is defined as the ratio (expressed as per cent) of the weight of the actual deposit to the weight calculated from the current flowing (by Faraday's law). Current efficiency in multiple refining is usually above 90 per cent and may reach 95 or 96 per cent.

Table 1 gives some of the current and power requirements; these are calculated on a 93 per cent current efficiency and for voltages as indicated.

The current efficiency varies inversely with the current density, the most efficient refining being done with low current densities. However, low current densities mean more plant space for a given capacity, and therefore the current densities used in practice are those which give the best balance between plant capacity and current loss. We have noted that multiple refining operations aim to maintain an efficiency

greater than 90 per cent; series refining efficiencies are about 20 per cent lower, as we shall see later.

TABLE 1

ELECTRICAL REQUIREMENTS FOR COPPER REFINING AT 93 PER CENT CURRENT EFFICIENCY

	Cell Voltage					
	0 15	0 20	0 25	0 30	0 35	0.40
Ampere-hours per pound of copper	411	411	411	411	411	411
Kilowatt-hours per pound of copper	0 062	0 082	0 103	0 123	0.144	0.165
Pounds of copper per ampere-day	0 0585	0 0585	0 0585	0 0585	0.0585	0.0585
Pounds of copper per kilowatt-day	387	292	233	195	167	145

Anode Impurities. Copper anodes usually contain about 0.5 per cent total impurities, and these may include a number of base elements as well as precious metals (Table 2). As the object of refining the copper electrolytically is to remove these impurities and produce pure cathode copper, it is important to know how these impurities behave as the electrolysis proceeds. As the anode corrodes, one of three things happens; the impurities may:

1. Dissolve with the copper and remain in solution.
2. Dissolve and be reprecipitated chemically by ions in the electrolyte.
3. Remain undissolved and drop to the bottom of the tank as solid particles.

Thus the contained impurities will collect principally in one of two places, either (1) dissolved in the electrolyte, or (2) in the deposit of *anode mud,* which accumulates on the bottom of the tank. Some of the suspended solid particles may be occluded in the cathode deposit and contaminate it; also some of the dissolved impurities may be plated out with the copper.

As a general thing, those metals which are below copper in the electromotive series do not dissolve but pass directly into the anode mud; all the precious elements are included in this group. Selenium and tellurium are present in the anode as selenides and tellurides of silver and copper; sulfur is present as copper sulfide, and oxygen as copper oxide. These compounds are insoluble and go into the anode mud.

Lead is soluble, but it is immediately precipitated as the insoluble lead sulfate, $PbSO_4$. Arsenic and antimony are soluble, arsenic as As_2O_3, and antimony as H_3SbO_3. Nickel, iron, and bismuth also dissolve in the electrolyte. Small amounts of NaCl or HCl added to the electrolyte precipitate the bulk of the antimony as the oxychloride, bismuth as the oxychloride, and any dissolved silver as the chloride. The precipitation of antimony (and bismuth, when present) is not complete, but the presence of chlorine ions in the electrolyte keeps the amount of dissolved antimony below the point at which it would precipitate on the cathode.

Table 2 gives the approximate distribution of the various impurities.

TABLE 2[a]

APPROXIMATE DISTRIBUTION OF COPPER ANODE IMPURITIES

	In Anode Mud (per cent)	In Electrolyte (per cent)		In Anode Mud (per cent)	In Electrolyte (per cent)
Gold	100	None	Arsenic	40	60
Silver	100	None	Antimony	90	10
Lead	100	None	Selenium	100	None
Nickel	5	95	Tellurium	100	None
Iron	None	100			

[a] Creighton, H J , and Koehler, W A , op cit , p 163

The Electrolyte. We have already given the approximate composition in terms of its free acid and copper content. The electrolyte found in an operating cell, however, will contain small amounts of other substances — chlorine added as a precipitant, and the soluble impurities from the anode. Table 3 gives the average composition range of these electrolytes. As a rule the total amount of dissolved impurities should be kept below 25 grams per liter.

TABLE 3[a]

COMPOSITION RANGE OF COPPER REFINING ELECTROLYTES

Free H_2SO_4	180	to	220 g/l
Copper	38	to	45 g/l
Nickel	6	to	10 g/l
Arsenic	4	to	12 g/l
Antimony	0.4	to	0.6 g/l
Iron	0.2	to	1.2 g/l
Chlorine	0.020	to	0.052 g/l
Specific gravity	1.240	to	1.280

[a] Creighton, H. J., and Koehler, W. A., Electrochemistry, 3d ed., Vol. 1, p. 162, John Wiley and Sons, Inc., New York, 1935.

The sulfuric acid is used to increase the conductivity of the electrolyte, and the electrolyte is also heated to about 60° C as this increases its conductivity, makes a firmer and denser cathode deposit, and causes more uniform corrosion of the anodes. The heating of the electrolyte, however, increases the chemical corrosion of both anodes and cathodes.

Circulation of the Electrolyte. It is necessary that the electrolyte be kept continuously in circulation to avoid the segregation of salts which would take place if electrolysis were to be conducted in a stationary electrolyte. Without circulation the heavy copper sulfate would tend to become more concentrated near the bottom of the tank, the solution near the cathodes would be impoverished in copper ions, and the solution near the anodes would increase in copper content until the hydrated copper sulfate would precipitate on the anode and impede the dissolution of the copper.

The solution is drawn from the tanks and pumped by means of air lifts or centrifugal pumps to an elevated storage tank from which it feeds back into the electrolytic tanks by gravity. In some plants the tanks are set on different floor levels so that it is possible for the electrolyte to flow through several tanks by gravity. The group of cells served by a single pump or air lift is known as a *circulation cascade.* The flow through any one tank is usually from an inlet pipe at the bottom of the tank near one end to an overflow pipe or weir at the top of the tank on the opposite end. Somewhere in the circulation system will be the device used to heat the electrolyte; the heating is usually done by steam coils either in the sump tank or the overhead storage tank. Lead pipe is commonly used for transporting the electrolyte, but the connections which enter the tanks must be made of rubber or other insulating material to prevent current leaking out on the pipe line.

Circulation commonly amounts to 3 to 5 gallons per minute flowing into each tank. This gives a gentle flow with little turbulence in the cells, so that there is not so much interference with the settling of the slimes. Bottom-to-top circulation as described above is most common, although this causes the electrolyte to flow opposite to the settling of the slimes; circulation systems with inlet at the top and outlet at the bottom have also been used.

Purification of the Electrolyte. For best operation of the electrolysis it is essential that the per cent of soluble substances in the electrolyte be kept within certain limits; copper and free acid should be held at definite values, and the soluble impurities must be kept below certain critical percentages (Table 3). In the copper coulometer there is no

appreciable change in the composition of the electrolyte, but in commercial refining tanks several factors affect the electrolyte composition.

1. Evaporation from the exposed surface of the heated electrolyte removes water and hence increases the concentration of all dissolved substances.

2. Soluble impurities which are not precipitated by ions in the electrolyte build up in concentration as the electrolysis proceeds. Nickel, arsenic, and iron are the principal elements in this group.

3. The copper content of the solution may either increase or decrease depending upon the nature of the anodes. With fairly pure anodes, the copper will tend to increase in concentration because of the chemical corrosion of both anode and cathode by the sulfuric acid plus dissolved oxygen; this will also decrease the free acid content of the electrolyte. If the anodes are relatively impure and contain larger amounts of nickel and iron, an appreciable portion of the current will be consumed in corroding or "ionizing" these impurities at the anode. Practically all of the current is plating copper at the cathode, which means that copper is being plated faster than it is dissolving, and the electrolyte becomes depleted in copper sulfate. In most refineries, however, the anodes are pure enough that this second effect is not noticed; as a general rule it will be found that dissolved copper tends to build up in the electrolyte.

Regulation of the electrolyte composition is attained by "bleeding" a certain amount of electrolyte from the main circuit and replacing this by fresh "make-up" solution of the proper composition. The foul electrolyte is then treated to recover as much of the acid and metal content as possible. Several methods have been used for treating foul electrolyte, the choice depending upon the nature and amount of the impurities. These methods utilize (1) crystallization of the salts by evaporation of the liquid, (2) electrodeposition using insoluble anodes, or (3) some combination of (1) and (2).

The purpose of crystallization is to remove the excess copper sulfate as crystals of $CuSO_4 \cdot 5H_2O$ ("blue vitriol"). This is done by first neutralizing the free acid by agitating with air in the presence of metallic copper, evaporating part of the water in the liquid, and then allowing it to cool so that the crystals may separate. In electrodeposition with insoluble anodes, the copper content of the electrolyte is depleted as there is no copper dissolved from the anode. This is a relatively expensive method from the standpoint of power costs because of the higher voltage and lower current efficiency — it usually takes from 8 to 10 times as much power to separate a pound of copper using insoluble anodes as it does with soluble anodes.

In the description of refining plants which is to follow we shall give some examples of the methods used in purifying electrolytes.

Electrolytic Tanks. The tanks used in electrolytic refineries are made of either wood or reinforced concrete; reinforced concrete is superior to wood and is used in most of the newer installations. All tanks are lined with sheets of antimonial lead containing about 6 per cent antimony; this resists the corrosive action of the acid and copper sulfate in the electrolyte and protects the wood or concrete from attack. Series cells are from 8 to 14 feet long, 2¾ to 3½ feet wide, and 3½ to 4 feet deep. The tanks must be sturdily constructed to support the weight of the electrodes. An average tank will contain about 10 tons of electrodes and 3 tons of electrolyte (570 gallons).

Piers of concrete or brick of sufficient height to provide 8 or 10 feet of head room below the tanks are commonly used for support. Each tank is fitted with a drain in the bottom so that the anode mud can be sluiced out. The floors of tank house and basement are generally covered with asphalt or other acid-resisting material.

Anodes and cathodes are hung in the tanks spaced closely together. The *electrode distance* is usually about 4 to 4½ inches. This is the distance from center to center of two adjacent anodes, and it means that each anode surface is separated from the adjacent cathode by a space of about an inch. This space will remain relatively constant as the electrolysis proceeds, because as the cathode deposit builds up the anode thickness decreases at about the same rate. Too close a spacing of electrodes may result in current losses caused by short-circuiting due to bridging of the gap between anode and cathode by crystals growing out from the cathode; too wide spacing of electrodes means more power loss, because the resistance is greater through the longer column of electrolyte, and less efficient utilization of the tank space. The tanks are wide enough to allow about an inch between the electrodes and the side walls, and deep enough to give a space of 6 to 8 inches from the bottom of the electrodes to the tank floor. In this space the anode mud collects.

Anode Corrosion. The copper and impurities dissolve from the anode under the action of the electric current, and the portion below the surface of the electrolyte gradually becomes thinner. Just before the corroded anodes are removed from the tank there will be only a thin sheet of the original anode left. The *anode scrap,* therefore, consists of the lugs and upper part of the original anode plus a small amount of the submerged portion (Fig. 7). Impure anodes corrode unevenly, and as the anode becomes thin there is a tendency for pieces of it to slough off and fall to the bottom of the tank. To avoid

this the corroded impure anodes must be removed sooner than purer anodes. The weight of anode scrap will be from 6 to 15 per cent of the weight of the original anodes, depending on their purity. Anode scrap is washed free of adhering slime and returned to the anode furnace.

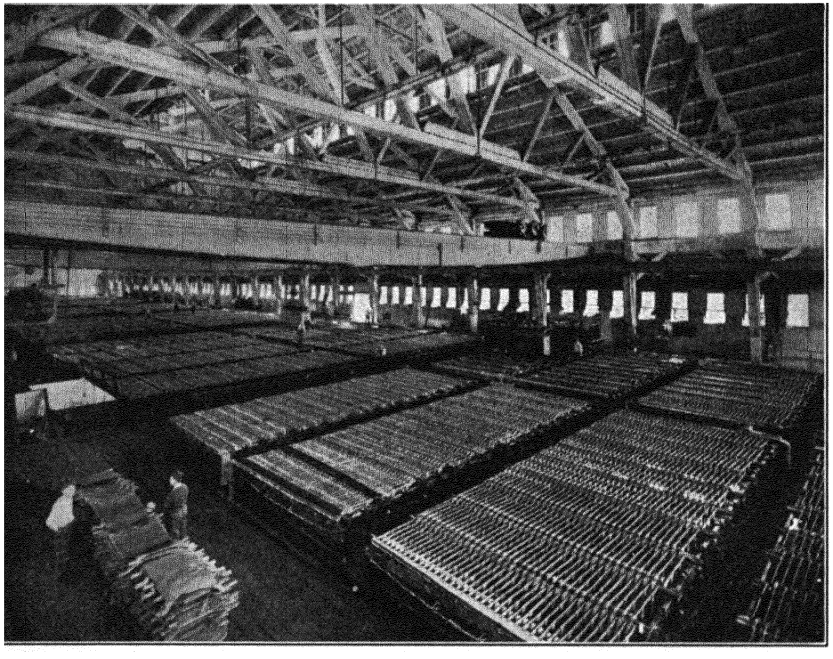


FIG. 7. View in the Tank Room of an Electrolytic Refinery.

The tanks are arranged in "nests" of ten and are connected by the Walker system. Busbars are tapered. In the foreground is a car of anode scrap to be sent back to the anode furnaces. Anodes and cathodes are handled by the overhead cranes.

The Cathode Deposit. Two things are of importance in deposits of cathode copper — (1) the chemical composition of the copper, and (2) the physical condition of the deposit.

The cathode carries a negative charge, and in the adjacent electrolyte there are numbers of cations carrying positive charges — copper and hydrogen ions especially, together with some nickel and iron. Theoretically, all the metallic atoms *below* copper in the electromotive series should not dissolve at all, and the atoms of metals *above* copper in the series should dissolve but should not be discharged at the cathode as long as copper ions are present. Practically, this rule holds fairly well; thus hydrogen ions are not neutralized to any extent at the cathode, as hydrogen is well above copper in the electromotive

series. The theoretical rule could be expected to hold only if the voltage drop between anode and cathode were very small; this, however, would mean an extremely small current (Ohm's law), and the deposition would not be rapid enough for commercial refining.

With higher voltages there is a tendency for other metallic ions to be neutralized (nickel, iron, etc.) and form part of the cathode deposit, and the greater the concentration of these ions in the electrolyte, the more that will be discharged. The higher the current density (and consequently the voltage) and the higher the concentration of soluble impurities, the less pure will be the cathode deposit. The limits of current density and impurity content that we have mentioned before are those which experience has shown will yield a deposit of the purity required in electrolytic copper.

In addition to the impurities deposited electrolytically, suspended particles of anode mud may become attached to the cathode and be mechanically occluded in the cathode deposit. The amount of impurities thus carried into the cathode copper will depend upon the amount of the anode mud and the rapidity with which the particles settle out. Arsenic and antimony tend to form *float slimes* of basic compounds which are particularly troublesome because they do not settle rapidly. More impurities are occluded near the bottom of the cathode than at the top, because the suspended particles are more concentrated at the bottom.

When copper ions are discharged at the cathode, the neutral atoms assemble into crystals of copper, and if a crystal is already started, the atoms tend to line up in its crystal lattice rather than to form new crystals. The growth starts by the formation of a large number of small crystal nuclei closely spaced over the cathode surface, and the crystals grow in a direction normal to the plane of the cathode surface. As these crystals grow, the more favorably oriented crystals increase in size, and the other crystals cease to grow — thus the crystals appear to "fan out" as they get away from the original surface and instead of a large number of small crystals we have a smaller number of large crystals. The thicker the deposit the coarser the crystals will be, and the more irregular the surface of the deposit.

Figure 8 is a photomicrograph of a cross-section of a copper cathode showing the starting sheet. One boundary of the starting sheet is straight, and the other is somewhat irregular. The straight side was originally adjacent to the starting blank in the stripper cell. Note that the crystals are small on this side and that they grow larger as their length increases; the "outer" side of the starting sheet is irregular because of the coarser crystals. The deposit formed in the

commercial cell builds up on the starting sheet and begins with the formation of a new set of crystals. These also grow in size and eventually become much larger than those in the starting sheet because the deposit is much thicker. For this reason the surface of the finished cathode is much more irregular than the surface of the starting sheet.

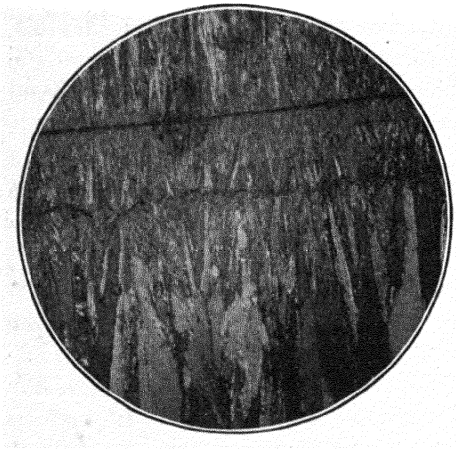


FIG. 8. Magnified Section Through the Center of a Copper Cathode.

Because copper crystals grow normally to the depositing surface, a groove on the starting sheet will result in a line of weakness in the sheet of deposited copper. This fact is often utilized by making a small groove in the surface of starting blanks about ½ inch from the outer edge, so that the deposited copper will part readily along the line of this groove when the starting sheet is being stripped from the blank. Crystal growth is always greatest at sharp points and corners, because the current density is greatest here. This often results in the formation of " bumps " and " warts " on the cathodes, and these may grow large enough to short-circuit the anode and cathode.

In the ordinary deposit the copper crystals are firmly interlocked, and the deposit is strong and tough. Low current densities, hot solutions, and the addition of a small amount of glue (or similar colloid) to the electrolyte all promote greater smoothness and toughness in the cathode deposit. Small amounts of glue are used in practically all electrolytes, and it has a pronounced effect on the physical properties of the cathode deposit. The glue, however, increases the resistance of the electrolyte, and even the small amounts used may increase the resistance by 10 or 20 per cent.

Brittle Cathodes.[5] The process for producing copper shapes by coalescence and extrusion of cathode copper requires that the cathodes be cut or broken into small pieces. The ordinary tough cathode deposit is unsuitable, and a process has been developed to produce a brittle cathode.

[5] Tyssowski, John, The Coalescence Process for Producing Semifabricated Oxygen-Free Copper: Am. Inst. Min. & Met. Eng. Tech. Paper 1217 (Metals Technology), June 1940.

The production of brittle cathodes resembles the standard multiple refining process in most respects — tanks and electrical connections, use of salt to provide chlorine, rate of circulation of electrolyte, acid content of electrolyte, temperature of electrolyte, length of deposit cycle, size and spacing of anodes, and removal of the anode mud. In fact, the two processes differ only in that (1) a depositing blank is used instead of a starting sheet, the deposit is shaken or knocked off, and the starting blank used again, (2) the composition of the electrolyte differs in certain minute but important details.

Glue is omitted from the electrolyte, and in its stead there is added a small amount of an *embrittling agent*. This is a reagent which shows a greater ability to wet copper than does the electrolyte; it should form a film on the copper which has a definite insulating value. A mixture of corn oil, castor oil, gasoline, and carbon tetrachloride has been found to be a suitable embrittling agent.

The starting blanks of ⅛-inch polished cold-rolled copper are dipped in the embrittling mixture before being placed in the tanks. The current is then able to puncture the insulating film only at a number of widely spaced points — widely spaced as compared to the number of crystal nuclei that would form on an un-oiled sheet — and there are fewer points at which crystal growth can start. As the crystals grow, the embrittling agent in the solution coats their surfaces and prevents them from growing together and forming a coherent mass.

After the cathode deposit has reached the proper thickness, the cathodes are removed, and the deposit removed from the blank by shaking or knocking it; the friable deposit is then broken to the desired size, and the blanks are used again for the next cycle.

The method for producing brittle cathodes compares quite favorably with standard refining practice. The process requires somewhat more labor in applying the embrittling agent and removing the cathode deposit, and the rough surface of the cathodes increases the possibility of entrapping slime particles. On the other hand, because of better electrical connections at the cathode (use of solid connections instead of loops and rods), and the increased conductivity of the electrolyte caused by the omission of glue, the voltage required is lower. Brittle cathodes require only 75 to 85 per cent of the power required to produce tough cathodes under similar operating conditions.

Plant Operations. The important operations in an electrolytic refining plant are as follows:

1. Charging of new anodes and starting sheets in the tanks. Anodes are handled by means of overhead cranes which are equipped

to move an entire tankload at one time. Starting sheets are usually placed by hand (Fig. 2).

2. Removing cathodes when finished, and washing them with a water spray to remove electrolyte and adhering slime. All the cathodes in a tank are removed at one time by the crane.

3. Removing the remnants of copper anodes, washing them and returning the scrap to the anode furnaces. At the time the anodes are removed the anode mud is flushed out of the tank and collected.

4. Inspecting the operating tanks to discover and eliminate short circuits caused by growths on the cathodes or the warping of new starting sheets.

THE SERIES SYSTEM

Much of the previous discussion on the multiple system of refining applies equally to the series system, and in such things as electrolyte composition, composition of anodes, and nature of cathode deposits, there is no important difference between the two methods. Our discussion, therefore will be concerned principally with the outstanding differences between the two systems.

Intermediate or Bipolar Electrodes. If an anode and cathode are immersed in an electrolyte there will exist a potential gradient through the column of electrolyte between the positive and negative electrodes, and if another metal strip is inserted in the electrolyte between the two electrodes, a current will flow through it because the side nearest the cathode will assume a negative charge and the side nearest the anode will have a positive charge. The intermediate electrode has no metallic connection with either of the two end electrodes (Fig. 9). The charges on the various parts are, of course, relative, because there is a steady potential gradient in one direction. Thus the right side of the intermediate electrode A is positive with respect to the left side of A; however, the right side of A is *negative* with respect to the anode, and the left side of A is *positive* with respect to the cathode.

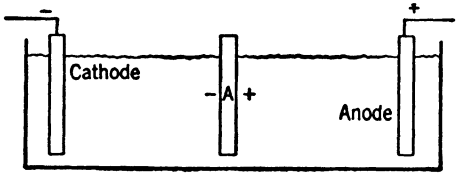


FIG. 9. An Intermediate Electrode.

If our solution contained dissolved $CuSO_4$ and the electrodes were of metallic copper we would find that when the current was passed through it, copper would dissolve from the anode and plate out on the cathode. Also, copper would plate out on the right side of A, and

copper would be dissolved from the left side. A large number of intermediate electrodes might be inserted in the tank, in which case copper would dissolve from one side of each and plate out on the opposite side of the adjacent electrode. The electrodes in a series refining tank are a number of intermediate electrodes, and only the two end electrodes are connected to the electrical circuit (Fig. 9).

Electrodes. There are no separate anodes and cathodes in series refining tanks, as each of the bipolar electrodes serves as both anode and cathode, and no starting sheets or special depositing sheets are needed. The impure copper is carefully cast into the required shapes, or the electrodes may be made by a rolling process which yields a smoother and more perfect electrode. As the electrolysis proceeds, the copper dissolves from one side of each electrode and deposits on the next electrode; the electrodes are removed when the transfer is practically complete and the small amount of unrefined copper adhering is stripped off and scrapped.

Series electrodes are smaller than the anodes used in multiple system, weighing about 100 pounds each. The busbars or cables which bring the current into the cells are not nearly as heavy as the busbars used in the multiple system, as the amperage per tank is much less.

Series electrodes as cast or rolled are commonly called *anodes*, although this nomenclature is not strictly correct.

Tanks. Series tanks are usually somewhat larger than multiple refining tanks but are of the same general construction. They also are constructed of wood or reinforced concrete, and the concrete appears to be the more satisfactory material. An important difference is the tank lining. A metallic lining cannot be used because this would bypass a part of the current around the electrodes, so a non-conducting lining is necessary.

Current Efficiency and Power Consumption. The overall current efficiency in the series process is lower than is common in multiple refining, generally in the neighborhood of 70 to 80 per cent. In spite of the lower current efficiency the series process generally yields a greater weight of refined copper per unit of electric power. This is due to the lower voltage required; from 10 to 30 per cent of the total voltage drop in a multiple cell is due to the contact losses at the points where the anodes and cathodes rest on the conductors which carry the current — these contacts are not needed in series refining.

In most other respects there is no great difference between the two systems, and in another section we shall present a description of a plant using the series system which will illustrate the important details.

TREATMENT OF ANODE MUD OR SLIME

The weight of anode mud or slime produced in electrolytic refining of copper will range from 0.5 to 3.0 per cent of the original anode weight, depending on the purity of the anode copper. In addition to the elements we have already mentioned, a certain amount of metallic copper enters the slime. Part of this is in the form of small nodules which break off the cathode deposit, and part of it comes from the precipitation reaction:

$$2Cu^{+} \rightarrow Cu + Cu^{++}$$

This is due to the solution of a small amount of copper as cuprous ions which exchange charges to form a cupric ion and a neutral copper atom.

Table 4 gives the average composition range of copper anode slimes as they come from the tanks. The principal value of these slimes is in their precious metal content.

TABLE 4[a]

COMPOSITION RANGE OF COPPER ANODE SLIMES

Gold	0.0548	to 0 6855%;	16 to 200 oz/ton; $560 to $7000/ton
Silver	10.28	to 15 07%;	3,000 to 14,900 oz/ton
Copper	16	to 24%	
Nickel	0.05	to 5 25%	
Lead	1	to 16%	
Antimony	2.3	to 8.0%	
Tellurium	0 8	to 6 0%	
Selenium	1 5	to 9 0%	
Arsenic	2 7	to 3 9%	
Bismuth	0.26	to 0 46%	
Iron	0 17	to 0.27%	

[a] Creighton, H J , and Koehler, W. A., Electrochemistry, 3d ed , Vol 2, p 168, John Wiley and Sons, Inc , New York, 1935

The treatment of slime varies in different refineries, depending upon the analysis of the material; in general, however, the slimes are submitted to three basic operations.

1. Roasting to convert copper to copper oxide, and leaching with sulfuric acid to remove the copper.

2. Subjecting the residue to a series of oxidizing fusions. This oxidizes the base metal impurities and leaves a *doré bullion* of silver, gold, and platinum metals. Base metals pass into either slags or furnace fumes.

3. Parting the doré to recover fine gold, fine silver, and platinum metals.

Roasting and Leaching. The slimes are first screened to remove any large pieces of copper and then filtered to give a dense cake containing about 35 per cent moisture. This cake is then roasted at about 300° C, and the copper present is oxidized to CuO. The roasted slimes are then leached with hot sulfuric acid (10 to 15 per cent acid) in lead-lined kettles, and the leached slimes are filtered and sent to the doré furnaces. The solution from the leaching is returned to the tank house after being passed over metallic copper to precipitate any selenium and tellurium that may have dissolved.

Oxidizing Fusion. The leached slime is melted down in a small reverberatory (doré) furnace, and the impurities are oxidized by air and by oxidizing fluxes, such as niter. Soda ash and silica are also used as fluxes.

The sequence of operations such as skimming and adding of fluxes depends upon the composition of the mud being treated; the process is a batch operation and must be adapted to the particular charge being treated. If much lead is present the first skimming will consist largely of lead oxide (litharge) formed as the charge melts down. Further oxidation by means of air and oxidizing fluxes oxidizes the remaining base impurities, which are removed as slags. The gases from the doré furnaces are cleaned by passing them through spray chambers and Cottrell treaters. The slags are re-treated to recover the impurities or sold for their metal content to lead smelters or other plants. Cottrell dust and the residue from the washing chambers are re-treated. Both the slags and the flue dusts contain considerable gold and silver as well as lead, selenium, and tellurium; all these refinery byproducts are too valuable to be discarded.

The metal remaining in the doré furnace is principally silver and gold containing small amounts of base metal plus any platinum metals in the original slime. This is then *parted* to separate and purify the gold and silver and to recover the platinum metals.

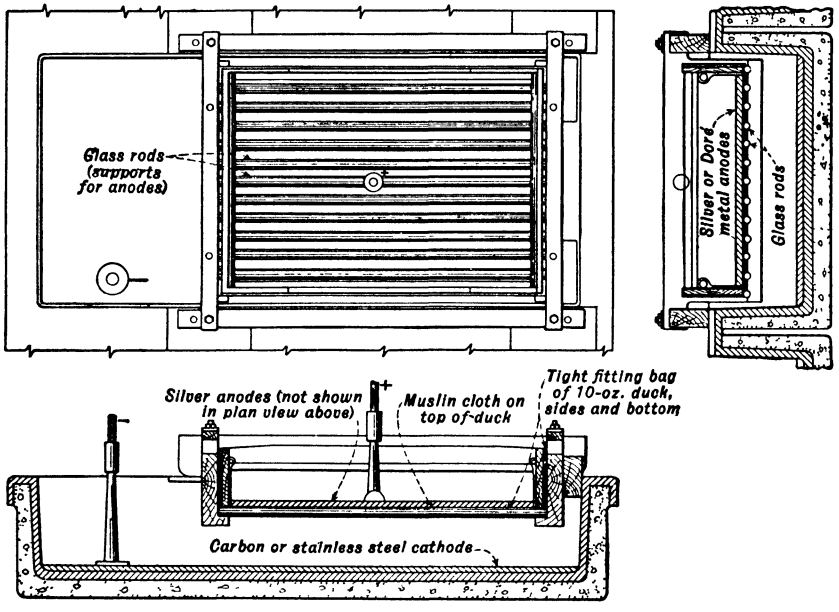
Acid Parting. The doré is boiled in cast iron kettles in strong sulfuric acid (66° Bé, or 96 to 98 per cent) to dissolve the silver and platinum metals. Gold remains undissolved, and the silver sulfate liquor is siphoned into a tank of water and boiled. The silver is precipitated in the form of crystals on copper plates hung in the tank, the copper (a less noble metal) going into solution. The silver crystals are collected and melted into bars of fine silver.

If the platinum metals are present in sufficient quantity they must be recovered by separating them from the silver — possibly by casting the silver into anodes and refining it electrolytically.

The use of acid parting is not common in large copper refineries —

most of them employ electrolytic parting and refining methods. These are the *Thum* and *Moebius* processes for silver, and the *Wohlwill* process for gold.

Thum and Moebius Processes. These two processes are electrolytic refining methods in which an anode of crude silver is electrolyzed and a deposit of pure silver is plated on the cathode. The two methods differ principally in the details of the cell construction.



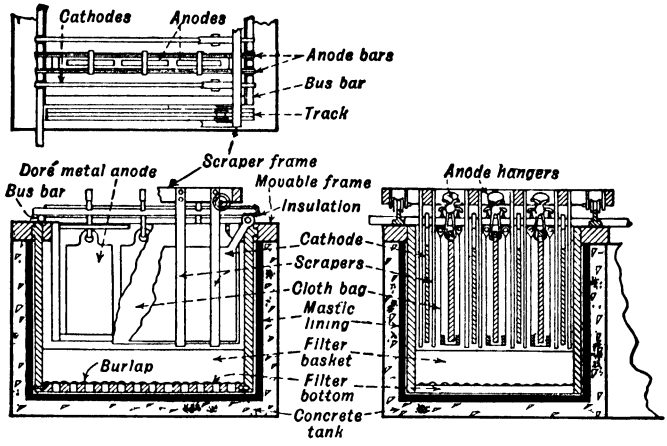
(*From Creighton and Koehler, Electrochemistry, John Wiley and Sons, Inc., New York*)

FIG. 10. Thum Cell for Silver Refining.

The Thum cell is a shallow tank about 52 by 24 inches and 9 inches deep made of acid-proof stoneware or concrete lined with mastic. A slab of carbon or graphite covering the bottom of the cell serves as the cathode; stainless steel may also be used for the cathode. A wooden or stoneware basket (Fig. 10) with a bottom of glass rods serves to hold the anodes which are laid horizontally on the bottom of the basket with a piece of muslin or duck beneath them to prevent the anode slimes from falling through the bottom of the basket. The anodes are small slabs of impure silver about 8 by 12 inches; the cathode deposit forms on the cathode plate as loose crystals, which are raked out at intervals.

The Moebius cell resembles a small multiple refining tank (Fig. 11), and the anodes and cathodes are hung from suspension bars. The anodes, which are about 14 by 5½ inches and are about ⅜ inch thick,

are hung in canvas bags that hold back the anode slime. The cathodes are plates of stainless steel or rolled silver; the cathode deposit forms as loosely adherent crystals which are knocked off by wooden scrapers and collected in a basket in the bottom of the cell. The cell shown measures 24 by 26 inches; its depth is 22 inches. These cells are constructed of the same material as the Thum cells.



(From Creighton and Koehler, Electrochemistry, John Wiley and Sons, Inc., New York)

FIG. 11. Moebius Cell for Silver Refining.

The voltage drop in the Moebius cell is about 2.7 volts, and in the Thum cell it is 3 to 3.5 volts. This difference is due to the slime settling on the muslin diaphragm, which increases the resistance of the cell. Moebius cells require small floor space, use less electric power, and consume less nitric acid than the Thum cells; however, they produce anode scrap which amounts to about 15 per cent of the weight of the anode and must be recast before it can be used in the Moebius cell. Anodes are completely consumed in the Thum cells because new anodes can be placed in the basket on top of the old ones, and all the fragments are thus dissolved. In most other respects there is little difference between the two systems, and the remarks which follow apply to both.

The anodes for these refining processes are made by casting the bullion from the doré furnaces; they contain about 95 per cent silver with the remainder mainly copper and gold. The silver and copper dissolve, and the gold remains behind as a slime. The cathode deposit contains 99.9 per cent (999 fine) silver, which is melted in graphite crucibles and cast into bars.

The cells operate with a current density of about 50 amperes per square foot. The electrolyte is a practically neutral solution of silver

and copper nitrates containing about 60 grams of silver per liter and 30 to 40 grams of copper. Part of the electrolyte is removed each day and replaced by fresh electrolyte in order to keep the impurities below the prescribed limits and to build up the silver content, as the electrolyte gradually becomes depleted in silver. Foul electrolyte is passed over copper to cement out the silver and then over metallic iron to precipitate the copper.

The anode slime collects on the diaphragms surrounding the anodes. It contains all the gold, platinum, and palladium. This is removed, washed, and treated with boiling sulfuric acid to remove any copper and silver; it is then washed again, dried, melted, and cast into anodes for refining by the Wohlwill process.

The Wohlwill Process. This process consists in electrolyzing impure gold anodes in a hot acid solution of gold chloride. Anodes are made from such materials as the anode slime from Thum and Moebius cells, and they will contain from 94 to 98 per cent gold. Cathodes are deposited on rolled strips of pure gold, and the resultant cathode gold will be from 999.5 to 999.9 fine.

The cells are made of glazed porcelain and are small in size because of the value of the electrolyte. Anodes and cathodes are suspended in the solution. The electrolyte contains 7 to 8 per cent gold as $AuCl_3$ and 10 to 16 per cent free HCl; it is maintained at a temperature of 70° C. High current densities (110 to 120 amperes per square foot) are employed to obtain rapid deposition and reduce interest charges on the gold in process; about 1 3 to 1.5 volts are required to give this current.

Part of the electrolyte is removed daily to control impurities, and gold chloride must be added to replace the gold lost by depletion of the solution. Platinum and palladium concentrate in the electrolyte; but some gold, silver chloride, lead sulfate, and the other metals of the platinum group are found in the anode slimes. These are recovered by several different methods.

The Wohlwill process utilizes an alternating current superimposed on the direct current used for the actual plating when the silver content of the anodes is high; this serves to prevent the silver chloride slime from adhering to the anodes.

All three of these processes are used by the United States Mint as well as by commercial refiners. There are some differences in operating methods, because the commercial refiners must put the metal through the process as rapidly as possible to minimize interest charges on the highly valuable metal and electrolyte; this problem does not confront the Mint.

ELECTROLYTIC REFINING PLANTS

To point up the discussion of the methods used in copper refining we shall present brief descriptions of several multiple refining plants and one series plant. A good deal of the material will be given merely as a summary, but parts of the descriptions that have not been considered previously will be given in more detail. The two Canadian plants described are the most recently constructed refineries on the North American Continent.

Raritan.[6,7] The Raritan plant of the Anaconda Copper Mining Company is located on tidewater at Perth Amboy, New Jersey. The plant receives crude copper from Africa, South America, Mexico, and the United States, and all but about 6 per cent of this comes by water. Byproducts include silver, gold, platinum, palladium, selenium, tellurium, copper sulfate, and nickel sulfate. This plant has a production capacity of 45,000,000 pounds of refined copper per month.

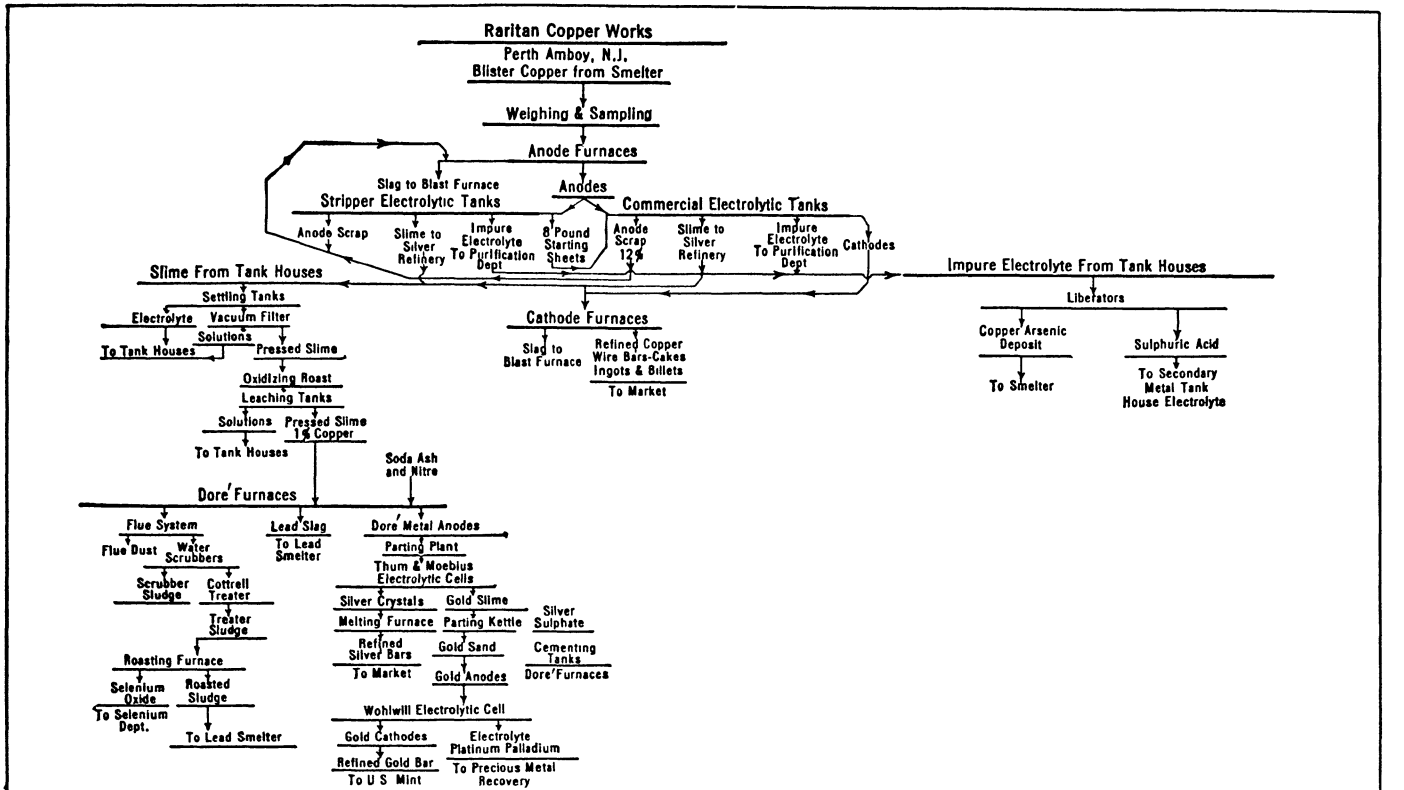
Electrical Plant. Power is produced by steam generated in three high pressure 1200-horsepower Stirling boilers which normally operate at 180 to 200 per cent of capacity at 385-pound pressure and deliver steam at 660° F. Four older B. and W. boilers of 760 horsepower each are kept in reserve, and the steam from the main boiler plant is augmented by steam from the waste-heat boilers on the eight copper furnaces. Power is generated as 60-cycle alternating current at 2300 volts in three turbine-driven alternators, one of 3125 kilovolt-amperes rating and the other two of 5000 kilovolt-amperes each.

Alternating current is converted to direct current at the tank houses by means of motor-generator sets. Tank house No 1 has two 2400-kilowatt sets; each of these consists of a synchronous motor (2650-kilowatt, 2300 volt, 720 revolutions per minute) direct-connected to two 300-volt, 4000-ampere direct-current generators. Thus the power supply to Tank house No. 1 amounts to 16,000 amperes at 300 volts.

Tank house No. 2 is served by two 1920-kilowatt motor generator sets each consisting of a synchronous motor (2150-kilowatt, 2300-volt, 720 revolutions per minute) direct-connected to two 240-volt 4000-ampere direct-current generators. These two provide current for the commercial cells, which amounts to 16,000 amperes at 240 volts. Tank house No. 2 contains all the stripper cells for making starting sheets, and these are supplied with 7000 amperes at 100 volts from a 1076-kilowatt rotary converter equipped for automatic constant-current control.

[6] Burns, W. T., Refining Anaconda Copper at Raritan and Great Falls: Eng. and Min Jour., Vol. 128, No 8, p 306, 1929

[7] Raritan Copper Works, Pamphlet issued by Raritan plant.



(*Courtesy Anaconda Copper Mining Company*)

FIG. 12. Flowsheet of the Raritan Refinery.

Current density used is 18 amperes per square foot of cathode in the commercial cells and 17 amperes in the stripper cells. Voltage drop per cell is about 0.25 volt, and the current efficiency (as calculated from the current delivered to the tank house and the weight of cathode copper produced) is 92 to 95 per cent.

Tanks. Tank house No 1 contains 1800 cells or tanks, and tank house No. 2 contains 1656 cells. There are 276 stripper cells for starting sheets, all in tank house No. 2, so that the total number of cells is 3180 commercial cells and 276 stripper cells.

Tanks are 9 feet 11 inches long, 2 feet 10 inches wide, and 4 feet deep. Most of the tanks are built of wood and are lined with ⅛-inch 6 per cent antimonial lead sheeting. The newer tanks are of lead-lined reinforced concrete; all replacements are to be concrete tanks.

Tank house No. 1 is divided into two electrical circuits of 900 tanks each. The commercial cells in tank house No. 2 are divided into two circuits, one of 660 cells and the other of 720 cells; stripper cells are on a separate circuit. The Walker system of electrical connections is used.

Each tank house is served by eight electrically operated cranes for handling anodes and cathodes. Commercial tanks each contain 28 anodes and 29 cathodes; stripper cells contain 25 anodes and 24 starting blanks.

Anodes. All anodes are cast into straight-line casting machines at the plant from four anode furnaces.

Composition:

Cu,	99.25%	Pb,	0.053%
O_2,	0.100%	Fe,	0 058%
Ag,	30 oz/ton	Bi,	0 003%
Au,	0 40 oz/ton	S,	0.004%
As,	0 060%	Se,	0 048%
Sb,	0 022%	Te,	0.038%
Ni,	0.050%		

Weight: 525 pounds
Size: 36 inches long, 28 inches wide, 1½ inches thick.
Life: 30 days — produce three crops of cathodes.
Anode scrap: 10 to 12 per cent.
Mode of suspension: cast lugs.

Cathodes. The starting sheets are deposited on sheets of rolled copper in the stripper cells; the blanks are greased to prevent the deposit sticking. At the end of 24 hours the blanks are pulled and an 8-pound starting sheet is stripped from each side. To each starting

sheet are riveted two small copper loops through which the cathode supporting bar is passed.

Commercial cathodes weigh 160 pounds and are pulled at the end of 10 days. These are washed and then melted and cast in one of four cathode furnaces.

Composition of cast electrolytic copper (wirebars, etc.):

Cu,	99.94 to 99.97%	O_2,	0.02 to 0.05%
Ag,	0.0010%	Fe,	0.0025%
Au,	0.00001%	Ni,	0.0015%
S,	0.0020%	As,	0.0015%
Sb,	0 0015%		

Electrolyte. The electrolyte is circulated by means of vertical centrifugal pumps and passes through the tanks at the rate of 4 gallons per minute.

Composition, in grams per liter:

Cu,	45	Ni,	8.5
As,	12 5	H_2SO_4,	200
Sb,	0.4	Cl,	0.03
Fe,	1.20		

Temperature: 55° C
Specific gravity: 1.26–1.28

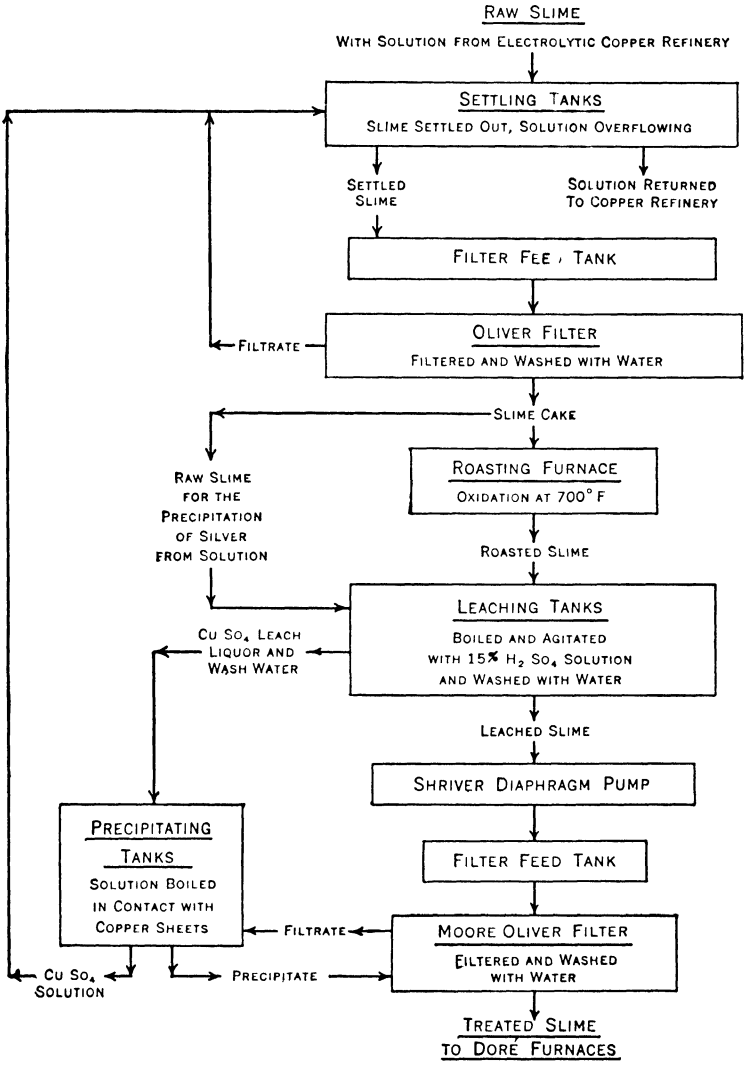
Anode Mud. The anode mud produced will average about 0.6 per cent of the weight of anodes. The mud produced from Anaconda anodes will be as follows:

Ag,	43 23% (12,610 oz/ton)	Te,	6 14%
Au,	0 234% (68 4 oz/ton)	Fe,	0 22%
Cu,	13 86%	Sb,	2 46%
Se,	1.46%	Pb,	3 96
Bi,	0 26%	Ni,	0.27%
As,	3.88%		

The Raritan silver refinery not only handles the anode mud produced in its own plant but also anode mud from the Great Falls refinery and doré bars from the lead refinery of the International Lead Company. The capacity of the silver refinery is 2,500,000 troy ounces of silver and 25,000 troy ounces of gold per month.

Slime is flushed out of each tank by removing a lead plug in the bottom, and the slime is carried through launders to a collecting tank in the basement, from which it is pumped to the silver refinery. This mixture of slime and electrolyte is thickened in settling tanks and the clarified electrolyte returned to the tank house. The slime is then filtered on an Oliver filter and given a light roast in an oil-fired furnace

to break up selenides and tellurides and oxidize the copper. The roasted slime is then agitated in lead-lined iron kettles with hot 10 per



(*Mosher, Am. Inst. Min. and Met Eng Trans., Vol 106, p 428, 1933*)

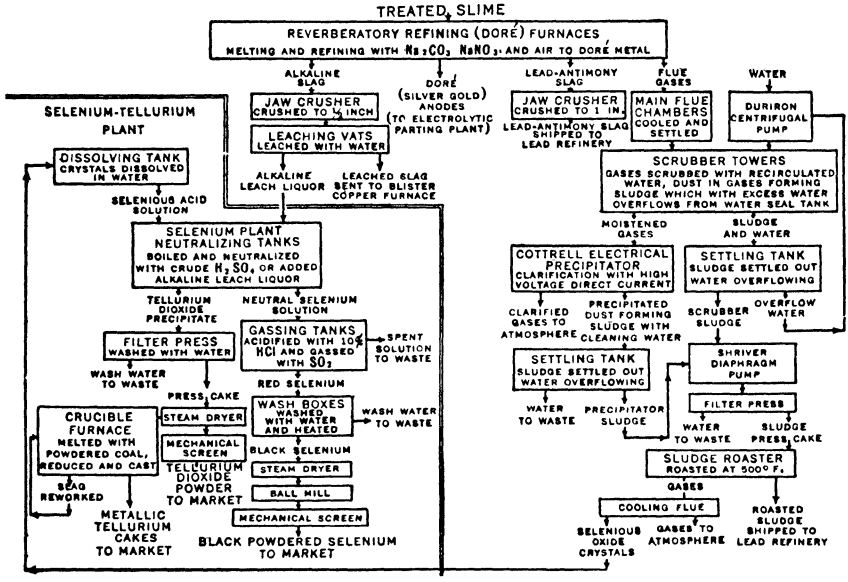
FIG. 13. Flowsheet of Treatment of Anode Mud or Slime.

cent sulfuric acid to dissolve the copper. After again washing and filtering on a Moore filter the decopperized slime goes to the doré furnaces.

The doré furnaces are small oil-fired reverberatories which hold

about 15,000 pounds of wet slime; treatment of this charge takes about 40 hours and results in the production of 3500 pounds of doré bullion containing 98.5 per cent silver, 1.0 per cent gold, and 0.5 per cent other metals. This doré is cast into anodes for the Thum and Moebius cells.

A flowsheet of the Raritan plant shown in Figure 12 indicates the number of products removed in the doré furnace. Lead and antimony are collected in slags and selenium and tellurium are recovered both

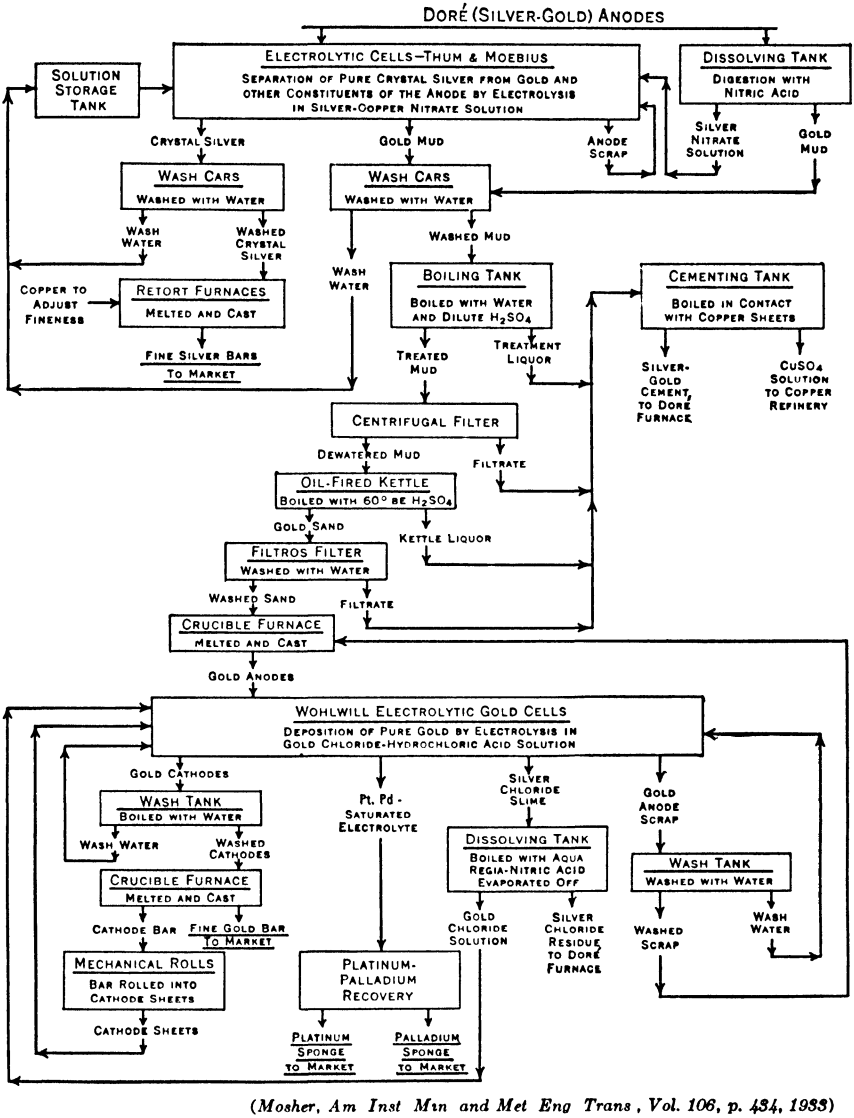


(*Mosher, Am. Inst. Min and Met Eng Trans, Vol 106, p 432, 1933*)

FIG. 14. Flowsheet of Furnace Refining and Recovery of Selenium and Tellurium.

from the flue dusts and in the alkaline slags produced by the addition of soda ash and niter. The amount of tellurium and selenium produced depends on the market for these elements. Although selenium and tellurium are present only as small percentages even in the anode slimes, the byproduction of these elements from copper refineries accounts for practically all the world's production; usually the supply has been greater than the demand. Most of the byproducts must be thrown into a commercially salable form or discarded; it is not possible in a refinery to keep impurities circulating in the system.

Both Thum and Moebius cells are used for parting the doré, and the cathode crystals are washed, melted in large graphite crucibles, and cast into standard thousand-ounce bars with a fineness of 999+. The gold slime is leached with boiling sulfuric acid to remove silver, washed, and cast into anodes for the Wohlwill cells. The silver sulfate



(Mosher, Am Inst Min and Met Eng Trans, Vol. 106, p. 434, 1933)

FIG. 15. Flowsheet of Electrolytic Parting and Refining of Precious Metals.

solution is cemented to remove the silver, which returns to the doré furnace.

The Wohlwill cells produce gold about 999.75 fine; this is melted in graphite crucibles and cast into standard bars. Platinum and palladium are recovered by working up the foul electrolyte from the Wohlwill cells.

A complete description of the silver refinery at Raritan has been given by Mosher.[8] We shall not go into further details on this plant beyond presenting three flowsheets (Figs. 13, 14, and 15), pages 281–283, which show these operations in more detail than Figure 12.

Purification of the Electrolyte. Impure electrolyte from the tank house is treated in insoluble-anode liberator cells, to produce a copper-arsenic deposit and sulfuric acid. The copper-arsenic residue goes to the smelter, and the acid joins the electrolyte in the secondary metal tank house, which is an electrolytic refinery for the treatment of secondary (scrap) copper.

Great Falls. The Great Falls refinery[9,10] of the Anaconda Company is located at Great Falls, Montana, about 200 miles from the smelter at Anaconda. It is smaller than the Raritan refinery and does not include a plant for treatment of slimes — anode slimes are shipped to the Raritan refinery. The plant has a capacity of about 27,000,000 pounds of refined copper per month — approximately half that of the Raritan plant.

Electrical Plant. The refinery is located near the hydroelectric plant of the Montana Power Company on the Missouri River, and power is purchased as alternating current at 6600 volts. The refinery substation contains seven synchronous motor-generator sets, each consisting of one 1730-horsepower 6600-volt alternating-current motor driving two 600-kilowatt 200-volt 3000-ampere direct-current generators which furnish power for the electrolytic circuit. This gives a total of 42,000 amperes at 200 volts available for the tank house. Current density is high — about 28 amperes per square foot of cathode — and the voltage drop per tank is 0.4 volt.

Tanks. The tanks are made of wood and are lead lined; inside dimensions are 10 feet 3 inches long, 2 feet 10 inches wide, and 3 feet 9 inches deep. Some of the tanks are of lead-lined reinforced concrete, and all replacements are to be concrete tanks. The plant is arranged in the two-cell system, i.e., a group of cells is arranged in double rows of ten, five in a cascade, with aisles between each double row. This is different from most other refineries which use the Walker or Whitehead systems requiring the tanks to be built in " nests " (Fig. 7). The Great Falls arrangement requires more busbars and more floor space; however, each tank is an independent unit, and when a tank is in need of repairs a new or rebuilt tank can be put in place in a few moments.

[8] Mosher, M. A., Recovery of Precious and Secondary Metals from Electrolytic Copper Refining: Am. Inst. Min. & Met. Eng. Trans, Vol. 106, p. 427, 1933.

[9] Burns, W. T., op. cit., p. 306

[10] Bardwell, E. S., and Lapee, R. J., Notes on Purification of Electrolytes in Copper Refining: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 417, 1933.

Worn tanks are continually being replaced by new ones, so that no wholesale replacing of old tanks need be made at any one time.

The tank house contains 1440 commercial tanks and 90 stripper cells for making starting sheets. These are divided up as follows:

1. There are four crane bays of 360 cells each served by seven 10-ton cranes of 60-foot span; a crane transfer at one end of the building makes it possible to transfer cranes from one bay to another. The 90 stripper cells are not under the cranes.

2. The tank house is divided into 12 sections of 120 cells each and the stripper section of 90 cells. Each section has a separate electrolyte, which is pumped by Pohlé air lifts.

3. The tanks (commercial and stripper cells) are divided into three electrical circuits of 540, 510, and 480 tanks.

Commercial cells each hold 25 anodes and 26 cathodes.

Anodes. Anodes are of the coped lug type and weigh 630 pounds each. Anodes are cast at the Anaconda smelter and shipped to Great Falls. The only anodes cast at Great Falls are those made from the anode scrap.

Composition: Table 5 gives typical analyses of the anode copper treated at Great Falls over a period of years. These anodes also contained about 67.0 ounces of silver and 0.3 ounces of gold per ton.

TABLE 5[a]

ANALYSIS OF ANODE COPPER TREATED AT GREAT FALLS

	Per Cent				
	1929	1930	1931	1932	1933
					(3 months only)
Copper	99.290	99 286	99 249	99 199	99 406
Zinc	0.0008	0 0010	0 009	0.0010	.....
Lead	0 015	0 020	0 012	0 008	.....
Arsenic	0.088	0 084	0 062	0 056	0.099
Antimony	0 072	0 073	0 075	0 072	0.062
Selenium	0 012	0 013	0 010	0 008	.... .
Tellurium	0 084	0 073	0.089	0 069	.....
Nickel	0.014	0.022	0 014	0.010	.....
Bismuth	0 0057	0 0060	0 0054	0.008	.....
Iron	0 0010	0 0011	0 0013	0.007	.....
Sulfur	0 0032	0 0027	0 0027	0 0024	.....

[a] Bardwell, E. S., and Lapee, R J , op cit , p 419.

Size: 36½ inches long, 28 inches wide, 2 inches thick.

Life: 24 to 26 days — produce four crops of cathodes.

Anode scrap: 9 to 11 per cent.

Mode of suspension: cast lugs.

Cathodes. Thirteen-hour sheets weighing 7 pounds apiece are made in the stripper cells. Riveted loops are attached to hold the cathode bar. Commercial cathodes are pulled every 6 days, and they weigh about 140 pounds.

Electrolyte. The electrolyte has a specific gravity of about 1.275; it is maintained at a temperature of 55° to 60° C and is circulated by means of air lifts. Average analysis of electrolyte for two different years is given in Table 6.

TABLE 6[a]

AVERAGE ANALYSIS OF ELECTROLYTE AT GREAT FALLS

Year	Specific Gravity	Grams per Liter						
		Free Acid	Cu	As	Sb	Fe	Ni	Cl
1930	1.272	218	39.1	8 2	0 72	2 9	9 7	0 027
1932	1.253	213	34.5	8.7	0 60	2 5	8 0	0 028

[a] Bardwell, E. S., and Lapee, R J , op. cit., p. 421

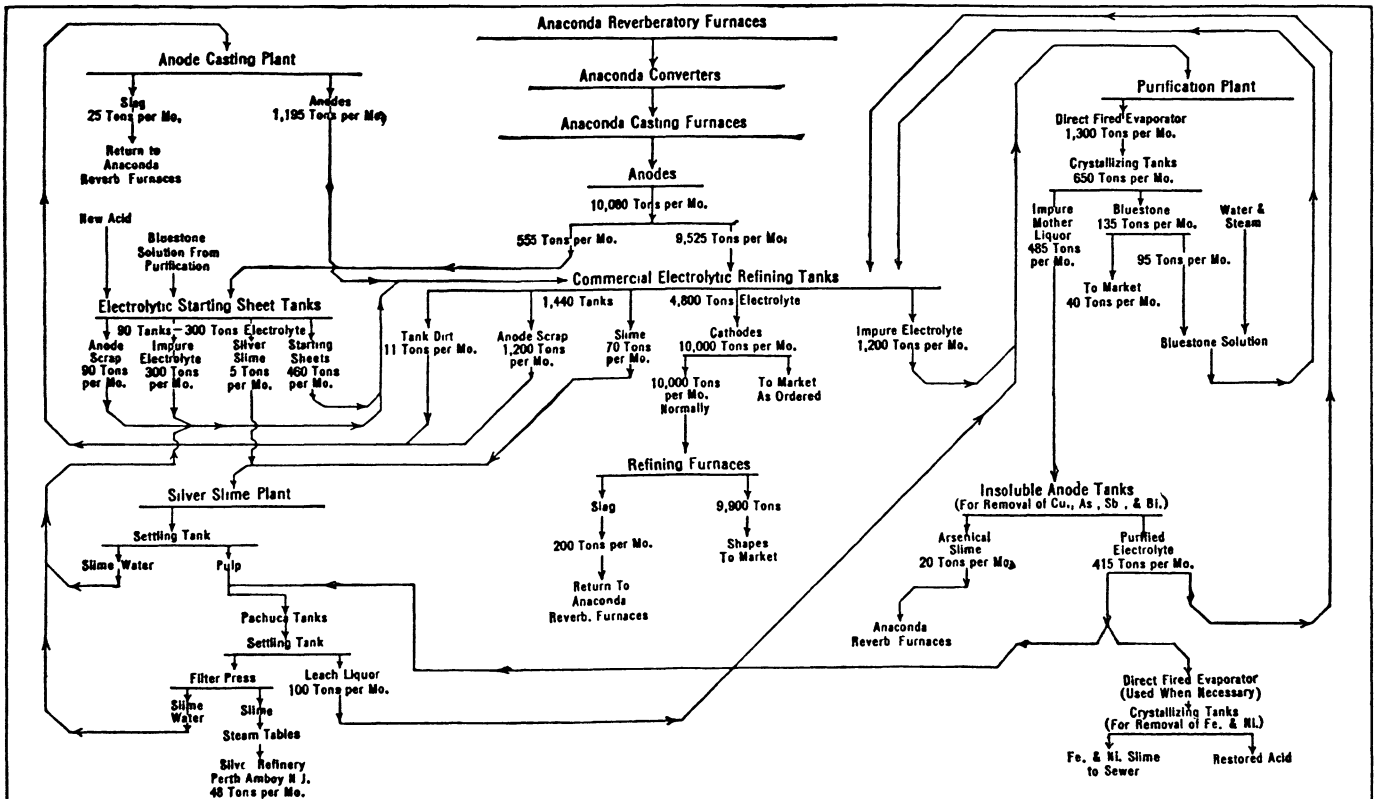
Anode Mud. The anode mud produced at Great Falls is leached to remove the bulk of the copper and then shipped to Raritan for refining. The leached slime will assay approximately as follows:

Cu,	1.5%	As,	5.0%	Se,	2 0%
Te,	15.6%	Pb,	4.6%	S,	2.7%
	Au, 75 oz/ton		Ag, 13,300 oz/ton		

Purification of the Electrolyte. The method adopted for purifying tank-room electrolyte at Great Falls is as follows:

Each day a certain volume of electrolyte is run off and sent to the purification tank, where it is boiled down to approximately 46° Baumé (specific gravity = 1.47). The concentrated electrolyte is then sent to crystallizing tanks, where the bulk of the copper is crystallized out as copper sulfate; part of this bluestone goes to market and part is dissolved and returned to the tank room (Fig. 16). The mother liquor is then passed through electrolytic tanks with insoluble anodes to remove the last of the copper and most of the arsenic and antimony. Spent electrolyte from the insoluble anode cells is then either returned to the tank room direct or boiled down to 55° Baumé (specific gravity = 1.61), the iron and nickel salts crystallized out, and the mother liquid returned to the tank-room circuit as restored acid.

Prior to 1930 all evaporating was done in lead-lined tanks provided



(Courtesy Anaconda Copper Mining Company)

FIG. 16. Flowsheet of Great Falls Refinery.

with lead heating coils through which 30-pound steam was passed. Since 1930, direct-fired evaporators have been used for this purpose.

The basic precipitate of antimony as sulfate and oxychloride carries with it arsenic and bismuth (probably as basic sulfates). Solubility of antimony in the electrolyte is very limited, and if enough antimony is present most of the arsenic and bismuth will be thrown into the anode mud; if there is little antimony present, however, the bulk of the arsenic remains in the electrolyte. Table 5 shows that in 1931 and 1932 the arsenic content of the anodes decreased while the antimony content remained constant. During 1930 the purification plant was operated continuously in order to hold down the arsenic content of the electrolyte. During 1931 and 1932 the purification plant was operated intermittently, and only for short periods, to control the acid content of the electrolyte. In 1933 the arsenic content increased and the antimony content diminished so that it was necessary to resume continuous operation of the purification plant

The 12 insoluble anode tanks which treat the mother liquor from the first crystallizing tanks are arranged in four cascades of three tanks each; antimonial lead is used for anodes and copper starting sheets as cathodes. The bulk of the copper is deposited in the first tank as impure cathodes, which are returned to the anode furnaces. The deposit in the other tanks is a sludge containing most of the copper and arsenic together with some silver and other metals; this sludge is sent back to the smelting furnaces at Anaconda.

If the tank-room solutions are low in iron and nickel the spent electrolyte from the insoluble-anode cells is returned directly to the main circuit. If nickel and iron are too high the solution is evaporated and a sludge of iron and nickel sulfates crystallized out; the restored acid then returns to the tank room. The sludge produced contains about 12 8 per cent nickel and 3.9 per cent iron; it is usually wasted, but it can be treated to remove the contained nickel if this becomes profitable.

Montreal East.[11] The electrolytic copper refinery of Canadian Copper Refiners, Ltd., is located at Montreal East, Quebec. The plant is designed for the production of 12,500,000 pounds of refined copper per month, and provision is made for doubling the plant capacity (Fig. 17). Crude copper comes principally from the Noranda and Flin Flon smelters.

Electrical Plant. Power is purchased from the Montreal Light, Heat, and Power, Consolidated, in the form of three-phase 60-cycle

[11] McKnight, H. S , Montreal East Plant of Canadian Copper Refiners, Limited: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 352, 1933.

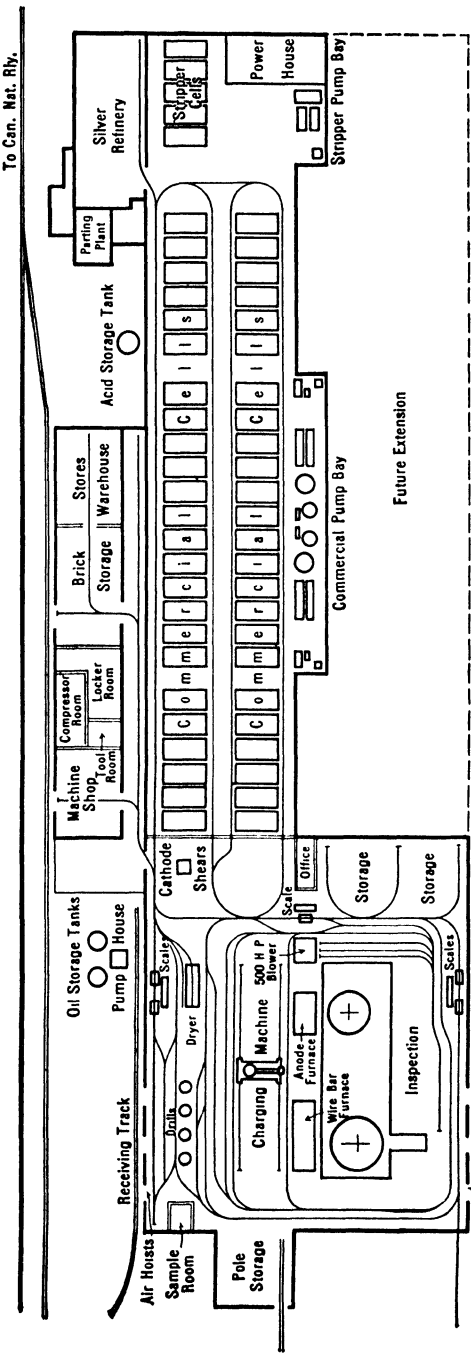
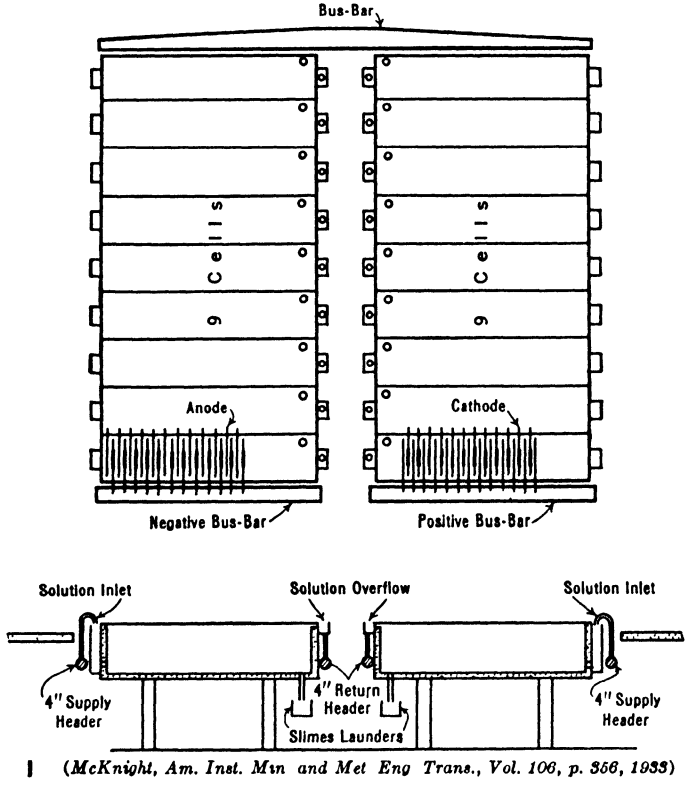


FIG. 17 General Layout of Plant at Montreal East Refinery.

(*McKnight, Am Inst Min. and Met. Eng. Trans., Vol. 106, p. 352, 1933*)

current at 12,000 volts. The incoming voltage is reduced to 2300 volts and 550 volts by two banks of outdoor transformers. The power for the main electrolytic circuit is supplied by three motor-generator sets consisting of 675-kilowatt 135- to 12-volt 5000-ampere direct-current generators driven by 980-horsepower 2300-volt synchronous motors. These sets operate in parallel and supply 15,000 amperes of current to



(*McKnight, Am. Inst. Min and Met Eng Trans., Vol. 106, p. 366, 1933*)

FIG. 18. Cell Tiers, Montreal East Refinery.

the circuit. The power for the purification circuit is supplied by a 125-kilowatt 25- to 3-volt 5000-ampere direct-current generator driven by a 225-horsepower 2300-volt synchronous motor.

About 300 tons of copper was used in the bus system, which is about 3500 feet long. The main runs under the working floor are made up of eight 10- by ½-inch copper bars spaced ½ inch apart and in parallel. The tank buses are of different sizes and shapes, the largest being 17 inches wide, 3 inches thick, and 19 feet long. The current is transmitted from bus to anode and from cathode to bus through knife-edge

contacts. These contacts consist of triangular sections of copper arc-welded to the 3-inch busbars.

The normal bus current is the full 15,000 amperes, and 15,000 amperes flows through each cell in the system, as all cells are in series in one electrical circuit. Cathode current density is 17 amperes per square foot, and the voltage drop per cell about 0.212 volt. Current density in the bus is approximately 375 amperes per square inch.

Tanks. The tanks are rather large, being 16 feet 7 inches long, 3 feet 7½ inches wide, and 4 feet 1½ inches deep, inside dimensions. They are built of reinforced concrete cast in place and lined with 6 per cent antimonial lead. Each tank holds 42 anodes spaced at 4½-inch centers and 43 starting sheets. The cells are supported independently of the working floor by concrete columns of such an elevation that the tops of the cells are 18 inches above the working floor. The columns are capped with a glass plate 1½ inches thick, a rubber sheet, and a lead shield to insulate the cells from the ground. The cell bottoms are 7 feet above the basement floor to provide ample space for inspection and headroom for solution lines and slimes launders.

There are 468 tanks — 432 commercial and 36 stripper tanks — arranged in *tiers* of 9 cells each and grouped in *sections* of two tiers or 18 cells. There are 26 such tiers, and all the cells are connected in series. The anodes and cathodes in any one tier are directly connected by means of "Baltimore grooves" cast in the top of one lug of each anode and accommodating the adjacent cathode bar. The electrical connections in a section are shown in Figure 18.

Anodes. About 60 per cent of the anodes come from the Noranda smelter already cast. The remainder are cast at the plant from Hudson Bay (Flin Flon) blister. The two lots have slightly different compositions, as may be seen in Table 7.

TABLE 7[a]

TYPICAL ANALYSES OF ANODES AT MONTREAL EAST[b]

	Cu	Ag	Au	As	Sb	Se + Te	Pb	Ni	Fe	S
Noranda	99 41	17 09	8 058	0 0024	0 0023	0 264	0.0016	0 0293	0.0065	0.0140
Domestic	99 49	31 40	4 577	0 0126	0 0073	0.183	0.0236	0.0143	0.0083	0.0155

[a] McKnight, H. S., op cit. p 355.
[b] Au and Ag in ounces per ton, all others in percentage.

Weight, 700 pounds.
Size, 36 by 36 inches on face; 1½ inches thick.
Life, 33 days — produce 2 crops of cathodes.
Anode scrap, 14 per cent.
Mode of suspension: cast lugs; Baltimore groove.

Cathodes. The starting sheets are 37½ inches square — slightly larger than the anode surface; these are deposited in stripper cells using anodes weighing 770 pounds (slightly larger than the anodes in the commercial cells). Each cathode weighs about 300 pounds and is removed at the end of 16 days. Two crops of cathodes are made from each anode, and when the first set of cathodes is removed the anode spacing is closed up to 4 inches and five additional anodes are added to each cell. Starting sheets are supported by a single large loop at the center.

Electrolyte. The electrolyte flows by gravity from head tanks through the electrolytic cell to sump tanks in the pump bay located below the basement floor. It is then elevated by centrifugal pumps to the head tanks, where it is heated by steam coils. The temperature is maintained at 140° F (60° C) and the flow through each cell is 4.5 to 5 gallons per minute. Commercial and stripper electrolytes are separate.

Circulation within the cell is from bottom to top (Fig. 18). The inlet to each cell is of rubber to prevent loss of current through the solution lines. The overflow line is broken by an air gap in a lead "boot."

TABLE 8[a]

TYPICAL ANALYSIS OF ELECTROLYTES AT MONTREAL EAST

Electrolyte	Temp (°F)	Deg Bé at 60° F	Free H_2SO_4 (%)	Cu (%)	Specific Gravity	Cl (%)
Stripper	140	22.50	12.96	3.16	1.19	0.00075
Commercial	140	27.30	16 60	3.20	1.24	0.00019

[a] McKnight, H. S., op cit., p 357.

Anode Mud. Slimes are removed at the end of the first cathode run, but the anodes are not moved. At the end of the second run the anode scrap is removed and the tanks are completely emptied and cleaned. The clear electrolyte is pumped from the cell to within a few inches of the bottom; then the plug is pulled and the slime and remaining electrolyte are conducted through lead-lined launders to tanks from which they are pumped to storage tanks in the silver refinery.

These slime-bearing solutions are pumped to a Dorr thickener, and the overflow solutions are returned through a settler to the tank room. The thickened slimes are filtered on an Oliver filter, roasted for 1½ hours at 500° to 650° F (260° to 343° C), and then leached for 3 hours

in 20 per cent acid solution made up chiefly of foul electrolyte from the tank room. The leached slimes are washed and filtered and delivered to the doré furnace.

TABLE 9[a]

TYPICAL ANALYSES OF SLIMES AT MONTREAL EAST, IN PER CENT

Slimes	Cu	Ag	Au	As	Sb	Se	Te	Pb	Ni	Fe	SO_4	SiO_2
Raw	45 0	8 0	2 5	0 120	0 222	24 61	3 77	1 91	0 037	0 338	6 21	2 18
Roasted	42 0	7 5	2 3	0 083	0 107	19 17	3.18	3.77	0 014	0 358	5 61	2 17
Leached	3 8	31 0	9 3	0 076	0 242	24.62	2.43	10 16	0.006	1 030	5.38	6 56

[a] McKnight, H S, op cit, p 365

The decanted leach solutions are filtered and passed through eight electrolyte cells employing lead anodes and lead cathodes. Practically all of the copper and selenium is removed in these cells in the form of a copper-selenium sludge. These solutions are then cemented with iron to remove the last traces of copper and are then discarded. The copper-selenium sludges are stored for possible future treatment to remove the selenium.

The leached slimes, containing about 25 per cent moisture, are treated in the doré furnace with the necessary fluxes of soda and niter. The first "scoria" or slags from the doré furnace are returned to the anode furnace for recovery of gold, silver, and copper contents. The soda and niter slags are leached with water, and the residue is returned to the doré furnace.

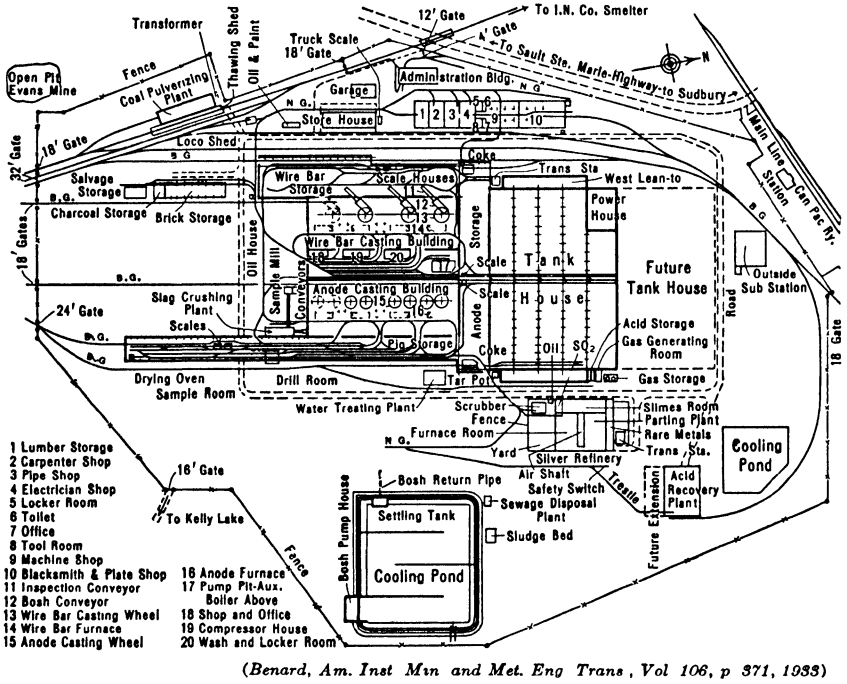
The doré bullion is cast into anodes and refined in 10 Moebius cells. Cathode silver is melted and cast into 1000-ounce bars of a fineness of 999+. The gold slime is boiled with concentrated sulfuric acid to remove silver and is then cast directly in bars that are 992+ fine.

Gases from the doré furnace and roasting furnace pass through cooling flues, a scrubber system, and a Cottrell treater. The Cottrell treater is of the pipe type and is made entirely of lead and lead-covered steel.

Ontario Refining Company.[12] The electrolytic copper refinery at Copper Cliff, Ontario, treats the crude copper from the smelting of the nickel-copper ores of the Sudbury district. The refinery has a capacity of 20,000,000 pounds of refined copper per month. The anodes contain larger amounts of nickel than that found at most refineries.

[12] Benard, Frederic, Electrolytic Copper Refinery of Ontario Refining Company, Ltd., at Copper Clift, Ontario: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 369, 1933.

Electrical Plant. Part of the power required is purchased, and part of it is generated by a 2500 kva turbogenerator at 2300 volts; the turbogenerator is operated by steam from waste-heat boilers and a pulverized coal-fired auxiliary boiler. Power is purchased at 30,000 volts which is stepped down to 2300 volts in a bank of three 2000-kilovolt-ampere transformers, with a fourth as a spare. Three motor-generator sets supply the electrolytic load; each consists of one



(*Benard, Am. Inst Min and Met. Eng Trans, Vol 106, p 371, 1933*)

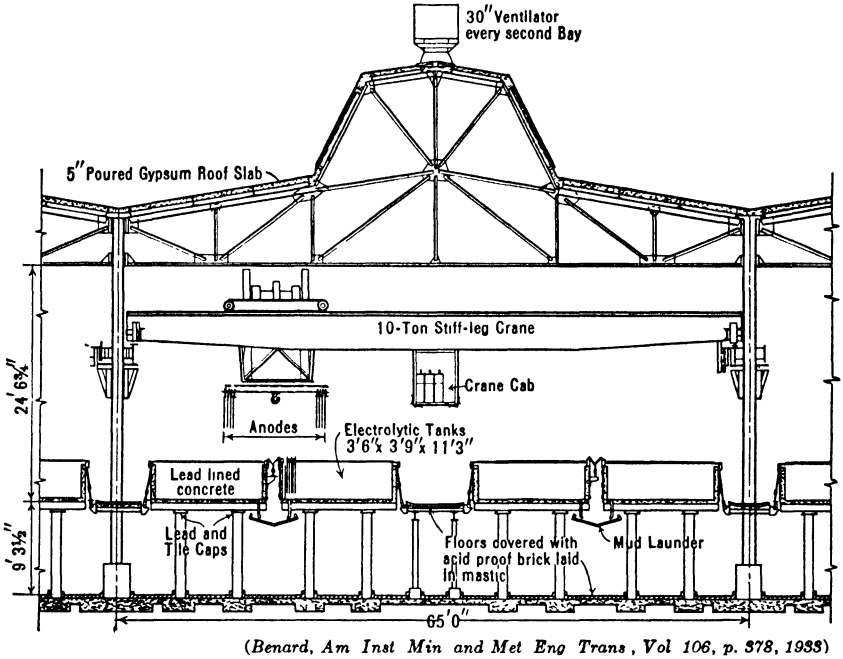
FIG. 19. General Plan of Refinery of Ontario Refining Company.

2880-horsepower 500-revolutions per minute synchronous motor driving two 6000-ampere 80- to 160-volt direct-current generators, and each set is rated at 2500 kilovolt-amperes. The third set is a spare and may be used interchangeably with the other two.

Current density is about 15 amperes per square foot with a voltage drop of 0.180 to 0.200 volt per cell. Current efficiency is 97 to 98 per cent.

Tanks. The tank house contains 1230 concrete tanks lined with 6 per cent antimonial lead. These are laid out in 32 sections of 38 tanks each, with two liberator units of six tanks each and two full-sized experimental tanks. The tanks are 11 feet 3 inches long, 3 feet 6 inches wide, and 3 feet 9½ inches deep, inside dimensions. The tanks are

supported by concrete piers with a 2-inch slab of vitrified tile and a lead cap between the pier and the tank sill; the tile is for electrical insulation from the ground and the lead cap for the protection of the pier from drip. There is 9½ feet of headroom between the basement floor and the tank bottoms.



(*Benard, Am Inst Min and Met Eng Trans, Vol 106, p. 378, 1933*)

FIG. 20. Cross-Section Through Tank House, Ontario Refining Company.

The tanks are arranged in two electrical circuits, which cross at right angles the two solution circuits. A current of 10,500 amperes passes through each electrical circuit. The tanks are connected by the Walker multiple system of contacts. Each commercial tank contains 38 anodes and 39 cathodes; stripper tanks contain 31 anodes, 30 mother blanks, and 2 end sheets. There are 76 stripper tanks (2 sections) and 1140 commercial tanks.

Anodes. The anodes are cast from incoming blister cakes, in two 36-foot Walker casting wheels.

Weight, 530 pounds.
Size, 36 by 36 inches; 1¼ inches thick.
Life, 28 days — produce two crops of cathodes.
Anode scrap, 12 per cent.
Mode of suspension, cast lugs.

Cathodes. Starting sheets are stripped every 24 hours and weigh 10 pounds each. Loops 4 inches wide of the same material are punched into them by electrically driven double-punch machines. Finished cathodes weigh 240 pounds and are pulled at the end of 14 days.

Electrolyte. The electrolyte is held at about 3 per cent copper and 13 per cent free acid. The solution is circulated at the rate of 2½ to 3 gallons per minute and is heated to 150° F (65° C). Glue, oil, and bindarine are added in small quantities to improve the toughness and smoothness of the cathode deposit. Circulation through the cells is from bottom to top.

Anode Mud. The analysis of the anode slimes are given below. The gold and silver assays are omitted because these are rather variable owing to the variation in custom material treated.

	Per Cent		Per Cent
Copper	24 70	Silica	0.18
Nickel	19 80	Lead	1.51
Selenium	15 03	Arsenic	0 24
Tellurium	3 61	Antimony	0 32
Iron	0 40	SO_4	5 48

Note the abnormally high nickel content. Every effort is made to throw as much of the nickel as possible into the electrolyte instead of the slime.

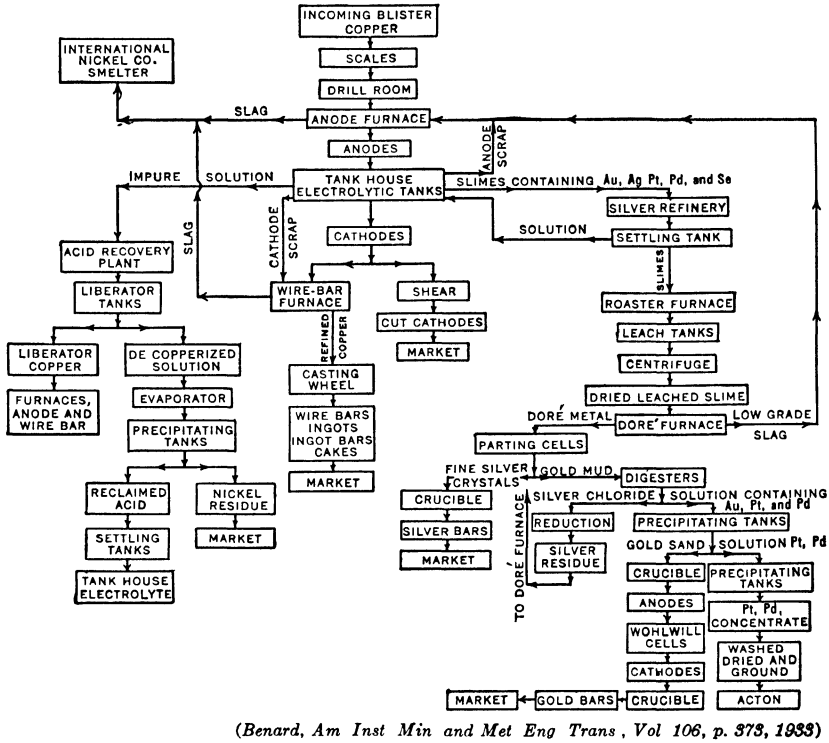
Slimes are roasted and leached to remove copper and nickel; this is done by mixing the raw slimes with concentrated sulfuric acid and roasting in a reverberatory furnace with a sectional cast iron bottom. The roasted slimes are given one leach with 10 per cent sulfuric acid and one water leach. The nickel and copper sulfate solution that results is treated with copper sludge to precipitate any selenium, tellurium, or silver, and returned to the tank house. The precipitate joins the regular slimes.

The treated slimes are refined to doré metal in an oil-fired reverberatory furnace which treats about 14,000 pounds of treated slime containing 20 per cent moisture. The slimes are mixed with a flux of 1 per cent sand and 2 per cent fluorspar, and slag is skimmed before the furnace is fully charged. After the charge is melted and the scoria slag skimmed, the matte is refined to doré, using soda ash and niter. The scoria slag is returned to the anode furnaces. Soda-niter slags are leached with water; the residue is returned to the doré furnace, and the leach liquor is pumped to the selenium plant.

The doré bullion is cast into anodes and refined in 40 Balbach

(Thum) cells. The gold slime is digested with aqua regia and the gold reprecipitated with ferrous chloride. This gold is then melted, cast into anodes, and refined in 6 Wohlwill cells. The solution remaining from the aqua regia leach is cemented on scrap iron to precipitate the platinum metals, and the platinum residues are shipped to a refinery in Acton, England.

The refinery also includes a plant for the recovery of selenium and tellurium from furnace slags and flue dusts.



(Benard, Am Inst Min and Met Eng Trans, Vol 106, p. 373, 1933)

FIG. 21. Flowsheet, Ontario Refining Company.

Purification of the Electrolyte. The principal impurity is nickel, and to remove this impurity a given amount of electrolyte must be removed from the tank house each day. Nickel markedly increases the electrical resistance of the electrolyte. By removing the nickel, the other impurities are easily held below the required limits.

The first step is to pass the solution through Pyne-Green segregating tanks, which have a bottom inflow, bottom outflow, and a small orifice near the top through which passes less than 10 per cent of the total flow. By means of the restricted circulation at the top, a segre-

gation takes place, and the upper layers of solution are depleted of their copper ions, the copper content being reduced from 3 to 1 per cent and the nickel and acid content being somewhat increased. This " segregated " solution is then delivered by automatic air lifts to the acid recovery plant.

The segregated solution is first passed through a nest of 10 tanks carrying 5000 amperes and using 25 lead anodes and 24 regular copper starting sheets. These tanks reduce the copper content from 12 grams per liter (1 per cent) to 8 grams per liter and produce commercial cathodes which go to the wirebar furnaces.

The same solution is then passed to 10 similar tanks which reduce the copper to 0.2 gram per liter and produce impure cathodes which go either to the anode furnaces or to the silver refinery for cementation purposes.

The decopperized solution is then evaporated from 23° Baumé to about 60° Baumé; nickel and iron residues are crystallized and precipitated, and the clear acid (54° Baumé) is returned to the tank house.

Phelps Dodge Refinery.[13] The refinery of the Nichols Copper Company at Laurel Hill, New York (now known as the Phelps Dodge Refinery), utilizes the *Nichols system* of series refining using cast anodes, and we shall present a description of this plant to illustrate the series system.

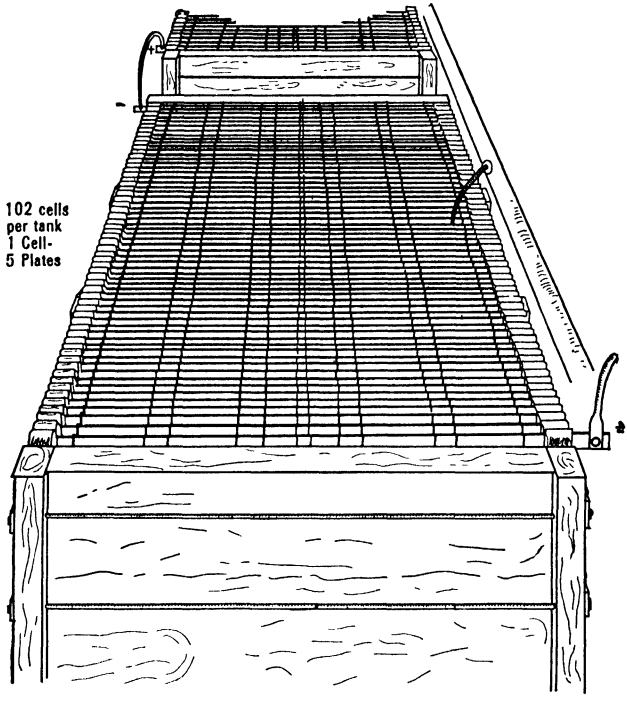
One tank room of the Baltimore plant of the American Smelting and Refining Company utilizes the *Hayden* series system in which the impure electrodes are rolled rather than cast. Certain impurities make it difficult to roll the copper properly, and the Hayden system is thus restricted to the refining of lean high-grade bullion. This restriction does not apply to the Nichols system. The Laurel Hill plant treats a wide variety of crude copper which is of the same type as that treated in refineries using the multiple system. This plant has a capacity of about 35,000,000 pounds of copper per month.

Tanks. The tanks used are either of wood or concrete construction and measure 16 feet long, 5 feet 4 inches wide, and 5 feet 2 inches deep, inside dimensions. The bottom lining is made of blown oil, asphalt, silica sand, and powdered silica; the side lining is a ¾-inch layer of blown oil mopped on in successive layers and burned on with a hot iron. The tank is capped with stationary wooden spacing blocks on each side forming slots into which the 102 iron suspension bars can fit; each bar carries 5 anodes (Fig. 23), and this group of 5 electrodes is known as a *cell.* Each tank, when loaded, contains 510 regular

[13] Harloff, C. S., and Johnson, H. F., The Nichols System of Electrolytic Copper Refining· Am. Inst. Min. & Met. Trans., Vol. 106, p. 398, 1933.

anodes in 102 cells; the charge amounts to 56,000 pounds of metal and 22,000 pounds of electrolyte per tank. The tanks are electrically connected in groups of about 44 in two parallel lines of 22 each (all groups are not uniform), and there are 417 tanks in the tank house. All are " commercial " cells, of course; starting sheets and " stripper " cells are not needed.

Tanks are loaded and unloaded by 5-ton cranes which will pick up 17 bars (85 anodes) at a load, thus requiring six loads per tank.



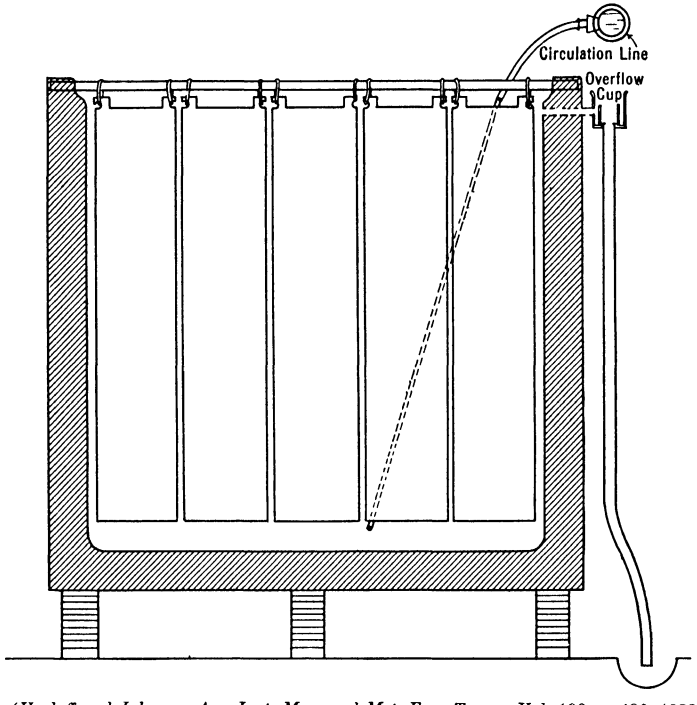
(Harloff and Johnson, Am. Inst. Min and Met Eng Trans., Vol 106, p. 401, 1933)

FIG. 22. Plan View of Loaded Series Tank Showing Set-up, Spacing Blocks, and Circulation Inlet.

A copper busbar 2½ inches by ¾ inch connected by a copper cable to the negative bus of the preceding tank serves to bring current into the tank at the positive end. Five 150-pound anodes are hung from the positive busbar, and here the current is introduced into the tank. At the negative end is a similar busbar from which are suspended five 45-pound depositing cathodes. The remaining electrodes in the tank are suspended from iron bars by means of copper links (Fig. 23). These electrodes weigh about 110 pounds each. Each of these 110-

pound electrodes serves as a *bipolar* or intermediate electrode, receiving a deposit of pure copper on one side while impure copper is being dissolved from the opposite side.

Electrodes. The electrodes are called *anodes* before they are put into the tank and *cathodes* after they are removed. The 110-pound anodes, which are 56 by 12 inches by $\frac{3}{16}$ inch with two ears forming the top part, are carefully cast by hand. The ears are subsequently punched out to form suspension lugs (Fig. 23). These anodes are suspended from steel hanger bars by acid-resistant cast links of copper alloy.



(*Harloff and Johnson, Am. Inst Min. and Met Eng Trans., Vol 106, p 402, 1933*)

FIG. 23. Elevation of Series Electrolytic Tank Showing Spacing of Plates, Circulation Glass, and Overflow.

After the casting and partial cooling, the warm anodes are punched, carefully straightened, assembled on the suspension bars, and spray-painted with a hot (180° F) 25 per cent solution of sodium resinate on the side which is to receive the pure copper deposit. This forms a cleavage zone that facilitates the removal of anode scrap without materially increasing the electrical resistance of the depositing surface.

Anodes are spaced $1\frac{13}{16}$ inches center to center with a 1-inch clearance on the side of the tank and ½ inch between adjacent anodes on the same suspension bar. New anodes are loaded into an empty tank and carefully adjusted so that all anodes are suspended properly. Electrolyte is then fed into the tank by a 2½-inch hose from a valve on the main circulating line until about 6 inches of the anodes is submerged. The cut-out bar is then disconnected, and current flows through the tank while the remainder of the electrolyte is added. This procedure is adopted in order to put an initial cathode deposit on the resinous paint as soon as possible; if this is not done the paint will dissolve in the hot electrolyte and the cathode deposit will cling to the anode so tightly that the anode scrap cannot be removed.

The current density will range from 13 to 26 amperes per square foot, depending upon the production desired; accordingly the tank cycle will range from 13 to 34 days. The cycle is so adjusted that when the cathodes are removed only a thin sheet of the original anode remains. The anode scrap is then stripped by hand from the cathode deposit and returned to the anode furnaces. Anode scrap amounts to 6 or 7 per cent of the original anode weight.

Electrolyte. The copper content of the electrolyte is maintained at 2.75 to 2 85 per cent copper and 17.5 to 18.5 per cent free acid. Part of the Cu_2O in the anodes is chemically dissolved in the electrolyte to replenish the copper loss, and by careful regulation it is possible to avoid the use of insoluble-anode cells to plate out excess copper from the electrolyte. A certain amount of the electrolyte is withdrawn and sent to the copper sulfate plant, and this keeps the impurities within the proper limits.

Cathodes of the desired purity have been produced by using an electrolyte containing up to 1.0 per cent nickel, 0.35 per cent arsenic, 0 06 per cent antimony, and 0.05 per cent iron. Sodium chloride is added daily to keep the chlorine content of the solution at 0 0003 to 0 0005 per cent. Glue and Goulac are added to improve the physical characteristics of the cathode deposit; about an ounce of glue and a pound of Goulac are added for every 50 tons of cathodes deposited.

The electrolyte is heated to 122° F (50° C) and is circulated through the tanks at about 3 5 gallons per minute. A glass tube introduces the electrolyte at a point about 5 to 8 inches above the tank bottom, and the solution overflows at the top of the tank.

It is necessary to add sulfuric acid and water to the electrolyte to replace the acid lost by chemical action and the water lost by evaporation. Part of the replacement water comes from that used to wash the cathode deposits.

Anode Mud. The anode mud is cleaned out of each cell whenever the cathodes are withdrawn. This will amount to about 0.8 per cent of the anode weight, depending on the purity of the anodes. This is screened and washed, roasted, and leached to remove the copper. The residue is shipped to another plant for treatment. The leach liquor is treated in the copper sulfate plant.

CHAPTER IX

HYDROMETALLURGY

INTRODUCTION

In general the *hydrometallurgy* of copper refers to those processes by which copper-bearing material is *leached* with a solvent to dissolve the copper, the solution being then separated from the residual solid or *tailing* and the copper precipitated from it. Solutions used have always been aqueous solutions, as the name *hydrometallurgy* suggests.

Of all the methods employed for recovering copper, leaching is one of the oldest, and it is the most complex of all, judging from the large number of experimental, semi-commercial, and commercial processes that have been developed. These include a wide variety of solvents and precipitation methods and a number of different methods of purifying solutions and mechanical handling of materials.[1,2] Leaching methods have been used on ores (both mined ore and ore still in place) on concentrates, calcines, mattes, and other products.

We shall find it necessary to confine our discussion largely to those methods which are in commercial use today. It is to be noted that leaching processes depend upon the nature of the ore being treated in an even greater degree than pyrometallurgical treatment. Except for relatively minor differences, it is possible to discuss copper roasting, smelting, converting, and refining in a general way and still not deviate too much from the practice found in special cases. Hydrometallurgical processes, however, differ from one another to such an extent that it is difficult to give a general discussion that will include all processes.

Crude ore in which the copper occurs as oxidized minerals (or oxidized minerals plus some sulfides) and some native copper tailings and ores constitute the two large classes of materials which are subjected to leaching. The leaching agents are generally either (1) sulfuric acid or (2) ammonia. The most widely used method of precipitating the dissolved copper is by electrolysis; the only other method of importance is cementation on scrap iron.

[1] Hofman, H. O., and Hayward, C. R., Metallurgy of Copper: McGraw-Hill Book Co., New York, 1924.

[2] Greenawalt, W. E., The Hydrometallurgy of Copper: McGraw-Hill Book Co., New York, 1912.

We shall consider the question of electrolysis later in the chapter, but at this point we shall mention the fact that this process differs from the electrolytic refining of copper in many respects. The recovery of copper by electrolysis is often called *electrowinning* as distinguished from *electrorefining* discussed in the preceding chapter. To the combination of leaching and electrolysis the term *electro-hydrometallurgy* is often applied.

General Considerations. In any leaching operations there are three important steps:

1. Bringing the solvent in contact with the material to be leached to permit dissolution of the metal.
2. Separating the *charged* or *pregnant* solution from the solid residue.
3. Precipitating the metal from the solution. As a general rule these follow in the order indicated, but sometimes the order of the last two are reversed, i.e., copper is precipitated while still in the ore-water mixture and is then separated from the pulp by flotation.

The *solvent* used for leaching must have the following characteristics:

1. It must be cheap and available in adequate quantities.
2. It must have a selective action, i.e., it should attack the ore minerals but not the gangue minerals.
3. In general it must be effective when used in cold dilute solutions.
4. If possible it should be regenerated by the precipitation operation.

These characteristics are modified by the nature of the material being leached. It is possible to treat roasted anode mud by boiling in concentrated sulfuric acid, but this method would hardly be applicable to the treatment of a 1 per cent copper ore — this would perhaps be treated by a prolonged leaching with cold dilute acid. Aside from the expense involved, the boiling sulfuric acid would probably not show a selective action with reference to either the ore or the leaching tanks.

The *leaching method* employed will also depend upon the nature of the ore involved, and in general there are two:

1. *Percolation* or *sand leaching.*
2. *Agitation* or *slime leaching.*

The terms *sand* and *slime leaching* are used principally in the cyanide leaching of gold and silver ores; sand (usually fairly coarse material) will allow solution to flow or *percolate* freely through the interstices, but slime (fine material) will pack in a vat or tank and impede the circulation of the liquid. Sands may be leached by simply allowing the liquid to stand on the material for a given time, but slimes require that the slime-liquid pulp be kept in agitation during the

leaching period to prevent the solids from settling and packing. We shall find applications of both methods in the leaching of copper ores.

The *precipitation method* used may be either (1) electrolytic or (2) chemical. Electrolytic precipitation is expensive but it yields a pure copper equal in grade to electrorefined copper, and it regenerates the sulfuric acid used as a solvent. Electrolytic precipitation is not used with ammonia leaching. Chemical precipitation is usually cheaper than electrolysis and can be used on some solutions which contain too little copper for satisfactory electrolysis. It produces an impure precipitate which must usually undergo further smelting and refining.

ORES SUITABLE FOR LEACHING

Hydrometallurgy has many advantages over pyrometallurgy — it generally requires no fuel or expensive furnaces, and often the principal expense is for the reagents used in the solvent. The principal disadvantage is simply the fact that many copper ores do not respond to leaching methods well enough so that the hydrometallurgical processes can compete with pyrometallurgy. Today only a rather small class of ores is being treated by leaching, but eventually processes may be developed which will widen the scope of leaching methods as applied to copper ores.

Commercial leaching plants operating today treat ores in which the copper minerals are (1) oxidized (soluble in water or dilute sulfuric acid), (2) partly oxidized and partly sulfide (sulfides are soluble in acid ferric sulfate), or (3) native copper or carbonate minerals (soluble in ammoniacal solutions). The choice of solvent to be used and purification and precipitation methods depends on a number of factors; among the most important are:

1. **Solubility of the Ore Minerals.** The only practical solvent for copper is an ammoniacal solution; ammonia can also be used to dissolve carbonates. Chalcanthite ($CuSO_4 \cdot 5H_2O$) is soluble in water; other oxidized copper minerals are soluble in dilute acid. Sulfide minerals can be dissolved in acidified ferric sulfate solution.

2. **Solubility of the Gangue Minerals.** The gangue must be only slightly soluble in the solvent to avoid the use of excess reagent and to prevent serious fouling of the solution. Thus, for example, ores with a gangue of dolomite or limestone must be leached with ammonia because these substances are very soluble in acids.

3. **Nature of the Copper Minerals.** Copper in the form of chalcanthite dissolves without consumption of acid and actually generates free acid in the circuit when electrolytic precipitation is used. Oxidized

minerals dissolve in sulfuric acid, and the acid consumed is regenerated by electrolytic precipitation.

4. Soluble Impurities in Gangue and Ore Minerals. When copper is to be precipitated electrolytically the impurities in the solution must be carefully controlled by means of a purification system. The impurities which are most harmful to the electrolysis are:

(*a*) *Chlorine Ions.* Chlorine ions are usually found when the ore contains atacamite ($CuCl_2 \cdot 3Cu(OH)_2$).

(*b*) *Nitrate Ions.* Nitrate ions are formed from soluble nitrates in the ore.

(*c*) *Iron.* The concentration of both ferric and ferrous iron is important.

(*d*) *Molybdenum.*

5. The Per Cent of (*a*) Total Copper, (*b*) Sulfide Copper and (*c*) "Acid Soluble" Copper in the Ore.

SOLVENTS

With the exception of certain solvents used in special processes, e.g., using strong sulfuric acid to leach copper from roasted anode mud, the important leaching agents used on copper ore are water, sulfuric acid, and ammonia; ferric sulfate is of some importance, but it is used with sulfuric acid, and the acid is the principal solvent.

Sulfuric Acid. Acid used for leaching will usually contain 25 to 70 grams of free acid per liter of solution, although this will vary, depending upon the stage of the operation. A given charge of ore will usually be treated with a succession of solvents of different strength. The chemical action of sulfuric acid upon the common oxidized minerals is given below:[3]

Azurite and Malachite. Both azurite and malachite dissolve readily in dilute acid according to the equations

Azurite:

$$Cu_3(OH)_2(CO_3)_2 + 3H_2SO_4 \rightarrow 3CuSO_4 + 2CO_2 + 4H_2O$$

Malachite:

$$Cu_2(OH)_2CO_3 + 2H_2SO_4 \rightarrow 2CuSO_4 + CO_2 + 3H_2O$$

Tenorite (melaconite). Tenorite (CuO) dissolves readily in dilute acid according to the equation

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

[3] Sullivan, J. D., Chemical and Physical Features of Copper Leaching: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 515, 1933.

Cuprite. Cuprite (Cu_2O) does not dissolve as readily as tenorite, and in a solution containing only sulfuric acid only half of the copper goes into solution:

$$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu + H_2O$$

If the solution contains an oxidizing agent, the precipitated copper will oxidize and then dissolve as $CuSO_4$. Oxygen from the air or dissolved ferric sulfate will serve to oxidize the copper and permit complete dissolution; ferric sulfate is much more active than oxygen from the air dissolved in the solution.

Chrysocolla. The mineral chrysocolla is easily dissolved in sulfuric acid with the formation of $CuSO_4$ and liberation of silica:

$$CuSiO_3 \cdot 2H_2O + H_2SO_4 \rightarrow CuSO_4 + SiO_2 + 3H_2O$$

The term " chrysocolla " is properly applied only to the mineral whose composition is given above. The name " chrysocolla " is often given to all copper silicates, and it is stated that some forms of chrysocolla are soluble in sulfuric acid whereas other forms are not. True chrysocolla is readily soluble; *dioptase,* another copper silicate, dissolves much more slowly than chrysocolla. Other minor silicates of copper are *bisbeeite, cornuite* (the amorphous equivalent of crystalline chrysocolla), *plancheite,* and *shattuckite*; the chemical properties of these minerals are not definitely known.

Brochantite. Brochantite is a basic sulfate, the most important mineral at Chuquicamata, Chile, and is readily soluble in sulfuric acid.

$$Cu_4(OH)_6SO_4 + 3H_2SO_4 \rightarrow 4CuSO_4 + 6H_2O$$

The sulfate *chalcanthite* ($CuSO_4 \cdot 5H_2O$) is soluble in water.

Atacamite. The basic chloride, atacamite, dissolves in sulfuric acid according to the reaction

$$Cu_2Cl(OH)_3 + 2H_2SO_4 \rightarrow 2CuSO_4 + HCl + 3H_2O$$

Note that this dissolution adds chlorine ions to the solution.

These are the important reactions for the dissolution of copper minerals in sulfuric acid, and they all involve simple double decomposition with the formation of soluble $CuSO_4$. Other minerals can be dissolved by the combined action of sulfuric acid plus an oxidizing agent; these we shall consider later.

In addition to the copper minerals, the various oxides, silicates, and carbonates in the gangue are attacked by the acid to form soluble sulfates of iron, aluminum, magnesium, etc. The amount and composition of these dissolved impurities depend upon the nature of the

ore; they result in increased consumption of acid and they contaminate the solution.

Water. The only copper mineral soluble in water is chalcanthite, $CuSO_4 \cdot 5H_2O$. This is not a common mineral in natural ores, but it is formed by slow oxidation and weathering of sulfide ores, and hence is quite important.

When copper sulfate solutions are electrolyzed using an insoluble anode, one mol of H_2SO_4 is generated for each mol of $CuSO_4$ decomposed. Hence such sulfates as chalcanthite and brochantite are *acid-forming* minerals because less acid is required to dissolve them (none for chalcanthite) than is generated in the electrolytic cells when the dissolved copper sulfate is decomposed.

Acid Ferric Sulfate. The combination of H_2SO_4 plus an oxidizing agent will dissolve many copper minerals which are not soluble in acid alone. The most common oxidizing agent is ferric sulfate, and this is not added as a reagent but is formed by the dissolution of iron-bearing minerals in the ore. The essential reaction involved is the oxidation of material by the ferric sulfate which is itself reduced to ferrous sulfate.

Cuprite. Sulfuric acid alone, as we have noted, attacks cuprite to form Cu and $CuSO_4$, thus putting only half of the copper in a soluble form. Ferric sulfate will attack the metallic copper:

$$Cu + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4$$

Ferric sulfate also assists the reaction

$$Cu_2O + H_2SO_4 \rightarrow Cu + CuSO_4 + H_2O$$

because the precipitated copper is dissolved before it can form an impervious coating on the outside of the cuprite particle.

Chalcocite. Chalcocite will dissolve in ferric sulfate according to the reaction

$$Cu_2S + 2Fe_2(SO_4)_3 \rightarrow 2CuSO_4 + 4FeSO_4 + S$$

Chalcocite dissolves in two distinct stages; at first it dissolves rather rapidly until about half the copper is gone (atomic ratio Cu : S = 0.9 : 1) after which the dissolution of copper proceeds more slowly, indicating that the previous reaction may take place in two stages:[4]

$$Cu_2S + Fe_2(SO_4)_3 \rightarrow CuS + CuSO_4 + 2FeSO_4$$
$$CuS + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 + S$$

[4] Sullivan, J. D., op. cit., p. 522.

The sulfur liberated when chalcocite is leached remains behind as a solid; completely leached chalcocite appears as porous lumps of sulfur of about the same size and shape as the original chalcocite particles, but these will dissolve almost completely in carbon disulfide (a solvent for elemental sulfur). Aerated sulfuric acid has only a very slight solvent effect on chalcocite, and it appears that the oxidation of chalcocite by "weathering" or natural agencies is due to the presence of ferric salts.[5]

Chalcocite is the most significant sulfide as far as leaching operations are concerned because it is associated with the oxidized copper minerals in many of the commercially important deposits.

Bornite. Bornite (Cu_5FeS_4) responds to an acid ferric sulfate leach in much the same way as chalcocite, and the copper is dissolved at about the same rate.

Covellite. The reaction given for the dissolution of this mineral is the same as the second stage in the dissolution of chalcocite:

$$CuS + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 + S$$

Even though this reaction represents the slower stage in the dissolution of chalcocite, the "artificial covellite" dissolves much more rapidly than natural covellite. Covellite dissolves in acid ferric sulfate much less readily than chalcocite or bornite.

Chalcopyrite. Under ordinary conditions this mineral is practically insoluble in acid ferric sulfate solutions unless the ore is first roasted or hot solutions are used. It appears that when dissolution does take place there is no selective dissolution of any part of the molecule; part of the sulfur is oxidized and part is liberated according to the reactions

$$CuFeS_2 + 2Fe_2(SO_4)_3 \rightarrow CuSO_4 + 5FeSO_4 + 2S$$

$$CuFeS_2 + 2Fe_2(SO_4)_3 + 2H_2O + 3O_2 \rightarrow CuSO_4 + 5FeSO_4 + 2H_2SO_4$$

Tetrahedrite, Tennantite, Enargite. Enargite is one of the most difficultly soluble copper minerals; pure samples of tetrahedrite and tennantite are difficult to obtain and there are not many data on the solubility of these two minerals. Apparently tennantite is relatively insoluble in acid ferric sulfate, and tetrahedrite is somewhat more soluble.

Ammonia. Native copper and copper carbonates (malachite and azurite) will dissolve in ammoniacal solutions to give the familiar deep blue solution in which the copper is present as a complex copper-

[5] Sullivan, J. D., op. cit., p. 524.

ammonium ion. The solvent used is ammonium carbonate formed by the dissolution of NH_3 and CO_2 gases in water,

$$2NH_3 + CO_2 + H_2O \rightleftharpoons (NH_4)_2CO_3 \rightleftharpoons 2NH_4^+ + CO_3^{--}$$

and there is an excess of ammonia dissolved in the solution which hydrolyzes to form ammonium hydroxide. Thus the two effective reagents in the solution are ammonium carbonate $(NH_4)_2CO_3$ and ammonium hydroxide NH_4OH.

The natural carbonates azurite and malachite contain copper in the cupric state, and these minerals dissolve directly in the solution to form the soluble cupric ammonium carbonate.

Azurite:

$$Cu_3(OH)_2(CO_3)_2 + (NH_4)_2CO_3 + 10NH_4OH \rightarrow 3Cu(NH_3)_4CO_3 + 12H_2O$$

Malachite:

$$Cu_2(OH)_2CO_3 + (NH_4)_2CO_3 + 6NH_4OH \rightarrow 2Cu(NH_3)_4CO_3 + 8H_2O$$

Native copper is first dissolved by cupric ammonium carbonate in the solution to form cuprous ammonium carbonate; this is a common type of reaction in which cupric salts oxidize metallic copper to form cuprous salts.

$$Cu + Cu(NH_3)_4CO_3 \rightarrow Cu_2(NH_3)_4CO_3$$

After this step the cuprous compound is oxidized to the cupric ammonium carbonate by reaction with oxygen and ammonium carbonate.

$$2Cu_2(NH_3)_4CO_3 + 4(NH_4)_2CO_3 + O_2 \rightarrow 4Cu(NH_3)_4CO_3 + 4H_2O + 2CO_2$$

The oxygen is absorbed from the air by passing the solution through aerating towers. Thus the effective reagents in the dissolution of carbonates are ammonium carbonate plus ammonium hydroxide. Carbonate ions are contributed to the solution from the minerals. In dissolving native copper the effective reagents are ammonium carbonate and oxygen, with cuprous ammonium carbonate as an intermediate product, and no carbonate ions are supplied to the solution. Solutions must be aerated in dissolving native copper, but this is not necessary for dissolving copper carbonates.

The complex ions $Cu(NH_3)_4^{++}$ and $Cu_2(NH_3)_4^{++}$ may not always hold four ammonia groups for each copper ion in these ammonia-carbonate solutions. This does not affect the general nature of the

reactions; for example we may rewrite the last two reactions thus:

$$Cu + Cu(NH_3)_nCO_3 \rightarrow Cu_2(NH_3)_nCO_3$$

$$2Cu_2(NH_3)_nCO_3 + n(NH_4)_2CO_3 + O_2 \rightarrow 4Cu(NH_3)_nCO_3 + nH_2O + (n-2)CO_2$$

The CO_2 formed according to these reactions would immediately react with any excess ammonium hydroxide to form ammonium carbonate.

Ammonia leaching is generally less satisfactory than acid leaching and is practiced only on ores which cannot be leached with acids. These include (1) ores having a carbonate gangue, and (2) tailings or ores of native copper; native copper does not dissolve readily in acid or acid ferric sulfate, so the oxygen-ammonium carbonate solution is the only practical solvent. There have been two ammonia leaching plants on the American Continents — Kennecott in Alaska and Calumet and Hecla in Michigan — and only one elsewhere — Bwana M'Kubwa in Northern Rhodesia. The Calumet and Hecla plant treats reclaimed tailings containing native copper, and the other two plants leach copper carbonate ores. The Kennecott plant has recently been closed down.

Ammonia leaching has one particular advantage in that there is little or no fouling of the leach solutions by dissolved impurities. None of the common elements form ammonium complexes such as those formed by copper, so there is little chance of finding anything in the ores except the copper minerals which will be attacked by these ammoniacal solutions.

Other Solvents.[6] Other solvents which have been employed for dissolution of copper minerals include hydrochloric acid, sulfurous acid, ferrous chloride, and ferric chloride. Some of these have been employed in connection with various types of roasting, and some were designed to dissolve precious metals as well as copper. The solvents that we have described previously, however, are the only ones that are commercially important at the present time.

PREPARATION OF ORE FOR LEACHING

Crushing. Before the ore can be acted upon by the *lixiviant* (leaching solution) it must be crushed fine enough so that the liquid has access to all particles of the copper minerals. For low-grade oxidized ores the ore is crushed in stages to about a ⅜-inch maximum size and is leached directly. These ores are porous enough so that the solvent penetrates the particles and gives satisfactory leaching results.

[6] Hofman, H. O., and Hayward, C. R., op. cit.

Grinding. Low-grade ores (containing about 1 per cent copper) cannot be economically treated by grinding because of the expense involved. Not only would there be the cost of the grinding itself, but the product would contain more "slimes" which would have to be leached by agitation instead of percolation. Higher-grade ore, such as that at Katanga, can be ground in ball or rod mills and then leached in agitators, but most of the leaching ores do not contain copper enough to warrant the additional expense. All the large acid leaching plants except Katanga prepare the ore by fine crushing (⅜ inch) without subsequent grinding.

Classification or Washing. When the crushed or ground ore contains too many slimes for direct percolation leaching it must be separated into sand and slime portions; the washed sand is leached in vats by percolation and the fine slimes are treated in agitators. Whether classification is necessary or not depends to a large extent upon the amount of "natural slimes" in the ore, as the crushing of hard coherent rock to ⅜ inch would not produce enough fines to interfere with percolation.

Roasting. The purpose of roasting a copper ore previous to leaching would be to convert sulfides to water soluble sulfates and acid soluble oxides, but for low-grade copper ores this would be prohibitively expensive. Roasting of high-grade copper concentrate to prepare it for leaching has been tried on experimental and semi-commercial scales only.

Weathering or the natural oxidation of sulfide minerals by the combined action of water, air, and iron salts in the ore is sometimes used as a method of preparation. The ore is crushed and piled in heaps in the open where it is exposed to the action of the atmosphere. The actual leaching takes place concurrently with the weathering, and the water draining from the heaps contains the dissolved copper sulfate. Alternate wetting and drying of the ore speeds up the oxidizing reactions. The water may be added to the heaps from time to time, or the process may depend simply upon natural rainfall.

Weathering is a slow operation and requires that the ore be kept in process for a long time; it is not subject to control or regulation, and it is wasteful unless the heaps are carefully drained and constructed to prevent the solution from seeping into the ground. Its advantages are its cheapness and the fact that most of the copper is oxidized to the water-soluble sulfate.

Occasionally broken ore remaining underground will oxidize so that much of the contained copper can be leached out by passing water through the old stopes and collecting it in the lower levels of the mine.

Mine fires sometimes occur in sulfide ores, and the water circulated through these "fire zones" contains dissolved copper sulfate.

LEACHING METHODS

There are three principal methods of leaching copper ores — (1) leaching in heaps or in underground stopes, (2) leaching in vats by percolation, and (3) leaching by agitation. We shall discuss these briefly here, and the details will be further illustrated in the description of plants which follows:

Heap Leaching. Heap leaching has been practiced at Rio Tinto, Spain, since 1752, at Bisbee, Arizona, and on mine dumps at other places. This method is applicable to low-grade ores which cannot be profitably treated by other methods; the ore must also contain sufficient pyrite to oxidize readily.

The heap is built up so that the solutions readily drain away, and the heaps are built to permit uniform seepage throughout. It is best to build the heaps on a layer of fine tailings which form an impervious layer and prevent the solution from seeping into the ground. The surface of the heap is covered with shallow basins or pockets to hold the leach liquors and promote even distribution.

The chemical action is largely oxidation brought about by the action of air and ferric salts. The piles are provided with ventilating flues to permit circulation of the air, and the ferric salts are produced by the oxidation of the pyrite and other iron sulfides. Copper is dissolved as $CuSO_4$ and is recovered in the solutions which drain from the bottom of the pile.

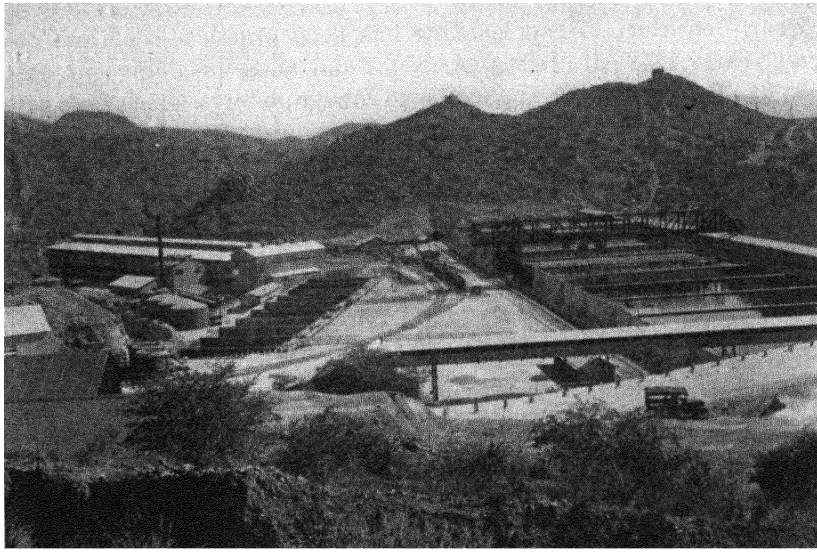
The leaching agent is water, which is run onto the surface of the piles at intervals, plus the natural rainfall. In some places the spent liquor from the precipitating tanks is run back on the piles; it is a more effective leaching agent than water because it contains some ferric sulfate.

The operations consist of alternate oxidation and leaching cycles, and for a large heap it may take several years to complete the leaching. Considerable heat is developed by the oxidation reactions, and the admission of air must be regulated to keep the heap from taking fire.

Leaching in Place. The leaching of broken ore in underground mines is similar to heap leaching in many respects. This method is used to recover copper from regions containing ore of too low grade for mining. Usually the ground to be leached is shattered by caving of nearby ore so that the rock is seamed and crevriced and hence exposed to the action of air and circulating water. The leaching and oxidation cycles proceed in about the same way as in heap leaching, and

the copper sulfate solution is collected in the lower workings and the metal precipitated; the solution may be first pumped to the surface or the precipitation may take place underground.

In many copper mines the natural mine waters contain dissolved copper even though no special provision is made for leaching some particular region. The mine waters from the Butte mines, for example, are treated to precipitate the dissolved copper.



(Courtesy Inspiration Consolidated Copper Company)

FIG. 1. Leaching Plant at Inspiration.

Leaching tanks and bridges visible at right.

Percolation. Most of the large commercial leaching plants treat the ore in leaching *vats*. These are large square or rectangular vats from 60 to 175 feet on a side and 16 to 20 feet deep. The vats are constructed of reinforced concrete; and because the acid solutions have a corrosive effect on the concrete, the vats must be lined with lead or mastic (asphalt and sand). These tanks all contain false bottoms or filter floors set above the tank bottom to protect the bottom lining from damage when charging or excavating ore and tailings. These false bottoms are usually made of 2-inch planks supported on timber uprights; these planks are drilled with a number of small holes to permit passage of the solutions. Tank bottoms contain openings through which liquor can be pumped into the tank or can be drained from the tank.

As far as the ore is concerned, the leaching operation is a batch process. New ore is charged into an empty tank by means of the loading bridge (Fig. 1), it is treated by a series of leaching and washing solutions, drained, and finally excavated and sent to the dump. This leached material is the *tailing*. Commercial leaching vats will hold from 5,000 to 10,000 tons of ore per charge.

There is no "flow" of ore through the leaching plant — it simply goes into one tank and stays there until it is completely leached; then it is removed and another charge added. The flow of leaching solutions, however, is generally much more complicated and a given batch of solution may pass through several tanks in one cycle All these large leaching plants employ a sulfuric acid leach and electrolysis for precipitation of the copper, and the leaching solutions and electrolyte are essentially the same. Spent electrolyte is used for leaching the ore, and the resulting solution passes to the tank houses where part of the copper is deposited and an equivalent amount of sulfuric acid is generated. The spent electrolyte (depleted in copper and enriched in acid) then returns to the leaching tanks. In other words, the liquid circulates in a closed system through the leaching plant and the electrolytic tanks.

There are two principal operations to be performed in these leaching vats — (1) the ore must be kept in contact with the solution long enough to dissolve the copper minerals, and (2) the copper-bearing solution must be separated from the tailing. If a tank containing 9000 tons of dry ore was allowed to drain completely, the wet tailings would still contain about 1000 tons of liquid, and if this was "strong solution," i.e., high in copper, it might contain up to 30 per cent of the total copper dissolved from the ore. There are two kinds of tailing losses in leaching operations — *chemical loss*, which represents the copper that is undissolved, and *mechanical loss* of copper which is dissolved but which remains in the liquid entrained in the wet tailing.

Filtration is out of the question for treating these huge masses of low-grade material, and the entrained copper solutions must be *washed* out of the ore while it is in the tank. The reason for using a number of different leaches and washes on each vat of ore is simply to obtain both efficient dissolution and washing and thus reduce both chemical and mechanical losses of copper to the practical minimum.

It is difficult to explain the flow of solutions in a leaching circuit without reference to a specific flowsheet, and we shall present descriptions of leaching plants in a later section, where it will be possible to consider these questions in more detail.

The liquid may flow or "percolate" continuously through a given

tank during the leaching, or the liquid may be run on, allowed to soak for a period, and then drained off. When liquid enters a tank through the bottom and overflows at the top, the system is known as *upward percolation;* in *downward percolation* the liquid enters at the top and is withdrawn at the bottom.

The tanks may be connected in series with the leaching solutions flowing from one tank to the next in a *countercurrent* system. The spent electrolyte, plus the new acid, first is placed on ore which has been almost completely leached; when this solution (strongest in acid) is removed the ore is completely leached and is ready for washing and excavation from the vat. The liquid from this vat passes to the next, which is less completely leached, and so on through the series. Newly charged ore is first leached by solution which is low in acid and high in copper. Thus the " flow " of ore and solvent (actually the ore does not " flow ") are in opposite directions; the acid solution acts on successively richer and richer ore, increasing its copper content and decreasing its acid content as it goes. From the last tank the copper-rich solution passes to the electrolytic plant.

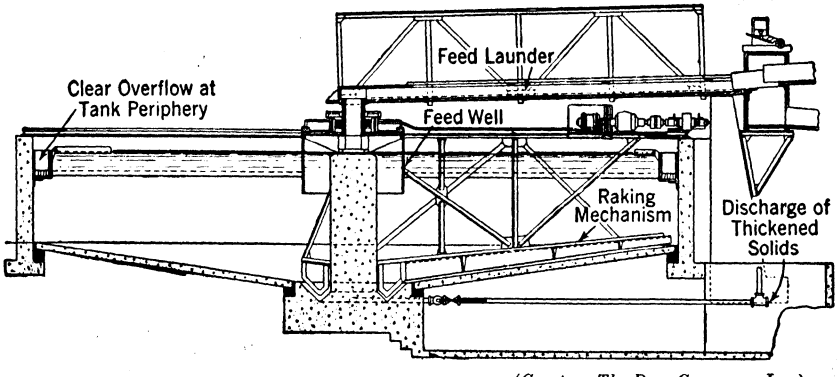
The leaching may be conducted as a batch process by means of which a series of leach solutions are placed on the ore in one tank, allowed to soak for a period, and then withdrawn. In this type of leaching the tanks are not connected in series.

Whatever leaching method is used, the dissolved copper and residual acid must be washed from the tailings. This is done by a series of washes with weak solutions and finally with water. Some of the first washes contain copper enough to join the main electrolyte; the last washes are usually treated with scrap iron to cement out the copper and are then discarded.

Agitation. When the ore to be leached is of such a nature that it will not permit free passage of solution through the interstices, it must be agitated and kept in suspension in the leaching tanks until the copper is dissolved. Agitation tanks are much smaller than the tanks or vats used in percolation leaching and must be equipped with a mechanical stirrer or air lift to keep the pulp in suspension. Mechanical agitators contain rotating paddles for agitation. *Pachuca tanks* are vertical cylindrical tanks containing a pipe which is coaxial with the tank; compressed air is introduced at the bottom of the pipe, and the rising column of air bubbles reduces the density of the column of pulp which is forced out the top of the pipe by the pressure of the denser pulp surrounding the pipe. The pulp drops back into the tank and is thus kept in circulation.

The separation of solid and liquid in slime leaching is a different

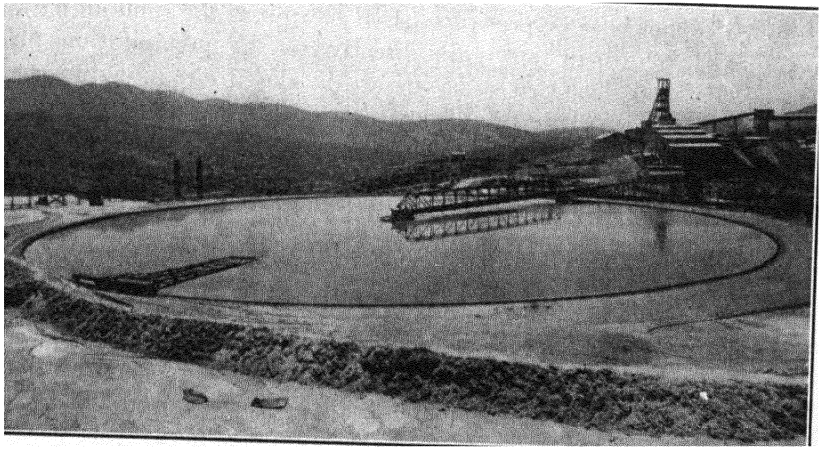
problem than the simple draining that suffices for sand leaching. The separation is usually carried out in *thickeners* (Fig. 2), which are essentially cylindrical settling tanks. Pulp flows continuously into the



(Courtesy The Dorr Company, Inc.)

FIG. 2. Section Through a Dorr Thickener.

thickener, and the solids settle slowly to the bottom of the tank; slow-moving arms sweep the thickened pulp toward the center of the tank where *thickened pulp* or *spigot product* is withdrawn continuously.



(Courtesy The Dorr Company, Inc.)

FIG. 3. A 325-foot Dorr Traction Thickener.

Clear liquid overflows at the top of the thickener. Thickeners take a dilute pulp and resolve it into two products — a clear solution and a thickened pulp.

When thickeners are used for washing a pulp they are generally used in series in a *countercurrent washing system.* The wash water flows through the thickeners in a direction opposite to the flow of pulp. The thickened pulp from one thickener is agitated (*repulped*) with weak solution; thickened again, repulped with a weaker solution, and so on until the values remaining in the liquid in the spigot product are too low to warrant use of another thickener. The spigot product from the last thickener is wasted as tailing. Wash water is added to the last thickener in the series, the overflow from this thickener is repulped with a spigot product to make the feed for the next to the last thickener, and so on. Figure 16 shows an example of a countercurrent slime washing system.

Filters may be used for more efficient removal of liquid from slimes, but this is not common in copper leaching.

TREATMENT OF THE LEACH SOLUTION

After the leaching and washing have been completed, the pregnant solution passes on to precipitation, but some pregnant solutions must be purified before the precipitation stage. The solution from copper leaching (even from slime leaching) is usually quite free of suspended matter, so that it is not necessary to *clarify* the solutions. It may be necessary to pass it through a settling tank, but it need not be filtered.

When copper is to be precipitated on scrap iron the solution requires no special treatment but goes directly to the precipitation plant. However, when the leach solutions are in closed circuit with electrolytic cells it is necessary to remove impurities picked up in leaching before the solution passes to the electrolytic cells. The most harmful of these soluble impurities are iron, chlorine, nitrates, and molybdenum. Rather elaborate installations are often required for purification of the electrolyte, and we shall consider these in connection with electrolytic precipitation.

If the ore contains no soluble sulfate minerals there will be a continual loss of acid in tailings, discarded wash water, cementation launders, etc., plus that consumed in dissolving gangue minerals. It will be necessary, then, to introduce fresh acid into the circuit. On the other hand, if the ore contains copper sulfate minerals, the leaching-electrolysis system will generate a certain amount of free acid; this may exceed the acid loss so that excess acid is produced.

CHEMICAL PRECIPITATION

Metallic copper may be precipitated from pregnant solutions by the addition of certain reagents and, if the solutions are ammoniacal,

copper oxide is precipitated by simply boiling the solution. Many different precipitants have been tried, but only two methods are of commercial importance — (1) cementation of sulfate solutions on iron and (2) boiling ammoniacal solutions to precipitate copper oxide.

Cementation. Cementation is a rather simple procedure which depends on the fact that a metal can be displaced from solution by a less noble element. Thus if a piece of metallic iron is placed in a solution of copper sulfate the iron dissolves and copper precipitates according to the reaction

$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu$$

Iron is the only metal used in practice for copper precipitation. Commonly scrap iron is used for this purpose although *sponge iron* produced by the direct gaseous reduction of solid iron oxide is a more rapid and efficient precipitant.

The scrap iron is loaded into tanks, towers, or launders, and the leach solution slowly flows or trickles over its surface. The deposit of *cement copper* forms as a loosely adherent granular deposit on the iron pieces. This is dislodged at intervals by shaking or washing and is flushed into settling tanks. When a sufficient supply of cement copper has accumulated it is excavated and shipped to a smelter for treatment. As a rule it is charged into the reverberatory furnace, but especially pure cements may be charged into the converters or anode furnaces.

If the scrap is badly oxidized the cement copper will contain a large amount of this oxide and will be quite impure; cement copper may contain from only 60 to over 90 per cent copper, the purity of the deposit being highest with clean scrap and clean solutions.

Scrap from " tin " cans is usually detinned before using, and heavier scrap is burned to remove any grease which would prevent the solution from wetting the metal. Precipitation with sponge iron is conducted in agitation tanks, and this method can be used with certain types of scrap iron.

According to the precipitation equation, one mol of copper is precipitated for each mol of iron, which would mean that one pound of precipitated copper would require $^{56}/_{64}$ or 0.875 pound of iron. Actually the consumption is greater than this, and commonly 1 to 2 pounds of iron is required to precipitate 1 pound of copper. Free acid and ferric salts in the solution will also consume iron.

$$H_2SO_4 + Fe \rightarrow FeSO_4 + H_2$$

$$Fe_2(SO_4)_3 + Fe \rightarrow 3FeSO_4$$

Cementation has a number of advantages which may be listed as follows:

1. The process is relatively cheap and simple, especially if an adequate supply of scrap iron is available. It requires little supervision and no elaborate equipment.

2. It can be used on copper sulfate solutions of any strength and particularly on solutions which contain too little copper to be electrolyzed successfully.

3. It can be used to "strip" solutions of all but a trace of copper so that the solution can be discarded. Electrolytic methods cannot be successfully used to strip solutions of their copper content.

Disadvantages of the cementation process are:

1. It produces a finely divided precipitate of metallic copper which must be melted and refined; often this cement copper is rather impure.

2. The metallic iron will consume any free acid in the solution, and therefore it cannot be used on acid solutions without excessive consumption of iron. Moreover, the acid is destroyed so that this method cannot be used in closed circuit with an acid leach.

Cementation is most commonly used (1) on leach solutions from heap leaching and underground leaching, and on mine waters, and (2) for stripping lean wash solutions from acid leaching.

Other Chemical Methods. Many other processes have been developed to precipitate copper either as a compound or in the metallic state. All these methods have one disadvantage in common with cementation — they yield a precipitate which must be resmelted (whether it is metallic copper or a copper compound). Some of these precipitants, however, have an advantage in that they do not consume the free acid in the solution (H_2S and SO_2, for example). The principal use of some of these methods is in the purification cycle in connection with electrolytic precipitation.

Hydrogen Sulfide. Hydrogen sulfide (H_2S) will precipitate copper as the sulfide, but the precipitant is difficult to handle and requires further smelting.

Sulfur Dioxide. Sulfur dioxide gas (SO_2) under pressure will precipitate copper from solution, thus:

$$CuSO_4 + SO_2 + 2H_2O \rightarrow Cu + 2H_2SO_4$$

This method yields a precipitate of metallic copper and generates sulfuric acid.

Lime. Burnt lime will precipitate copper as the hydroxide, but this gives a bulky precipitate which will be contaminated with other base metals and $CaSO_4$.

Precipitation from Ammoniacal Solutions. The copper dissolved in ammonia leaching exists in the form of a complex cupric ammonium carbonate which is soluble in excess ammonium carbonate and ammonium hydroxide. Some of the equilibria found in these solutions are indicated by the following reactions:

$$Cu(NH_3)_4CO_3 \rightleftharpoons Cu(NH_3)_4^{++} + CO_3^{--} \quad (1)$$

$$Cu(NH_3)_4CO_3 + 4H_2O \rightleftharpoons CuCO_3 + 4NH_4OH \quad (2)$$
$$\downarrow\uparrow$$
$$4NH_3 + 4H_2O$$

$$(NH_4)_2CO_3 + 3H_2O \rightleftharpoons 3NH_4OH + H_2CO_3 \quad (3)$$
$$\downarrow\uparrow \qquad\qquad \downarrow\uparrow$$
$$3NH_3 + 3H_2O \qquad H_2O + CO_2$$

$$H_2O + CuCO_3 \rightleftharpoons CuO + H_2CO_3 \quad (4)$$
$$\downarrow\uparrow$$
$$H_2O + CO_2$$

When such a solution is boiled the NH_3 gas is expelled and this causes reactions 2 and 3 to proceed to completion in the direction of the upper arrows. Thus both ammonium carbonate and cupric ammonium carbonate are hydrolyzed to yield carbonic acid and a precipitate of cupric carbonate (or basic carbonate). Carbonic acid readily decomposes into CO_2 and H_2O if there is not enough ammonia in solution to fix it as ammonium carbonate, and the slightly soluble CO_2 gas escapes from solution. Further boiling hydrolyzes the copper carbonate and drives off the CO_2, leaving a precipitate of CuO, as shown in equation 4.

The net effect of boiling these solutions is to expel the ammonia and carbon dioxide and cause the copper to precipitate as a carbonate, which becomes black copper oxide on further boiling. The ammonia and CO_2 can be recovered from the gases to be used again as a leaching agent.

The precipitated copper oxide is then shipped to a copper smelter, where it is charged to the smelting or refining furnace.

ELECTROLYTIC PRECIPITATION

The most widely practiced method for the precipitation of the copper dissolved in acid leaching is by electrolysis, using insoluble anodes. This method has one outstanding advantage over all other precipitation methods — it yields directly a product (cathode copper) which is of the same quality as the cathodes produced by electrolytic refining.

In some respects the process resembles the electrolytic refining of copper — the tanks and electrical connections are similar to the multiple refining process, the same type of starting sheets are used, and the finished cathodes are treated in the same way as cathodes from electrolytic refining. There are, however, several fundamental differences between the two systems, as we shall see. Briefly, these differences may be summarized as follows:

1. Insoluble anodes are used, and there is no appreciable corrosion of them (a good anode may last more than 10 years), and hence no " anode mud " is formed.

2. The copper in the electrolyte comes from the leaching plant, which is in closed circuit with the electrolytic cells, and because there is no copper dissolved from the anodes, the electrolyte becomes depleted in copper and its free acid content increases as it passes through the tank house. In the leaching cycle the opposite effect is found — acid is used up and more copper is dissolved.

3. Current efficiency is generally lower, voltage is much higher, and the power consumed per pound of cathode copper is much greater (Table 3). The cathode current density is less than that used in refining.

4. Concentrations of dissolved copper and free acid in the electrolyte are generally less than in refinery electrolytes, and the resistance of the electrolyte is greater.

5. The impurities found in the electrolyte are different from those found in refinery electrolytes, and the problem of purifying the solution is altogether different.

6. Electrolytic tanks are generally longer than multiple refining tanks, but anodes and cathodes have about the same dimensions.

The Cell Reaction. As we have mentioned before, electrolysis consists of two equivalent and opposite chemical reactions — oxidation at the anode and reduction at the cathode. In refining of copper the two reactions practically balance one another. Copper is plated on the cathode and an equivalent amount of copper is dissolved (corroded, oxidized) at the anode. With insoluble anodes, however, the cathode reaction is the same as in refining:

$$Cu^{++} + 2(e) \rightarrow Cu$$

but the anodic reaction is different:

$$SO_4^{--} + H_2O - 2(e) \rightarrow H_2SO_4 + \tfrac{1}{2}O_2$$

The *net* cell reaction is the sum of these two, or

$$CuSO_4 + H_2O \rightarrow Cu + H_2SO_4 + \tfrac{1}{2}O_2$$

The electrolysis liberates metallic copper at the cathode and gaseous oxygen at the anode; for every mol of $CuSO_4$ decomposed a mol of free H_2SO_4 is formed in the electrolyte.

The cell reaction if *endothermic,* i.e., if it proceeds from left to right, energy is absorbed:

$$CuSO_4 + H_2O \rightarrow Cu + H_2SO_4 + \tfrac{1}{2}O_2 - 55{,}030 \text{ cal}$$

In other words, copper will dissolve in oxygenated sulfuric acid and liberate 55,030 calories of heat for every gram-mol of copper dissolved. For the reverse reaction, as it takes place in electrolysis, 55,030 calories of heat are *absorbed* for every mol of copper that is deposited, and *this energy or its equivalent must be supplied by some external source.* In electrodeposition this is supplied as electrical energy, and if we assume that electrical energy is converted directly into " chemical energy " we can derive the following relations.

$$1 \text{ gram-calorie} = 4.186 \text{ joules or watt-seconds}$$

Hence 55,030 calories represents $55{,}030 \times 4\ 186 = 230{,}000$ watt-seconds of *electrical energy* that must be supplied for each gram-mol of copper liberated. From Faraday's law we know that the deposition of 1 mol of divalent copper (2 equivalents) requires 2 faradays or 2(96,500) coulombs of electricity. An expression of the amount of electrical energy is the product of two factors — a *capacity factor* (measured in coulombs) and an *intensity factor* (measured in volts); 1 joule is a volt-coulomb, or the amount of energy represented by 1 coulomb falling through a potential of 1 volt.

The voltage in our example is unknown; let us set it equal to V, and then we may write:

$$2(96{,}500)\ V = 230{,}000$$

Whence $V = 1.195$ volts.

This voltage is the *decomposition potential* or *chemical potential* of the indicated reaction, and it means that the voltage drop across the cell must be at least 1.195 volts if the reaction is to take place as indicated. If an insoluble anode is used, and there are no other reactions possible but the one indicated, then *no current will flow through the cell unless the impressed voltage from anode to cathode is greater than 1.195 volts.* After the voltage exceeds this value the current will flow, and the current flowing will follow Ohm's law — i.e., the current flowing will be directly proportional to the voltage above 1.195 volts.

This method of calculation is known as *Thomson's rule* and is based on the assumption that the *electrical energy* and *heat energy* involved in any given reaction are equal. We may write Thomson's rule as

$$E = \frac{U}{njF}$$

where E is the decomposition voltage, n is the valence, U is the heat of the reaction in calories, F is 96,500 coulombs, and j is the factor for converting joules to calories $= 0.239 = \frac{1}{4.186}$.

Thomson's rule is important because it illustrates the meaning of decomposition potential in terms of the energy change involved in a given reaction. It is not strictly accurate, however, because in a given reaction the chemical energy may not all be converted into electrical energy or vice versa; some heat energy may be absorbed from or given up to the surroundings. The correct formula is the *Gibbs-Helmholtz equation:*

$$E = \frac{U}{njF} + T\frac{dE}{dT}$$

where T is the absolute temperature of the cell. This equation is essentially Thomson's rule plus a correction factor which takes into

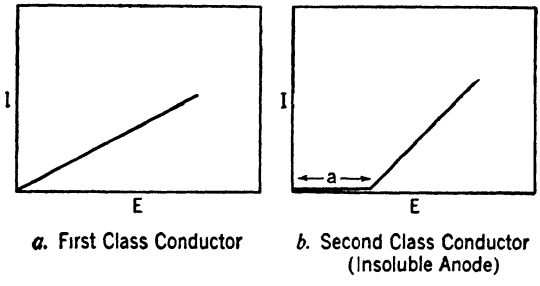


FIG. 4. Current-Voltage Curves for First-Class and Second-Class Conductors. The curve for an electrolytic cell using a soluble anode (refining) would resemble *a*, i.e., there would be no decomposition potential.

account the heat evolved or absorbed; the temperature coefficient dE/dT must be known if the Gibbs-Helmholtz equation is to be used. This may be either positive or negative.

The decomposition potential may be determined experimentally by gradually increasing the voltage and plotting current against voltage (Fig. 4). The first voltage at which an appreciable current begins to flow is the decomposition voltage.

The decomposition potential for copper sulfate between insoluble electrodes (platinum) as determined experimentally is given as 1.49 volts,[7] for a normal solution of copper sulfate.

Cell Voltage. The voltage across the deposition cell must be about 1.49 volts plus sufficient additional voltage to give the required current density, assuming that the concentration of the copper sulfate is normal and that the anode has the same characteristics as a platinum anode. Experimental determinations of decomposition potentials must also include the *gas* and *metal overvoltages.*

The *overvoltage* is the additional voltage required to deposit a metal or liberate a gas at an electrode; it depends upon the metal or gas to be liberated and also upon the nature of the electrode. In general, the metal overvoltages are rather small, but gas overvoltages are larger. In copper electrolysis we are interested in the anode overvoltage of oxygen; this will vary with the nature of the electrolyte, the composition of the anode, and the current density. At a current density of 1.0 ampere per square decimeter the oxygen overvoltage will range from 0.5 to 1.0 volt,[8] depending on the material in the anode.

The total cell voltage will then consist of three parts: (1) the decomposition potential as calculated from the Gibbs-Helmholtz equation, (2) the oxygen overvoltage at the anode, and (3) the voltage required to overcome the contact resistances and the ohmic resistance of the electrolyte. These will be approximately (1) 1.20 volts, (2) 0.30 to 0.60 volt, and (3) 0.20 to 0.30 volt, respectively, or a total of 1.70 to 2.10 volts.

Voltages used in practice range from 1.86 to 2 24 volts. The voltage will depend upon the nature of the anode, and it will vary slightly from time to time, depending on the condition of the anode surface.

Anodes. The function of the anode is simply to serve as a conductor to bring the current into the electrolyte; it should not react with the acid in the cell nor be oxidized by the liberated oxygen; and its oxygen overvoltage should be as low as possible. The anodes should also have sufficient mechanical strength and not be too brittle.

A number of different materials have been employed as anodes — antimonial lead, copper silicide and other copper alloys, magnetite, and cast irons. At present the most common material is antimonial lead, but part of the anodes at the Chuquicamata plant are of " Chilex," an alloy of copper, silicon, iron, and lead, with small amounts of tin and other metals. The anodes may be either cast or rolled, and they may

[7] Mantell, C. L., Industrial Electrochemistry, 2d ed., p. 61, McGraw-Hill Book Co., New York, 1940.

[8] Creighton, H. J., and Koehler, W. A., op. cit., Vol. 2, p. 47.

be supported by cast lugs (like those on copper refinery anodes), copper lugs, copper inserts, or riveted copper bars. The anodes may be solid slabs, or they may be in the form of a grid to save weight and material. As we have noted, they are about the same size as refinery anodes.

Cathodes. The cathode deposit is formed on starting sheets of the same type as those used in refining. The starting sheets are made in stripper cells which usually employ soluble copper anodes and operate in much the same way as stripper cells in refineries; insoluble anodes are used in some stripper cells.

Electrolyte. Table 1 gives the typical analysis of an electrolyte, and Table 2 shows the composition of electrolyte before and after it passes through the deposition cells.

TABLE 1[a]

ANALYSIS, IN GRAMS PER LITER, OF SPENT ELECTROLYTE AT CHUQUICAMATA

Cu	14.44	Al	1 75	K	2.30
Acid	78.54	As	0 242	Pb	0 011
Cl	0 21	Sb	0.009	Sn	0 004
Fe	4 60	Ca	0 475	Mn	0 135
SO_4	144 83	Mg	0 147	Mo	0.248
HNO_3	3 12	Na	6 74		

[a] Mantell, C L, op cit., pp 292, 301

TABLE 2[a]

ANALYSES, IN GRAMS PER LITER, OF ELECTROLYTES AT CHUQUICAMATA AND INSPIRATION

	Chuquicamata		Inspiration	
	Entering Tank House	Leaving Tank House	Entering Tank House	Leaving Tank House
Cu	22	18	32.6	28.1
Free H_2SO_4	55	61	22.2	26.2
Cl_2	0.10	0.10	....	....
Total Fe	2 5	2.5	16 8	....
Ferric Fe	0.9	1.3	4 2	8.4
Ferrous Fe	1.6	1.2	....	....

[a] Mantell, C L., op cit, p 294

Comparing these tables with the data in Table 3, Chapter VIII, which gives the composition of refinery electrolytes, we see that the electrolytes used in electrowinning contain about half as much dissolved copper and only one-third to one-fifth as much free acid. These have

a lower conductivity than refinery electrolytes, and they are also less corrosive.

These electrolytes are rather complex (Table 1) because of the number of substances dissolved from the ore; the concentration of these will build up in the closed circuit, so provision must be made to keep them below certain critical concentrations. The most harmful impurities found in these solutions are as follows:

Ferric Iron. Ferric iron oxidizes copper at the cathode according to the reaction

$$2Fe^{+++} + Cu \rightarrow 2Fe^{++} + Cu^{++}$$

or

$$Fe_2(SO_4)_3 + Cu \rightarrow 2FeSO_4 + CuSO_4$$

This corrosive effect is very pronounced and diminishes the current and power efficiencies. Addicks[9] found that in a solution containing 0.75 per cent ferric iron (about 9 grams per liter) at 51° C no cathode deposit was formed.

Under certain conditions the ferrous ions may be oxidized back to ferric ions in the electrolytic cells; this causes an increase in cathodic corrosion by the resultant ferric ions. The oxidation may take place at the anode:

$$Fe^{++} - (e) \rightarrow Fe^{+++}$$

but as this requires a higher potential than the normal anode reaction

$$SO_4^{--} + 2H_2O - 2(e) \rightarrow H_2SO_4 + \tfrac{1}{2}O_2$$

with moderate Fe^{++} concentration and well-circulated electrolyte there may be no anodic oxidation of the ferrous iron.

Ferrous iron is generally considered harmless and no effort is made to remove it, but all iron is simply reduced to the ferrous state. If the ore to be leached contains sulfides, the presence of ferric iron aids in the dissolution of copper, as we have noted. The practice at any particular plant, therefore, will depend upon whether or not it is desired to dissolve sulfide copper; ferric iron will improve the copper dissolution, but the tank house efficiency will suffer correspondingly.

Nitrates in the solution, particularly when catalyzed by small amounts of molybdenum, may cause a vigorous oxidation of ferrous ions.

Ferric iron in solution may be reduced to ferrous iron in one of two ways:

[9] Addicks, L., in Creighton, H. J., and Koehler, W. A., op. cit., Vol. 2, p. 198.

1. Bringing the solution in contact with SO_2 gas in reaction towers. The reaction involved is

$$Fe_2(SO_4)_3 + SO_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$$

This reaction reduces the ferric iron below 0.4 per cent and generates sulfuric acid.

2. Passing the solution over cement copper. This method can be used to remove all but a trace of ferric iron, but no acid is generated. This method is generally used in connection with dechloridizing operations. The reaction involved is

$$Cu + Fe_2(SO_4)_3 \rightarrow 2FeSO_4 + CuSO_4$$

Chlorine. Chlorine, especially when present in amounts over 0.5 gram per liter, causes difficulties in tank house operation. The anodes are attacked and corroded, insoluble cuprous chloride deposits on the cathode, and chlorine gas is liberated into the tank house atmosphere. Solutions are dechloridized by passing them over cement copper, which precipitates the chlorine as insoluble cuprous chloride (chlorine exists in solution as cupric chloride)

$$Cu + CuCl_2 \rightarrow 2CuCl$$

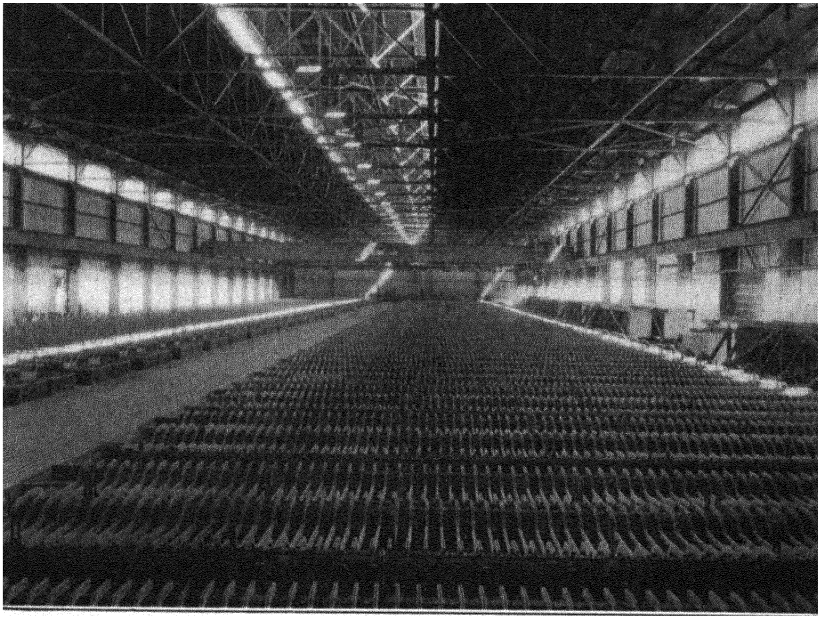
This reaction goes practically to completion in a few minutes if finely divided copper is present in excess. Cuprous chloride is practically insoluble in these dilute solutions, but it is soluble in a hot strong brine of ferrous chloride. The copper precipitated as CuCl is recovered by dissolving in strong ferrous chloride and then reprecipitating it as cement copper by cementing on iron. Note that the operation of this process results in the formation of excess cement copper, because in the cuprous chloride there is twice as much copper as the copper required to precipitate it.

Nitrates. Under certain conditions the nitrate ions cause severe oxidizing conditions in the electrolyte; ferrous ions are oxidized; anodes, cathodes, and lead pipes are oxidized; and fumes of nitrous oxide are evolved from the tanks. Molybdenum serves to catalyze these reactions, and when they get a start the nitrous oxide acts as a self-catalyzer. Nitrate and molybdenum are controlled by stripping and discarding a portion of the electrolyte; charging the electrolyte with SO_2 gas (a reducing agent) minimizes the oxidizing action of the nitrates.

Other Impurities. Most of the other impurities in these solutions are relatively harmless, and the discarding of a certain amount of

solution at regular intervals keeps their concentration within safe limits.

Purification with Limerock.[10] At the leaching plant of the Andes Copper Mining Company, Potrerillos, Chile, the solution from the leaching tanks is agitated with limerock and basic copper carbonate, which is obtained by stripping (precipitating) waste solutions with limerock. This precipitates most of the ferric iron, arsenic, phosphorus, molybdenum, and about 20 per cent of the aluminum; at the same time the copper in the carbonate precipitate is redissolved. This purification completely neutralizes all the free acid remaining in the leach solution. Practically all of the limerock enters the system at



(Courtesy Inspiration Consolidated Copper Company)

FIG. 5. Interior of Tank House at Inspiration.

the point where the waste solutions are stripped, and only a small excess is needed for the purification.

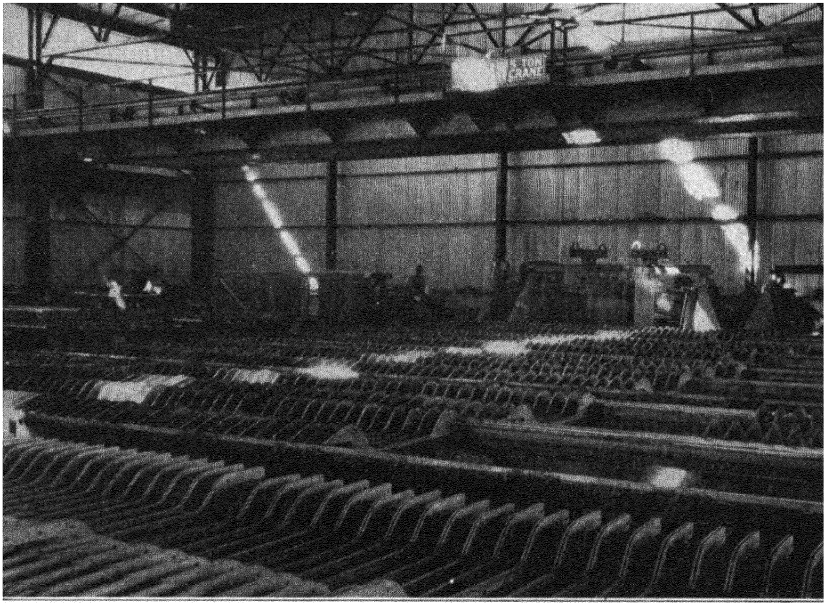
The neutralized solution is filtered and sent through the dechloridizing plant. Fresh acid is then added to bring the free acid content up to 10 or 15 grams per liter, and the solution proceeds to the tank house.

General. The electrolyte is maintained at a lower temperature (30°

[10] Callaway, L. A., and Koepel, F. N., Metallurgical Plant of the Andes Copper Mining Company: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 709, 1933.

to 40° C) than is used in refining practice; higher temperatures would decrease the resistance of the electrolyte and improve the leaching action, but they would also increase the corrosive and oxidizing action of the electrolyte.

The circulation of the electrolyte is much more rapid than is common in refining; this is permissible because there is no anode mud to be stirred up. The circulation rate will range from 25 to 200 gallons per



(Courtesy Inspiration Consolidated Copper Company)

FIG. 6. Starting Sheet Section, Inspiration Tank House.

minute, depending on the arrangement of the circulation cascades. A film of oil is usually used to cover the electrolyte to prevent the spraying of acid into the atmosphere by the escaping bubbles of oxygen.

Note (Table 2) that only a small part of the dissolved copper is removed from the electrolyte in the tank house. If it is desired to maintain the purity of the deposit and efficiency of deposition, the copper content must not fall below a certain minimum figure. Electrolysis is not suitable for completely stripping the copper from solution; cementation is commonly used for this purpose.

Electrolytic precipitation is best suited for treatment of the relatively high copper, high acid solutions obtained by acid leaching. The low-copper solutions containing little or no free acid, such as are obtained from heap leaching or leaching in place, are not suitable electrolytes

Current. The current densities used in electrowinning are lower than those used in refining — from 5 to 13 amperes per square foot of cathode surface. The current efficiency is also lower; it will be about 85 to 90 per cent when the ferric iron is kept down but only about 70 per cent when ferric sulfate is used as a leaching agent for sulfides.

Tanks are connected in about the same way as in multiple refining — electrodes in parallel, tanks in series — and the Walker system of connections is most common.

Power Consumption. Because of the high voltage and lower current efficiencies, much more power is required than in refining. Table 3 (analogous to Table 1, Chapter VIII) shows the power consumption for different cell voltages calculated for 90 and 70 per cent current efficiencies. Comparison of the two tables shows that from 8 to 10 times as much power is required per pound of copper in electrowinning. In extreme cases the electrowinning process might require 19 times as much power as electrorefining

TABLE 3

ELECTRICAL REQUIREMENTS FOR COPPER DEPOSITION USING INSOLUBLE ANODES

	Cell Voltage Current Efficiency = 90%				
	1 8	1 9	2 0	2 1	2 2
Ampere-hours per pound of copper	425	425	425	425	425
Kilowatt-hours per pound of copper	0 765	0 807	0 850	0 892	0 935
Pounds of copper per ampere-day	0 0565	0 0565	0 0565	0 0565	0 0565
Pounds of copper per kilowatt-day	31 4	29 7	28 2	26 8	25 6
	Current Efficiency = 70%				
Ampere-hours per pound of copper	545	545	545	545	545
Kilowatt-hours per pound of copper	0 980	1 035	1 090	1 143	1 20
Pounds of copper per ampere-day	0 0440	0 0440	0 0440	0 0440	0 0440
Pounds of copper per kilowatt-day	24.4	23 2	22.0	21.0	20.0

LEACHING-CONCENTRATION

Resembling in principle the Katanga process of first reducing copper oxides to metallic copper and then removing the metallic copper by concentrating methods, is an acid-leaching process in which the "normal" order of clarification and precipitation is reversed. This

process involves (1) leaching the ore to put the copper into solution, (2) precipitating the copper by treating the pulp with iron, and (3) removing the precipitated copper from the pulp by flotation.

This method is applicable to ores and old tailings which are not adapted to " standard " leaching methods for one or more of the following reasons:

1. The ore is of too low grade, and the resulting leach solutions too poor in copper to utilize acid leaching followed by electrolytic precipitation.

2. The ore may contain a mixture of sulfides and oxides — too much oxide for flotation alone, and too much sulfide for simple leaching.

3. The material may not settle readily enough to make thickening and clarification practical — this is particularly true of old weathered tailing dumps.

We shall give a brief description of the plant of the Ohio Copper Company at Lark, Utah, which treats an old tailing containing 0.42 per cent copper of which 22 to 25 per cent is water-and-acid-soluble. The oxide copper is dissolved, the copper precipitated, and the sulfides and metallic copper removed as a bulk flotation concentrate. A similar process is employed by the Miami Copper Company except that there sulfides and metallic copper are recovered separately in two flotation circuits.

Ohio Copper Company.[11] Figure 7 shows a flowsheet of the operation. Monitors wash the tailing from the dump, and the pulp flows through a surge tank into a washing trommel equipped with a 16-mesh stainless steel screen. Rock particles and debris remaining on the screen are rejected, and the undersize is pumped to the first of three conditioners connected in series. About 6 pounds of 60° Baumé sulfuric acid per ton is used; this is all added to the first conditioner. Of the total copper in the tailing, about 12 5 per cent is water-soluble, and 12.5 per cent acid-soluble. Thus about 12.5 per cent of the copper is dissolved before the pulp enters the conditioners, and 25 per cent is dissolved when the pulp leaves the last conditioner.

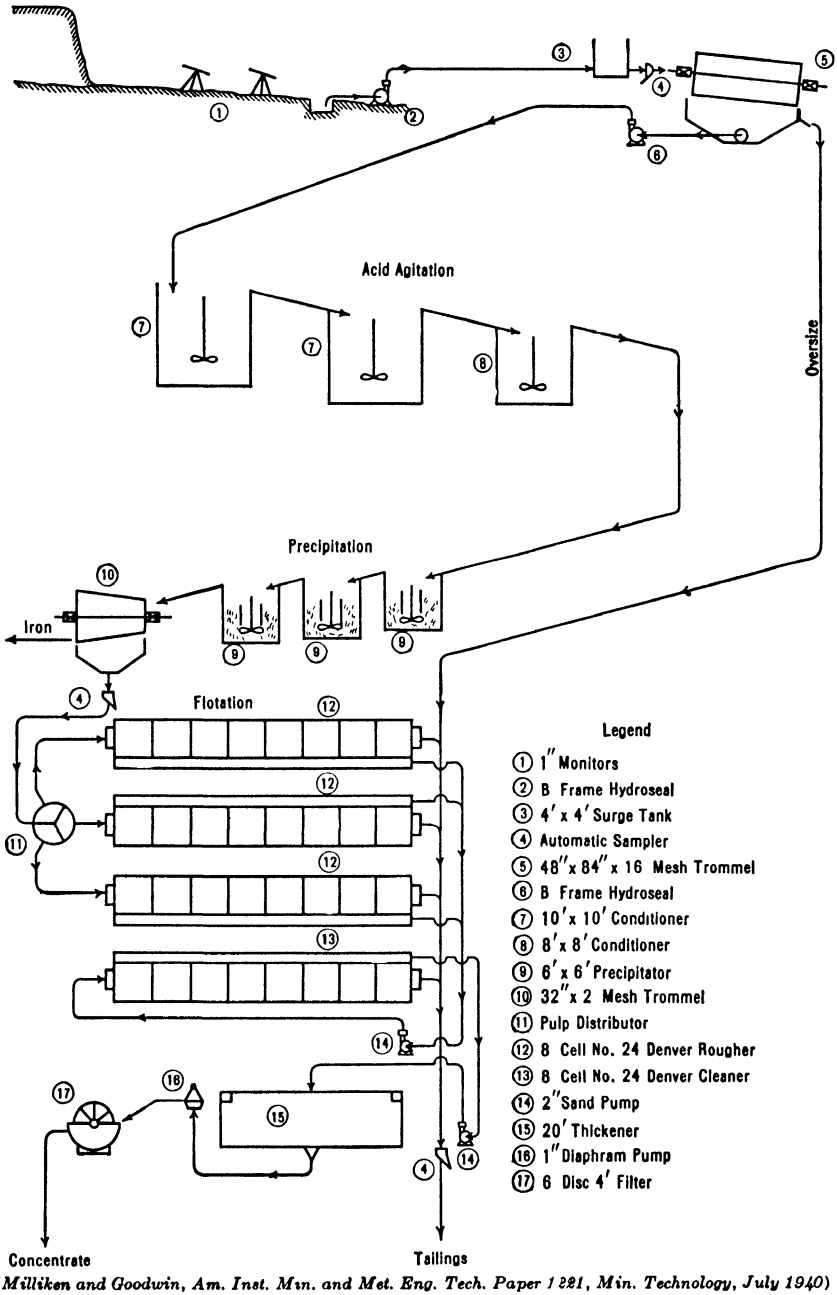
The conditioners are wooden, rubber-lined tanks, and the ship-type propellers are rubber covered; the acid agitation serves four purposes:

1. It dissolves the acid-soluble copper.

2. The acid cleans the surfaces of sulfide particles and renders them more floatable.

3. The tanks serve as conditioners for the flotation circuit; 0.025 pound of " Minerec " (collector for sulfides) is added here.

[11] Milliken, F. R., and Goodwin, Robert, Ohio Copper Company Tailings Re-Treatment Plant: Am. Inst. Min. & Met. Eng. Tech. Paper 1221 (Mining Technology), July 1940.



(Milliken and Goodwin, Am. Inst. Min. and Met. Eng. Tech. Paper 1221, Min. Technology, July 1940)

FIG. 7. Flowsheet of the Tailings Treatment Plant, Ohio Copper Company.

4. The conditioners act as surge tanks to prevent sudden changes in the density of the pulp flowing into the flotation circuit.

From the acid agitation the pulp flows through three precipitating tanks in series. These are rubber-lined wooden tanks equipped with white cast iron ship-type impellers rotating at 250 revolutions per minute. The iron used is known as "Premt" or "shredded iron" and consists of sheet iron obtained from discarded tin cans shredded into pieces about 2 inches square. Under the impeller action this iron moves as a boiling mass near the bottom of the tank and gives good contact with the solution. The action is less vigorous near the top so that very little of the iron is carried over with the pulp. Iron is added by hand as needed. About 2½ pounds of iron is consumed per pound of copper precipitated — this is higher than the consumption in the usual precipitation plant because the iron also neutralizes the free acid left in solution. With normal pulp flow the solution receives about 5 minutes contact with the iron, which suffices to precipitate 82.9 per cent of the dissolved copper.

The pulp passes over a trommel to remove the small amount of iron carried out of the last agitator and then to the flotation circuit. Pentasol xanthate (0.04 pound per ton) and amyl alcohol (0.15 pound per ton) are added as collector and frother respectively. Metallurgical results obtained are tabulated in Table 4. This process recovers 72 38 per cent of the total copper in the original tailing in a concentrate assaying 25.37 per cent copper.

EXAMPLES OF PRACTICE

To illustrate leaching methods we shall give brief descriptions of five commercial applications. These will include one operation leaching ore in place (Ray Mines), one ammonia leaching plant (Kennecott), and three acid-leach electrowinning plants (Chuquicamata, Inspiration, and Katanga).

Ray Mines.[12] Leaching of mined-out areas at the Arizona property of the Ray Mines Division, Kennecott Copper Corporation, was started on January 20, 1937, and by July 1, 1938, 10,000,000 pounds of copper had been produced by this method. The leaching operations are confined to the western part of the ore body and extend over an area of about 10 acres. The ore mined under this area averaged slightly more than 1 per cent copper and was extremely high in pyrite. Above the ore was an unaltered zone of primary or protore averaging 125 feet

[12] Thomas, R. W., Leaching Copper from Worked-Out Areas of the Ray Mines, Arizona: Mining and Metallurgy, Vol. 19, No. 383, p. 481, 1938.

TABLE 4

Metallurgical Results at Ohio Copper Tailings Re-Treatment Plant, August to November, 1939

Product	Solution			Solids			Total Solution + Solids				
	Tons	Cu per Ton, Lb.	Cu, Lb.	Tons	Per Cent Cu	Cu, Lb	Percentage of Total Cu as Soluble	Percentage Cu Based on Solids	Cu, Lb	Percentage of Total Based on	
										Dry Tons	Cu Content
Mill Overall											
Concentrate				1,340	25 37	679,900		25 37	679,900	1 17	72 38
Mill tails	305,000	0 110	33,600	113,260	0 100	225,800	12 95	0 115	259,400	98 87	27 62
Mill heads	261,700	0 527	137,800	114,550	0 349	801,500	14 67	0 410	939,300	100 00	100 00
Leaching and Precipitation											
Mill heads	261,700	0 527	137,800	114,550	0 349	801,500	14 67	0 410	939,300	100 00	100 00
Trommel oversize				4,500	0 220	19,800		0 220	19,800	3 93	2 11
Acid-leach feed[a]	276,000	0 499	137,800	110,050	0 375	781,700	14 99	0 418	919,500	96 07	97 89
Precipitation feed[b]	276,000	0 736	203,000[c]	110,015	0 326	716,300	22 10	0 418	919,500	96 04	97 89
Flotation feed[d]	276,000	0 125	34,600[c]	110,100	0 402	884,900	3 76	0 418	919,500	96 12	97 89
Flotation											
Concentrate				1,340	25 37	679,900[e]		25 37	679,900	1 17	72 38
Flotation tails	305,000[f]	0 110	33,600	108,760	0 095	206,000	14 02	0 110	239,600	94 94	25 51
Flotation feed	276,000	0 125	34,600[g]	110,100	0 402	884,900[e]	3 76	0 418	919,500	96 11	97 89
Tailings											
Rougher tails[h]	240,000	0 112	26,900	105,440	0 080	169,500	13 70	0 093	196,400	92 05	20 91
Cleaner tails[h]	65,000	0 103	6,700	3,320	0 550	36,500	15 51	0 651	43,200	2 89	4 60
Trommel oversize				4,500	0 220	19,800		0 220	19,800	3 93	2 11
Mill tails	305,000	0 110	33,600	113,260	0 100	225,800	14 02	0 115	259,400	98 87	27 62

[a] Trommel undersize. Increase in water tonnage due to trommel spray water and Hydroseal gland water.
[b] Acid-leach tailings.
[c] 82.93 per cent of soluble copper is precipitated.
[d] Precipitation tailings.
[e] Indicated recovery of solids in flotation is 76 83 per cent
[f] Increase in water tonnage is from cleaner tailings.
[g] Some additional copper precipitation during flotation indicated
[h] Distribution of rougher and cleaner tails approximate.

in thickness and containing about 0.6 per cent copper, and above this was a 50-foot leached zone or capping.

By 1933 there was no further mining in this section, and there was evidence that the remaining ore was broken and oxidized and that oxidation had extended into the protore zone. During 1935 and 1936 there was considerable rainfall, and the copper content of the surface water after percolating through this broken ground averaged 1 per cent copper, or 83 3 pounds per 1000 gallons. As no further mining was contemplated in this region it was decided to prepare the section for leaching; an estimate of the copper content of the abandoned ore and the protore above it indicated that the ground amenable to leaching contained over 50,000,000 pounds of copper.

Considerable underground work was required to prepare the area for leaching. Drainage drifts were driven and concrete dams installed in various underground tunnels to prevent the flow of the solution into active mining areas on the fourth level. It was also necessary to install on the third level a concrete ditch with a capacity of 500 gallons per minute, together with the necessary pump station and pumps for handling the water.

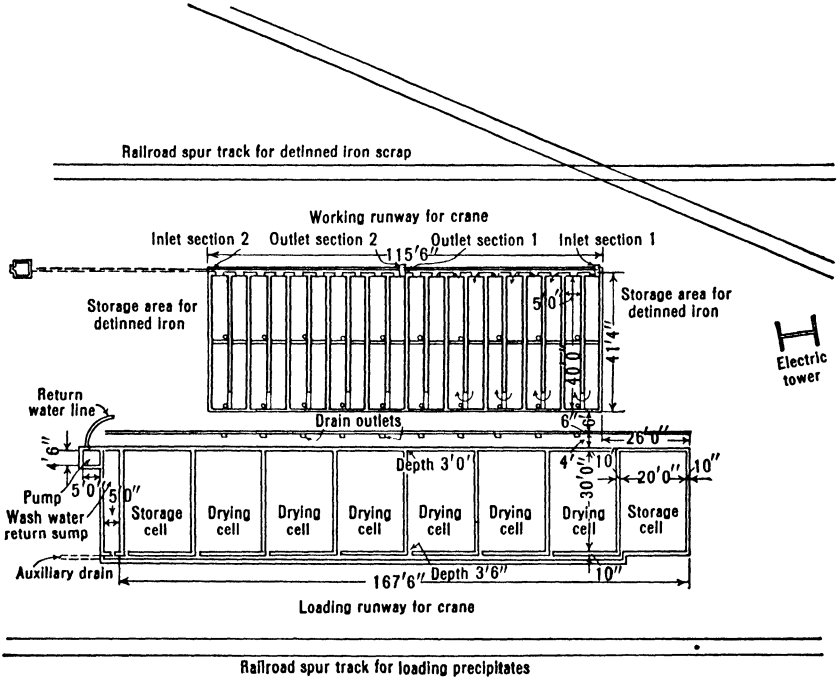
An underground pumping station delivers the solution to the surface through an 8-inch lead-lined pipe. Two centrifugal pumps made of Duraloy are used; these have a combined capacity of about 500 gallons per minute.

Water is pumped to the caved area by means of a four-stage centrifugal pump with a capacity of 340 gallons per minute; another pump can increase this supply to 500 gallons per minute when the water is available. The water was originally distributed over the caved area by a system of pipes equipped with rotating sprinklers, but it was found that when the water was allowed to run too long in one place, channels were formed, and the water ran through these without dissolving much copper. At present the sprinklers are placed in one section and allowed to remain there until the copper content of the liquid drops to 0.4 per cent; then they are moved to another section of the caved area. The caved area can be reworked repeatedly because the draining period between sprayings permits the old channels to seal themselves. The alternate periods of spraying and draining aid in the oxidation of the pyrite to ferric sulfate — the principal solvent for the copper minerals.

Leaching has been conducted entirely by fresh water, although it may be necessary to employ a leaching agent at some future time. Possibly the tailing water from the precipitation plant can be used for this purpose, taking advantage of the ferric sulfate formed by the oxi-

dation of ferrous sulfate. This tailing water would require conditioning, however, before it could be used as a leaching agent because when ferrous sulfate is oxidized a basic iron precipitate is formed, and this would tend to seal up the channels through the broken ore.

Figure 8 shows the general plan of the precipitating plant which was designed after considering the advantages and disadvantages of a number of other installations for recovering copper from mine waters. The precipitation is carried out in two sections each containing 5 cells 10 feet 8 inches wide and 40 feet long with an 8-inch dividing wall



(*Thomas, Mining and Metallurgy, Vol 19, p 482, 1938*)

FIG. 8. General Plan of the Precipitating Plant at Ray Mines.

down the middle. The cells are constructed of concrete and each cell is poured as a unit to avoid any cracks which might result in leaks. The cells have sloping bottoms, and at the lowest point is a discharge opening closed by a special lead discharge valve. Corrosion of the concrete by the copper sulfate is noticeable but not serious.

The scrap iron used is shredded iron made from detinned cans. This is loaded into the tanks by means of a ¾-yard clamshell bucket operated by a crane. Solution flows through the cells, and when the cement copper is to be removed a cell can be cut out and the copper

flushed out. These cells contain false bottoms consisting of wooden grilles upon which the scrap iron rests; the cement copper is washed through the grille and into the drying tank by means of an ordinary fire nozzle with 125-pound water pressure. Each flushing yields from 20,000 to 25,000 pounds of copper; and the operation takes about 45 minutes and requires 4500 gallons of water for each cell.

The copper precipitate settles in the first drying cell, and the clear water is drained off and returned to the precipitating cells. The cement copper is transferred to two other drying cells before it finally reaches the storage cell from which it is shipped. The rehandling of the precipitate is the major factor in eliminating the moisture content.

The plant is designed to handle 500 gallons per minute; the plant data for the period January 29, 1937, to July 1, 1938, are given in Table 5.

TABLE 5

LEACHING OPERATIONS AT RAY, JANUARY 20, 1937, TO JULY 1, 1938

Per cent copper in leach solution	0 923
Per cent copper in precipitation plant tailing water	0 0079
Indicated recovery, per cent	99 14
Copper produced, pounds	10,201,364
Scrap consumed, pounds	11,739,340
Ratio of scrap consumed to copper produced	1 15
Moisture content of precipitate, per cent	22 78
Copper content of dry precipitate, per cent	87 266

Kennecott.[13] The ammonia leaching plant of Kennecott, Alaska, was put in operation in 1916 and has operated until recently. This will serve as an illustrative example of an ammonia leaching operation.

The Kennecott ore contained both sulfides (chalcocite with some covellite) and copper carbonates (malachite and azurite) in limestone-dolomite gangue. The sulfides were removed by gravity concentration and flotation and the carbonates by leaching; ammonia leaching was used because the acid-soluble gangue precluded the use of an acid leach.

There are two essential differences between a plant such as this for copper carbonates and a leaching plant such as the Calumet and Hecla for native copper: (1) The necessary CO_2 for the formation of ammonium carbonate is supplied by the ore in carbonate leaching, but in leaching native copper the CO_2 must be provided from some other

[13] Duggan, E J., Ammonia Leaching at Kennecott: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 547, 1933.

source; and (2) the solution must be passed through aerating towers when native copper is being leached, to provide the necessary oxygen, whereas in leaching carbonates this latter step is not necessary.

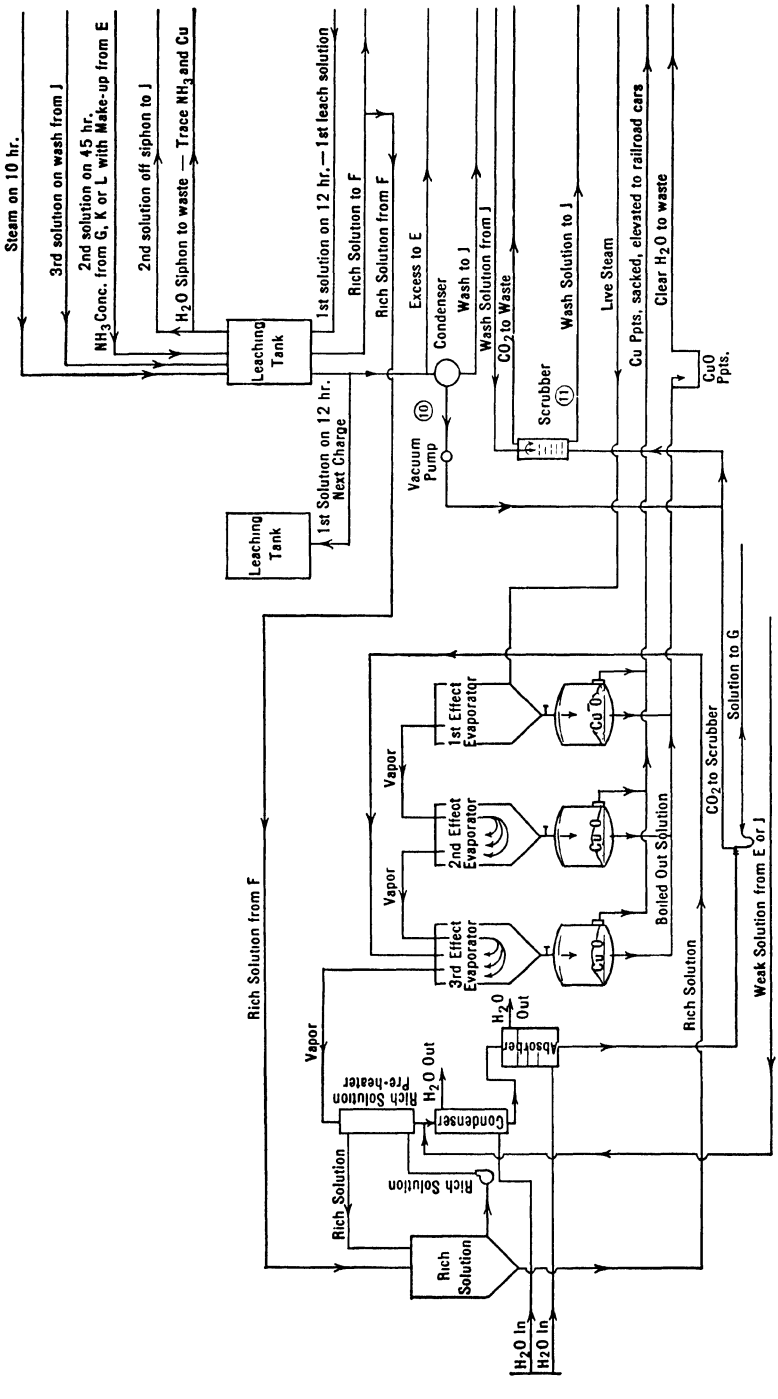
Leaching Feed. The feed to the leaching plant consisted of concentrator tailings containing about 1 per cent copper, mostly in the form of carbonates. Fine sand and slime were treated by flotation, and the leaching feed consisted of fairly coarse sands (about 20 mesh). This material was dewatered to about 5 per cent moisture in Esperanza classifiers and charged into a storage bin; from here it was conveyed to the leaching tanks by bucket elevators and horizontal chain-drag conveyors.

Leaching Tanks. Eight leaching tanks were used, each 30 feet in diameter; four of these held a charge 15 feet in depth (460 tons) and the other four held a charge 20 feet deep (575 tons). The leaching tanks were of all steel construction and vapor tight; a false bottom of screen was placed about 4 inches from the bottom of the tank, on which was placed a filtering medium of coco matting and 8-ounce duck. Mechanical excavators were used to remove the tailing after leaching, and when run in reverse these served as distributors. Feed was introduced through a door in the center of the top of the tank, and leached tailing was discharged through doors in the bottom to a system of conveyor belts which transported the tailings to the dump.

As in all sand leaching processes, the leaching operation was a batch process as far as the ore was concerned; a tank was filled with ore, leached and washed, and then the tailings were excavated and carried to the dump.

Chemistry of the Process. The solvent was ammonium carbonate containing a slight excess of ammonia, the leach liquors usually contained about 20 per cent more CO_2 than NH_3 by weight, which means a slight excess of NH_3 over that required by the formula $(NH_4)_2CO_3$. Ammonia was purchased as aqua ammonia containing about 30 per cent NH_3, and the CO_2 came from the dissolution of copper carbonates. This produced an excess of CO_2, and part of this gas was wasted in the evaporators.

The ore was leached by percolation in the usual manner, the copper carbonates going into solution to produce cupric ammonium carbonates. There was no fouling of the solution or building up of deleterious salts. After the enriched copper ammonia solution was withdrawn, the ore was washed first with a weak solution and then with live steam. The pregnant solution was boiled with steam to drive off the NH_3 and CO_2 and to precipitate copper as black oxide (CuO). The



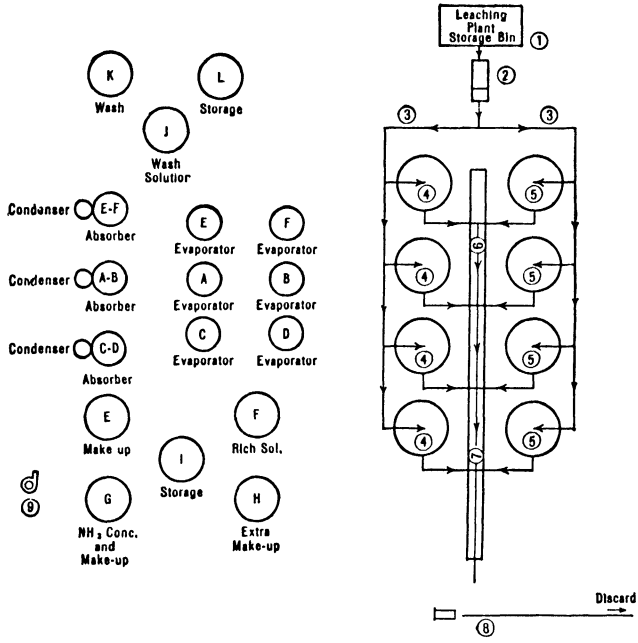
(*Duggan, Am. Inst. Min. and Met. Eng. Trans., Vol. 106, p. 554, 1933*)

FIG. 9. Solution Flow for Ammonia Leaching Plant, Kenneeott Copper Corporation.

10 Nash-Hytor No 1 vacuum pump. 11 Scrubber, 3 by 10 feet.

precipitate was filtered from the waste liquor and shipped; the ammonia was condensed and returned to the leaching circuit.

Leaching Process. Figures 9 and 10 show two flowsheets of the leaching plant. Figure 10 shows the sand flow through the plant and the relative positions of the various evaporators, condensers, and storage tanks. The " sand flow " is simple — the sand is merely charged into a tank, leached and washed, and then removed as tailing.



(*Duggan, Am Inst Min and Met. Eng Trans., Vol 106, p 555, 1933*)

FIG. 10. Sand " Flow " for Ammonia Leaching Plant, Kennecott Copper Corporation.

1. 300-ton storage bin.
2. 16-inch elevator
3. Drag distributors, one 50 ft long, two 100 ft long
4. Four 575-ton leaching tanks
5. Four 460-ton leaching tanks
6. Two 20-inch conveyors.
7. 20-inch conveyor.
8. Dragline scraper for tails.
9. Eight 2-inch centrifugal pumps for solution, one 4-inch centrifugal pump for rich solution, and one 3-inch centrifugal pump for circulating water.

The flow of solution is shown in Figure 9. The leaching was done in two steps. The " first leach " solution was a copper ammonia solution from another charge; this was a " still " leach, and the solution, which was not circulated, yielded the " rich ' or pregnant solution containing the maximum amount of dissolved copper; this solution then went to precipitation. After the first leach, the ore was leached with

strong ammonia to extract the rest of the copper; liquor from this leach then served for the first leach on the next tank of fresh ore. The second leach was a "circulation leach" in which the liquid was pumped to the top of the tank and allowed to flow through the ore column by downward percolation. After the second leach, the tailing was washed with water and steam and then discharged.

TABLE 6

TYPICAL OPERATING CYCLE FOR ONE CHARGE, KENNECOTT, ALASKA

Hours	Operations	Amount of Solution (tons)	NH_3 (per cent)	Cu (per cent)	CO_2 (per cent)
0– 12	Charge 575 tons ore @ 0.94 per cent carbonate Cu, 5 per cent H_2O				
12– 24	Draining				
24– 32	Pump to bottom first leach solution	192	10 50	6 30	12.40
30– 31	Siphon from top to waste	10	trace	trace	
31– 32	Siphon from top to wash storage	6	2.00	1.40	
32– 44	Still leach				
44– 46	Pump from bottom to rich solution storage	59	10 32	7 85	12.20
44– 46	Pump to top concentrated ammonia	23	26 00		22.00
44– 46	Pump to top make-up	36	4.00	2.50	4.30
46– 94	Circulation leach				
94–102	Pump from bottom to next charge	192	10 50	6.30	12.40
94– 96	Pump to top wash	30	1.50	1.00	
98–108	Steam wash, 28 tons steam to top				
102–104	Pump from bottom to make-up storage	36	4 00	2.50	4.30
104–108	Pump from bottom to wash storage	24	1 40	0 65	
108–120	Discharge tailing, 0.14 per cent carbonate Cu				

Table 6 shows a typical operating cycle for one charge of ore. The total cycle took about 5 days (120 hours). The first 24 hours was consumed in charging and draining the ore. The first leach solution was then pumped in from the bottom, and the residual moisture was siphoned off at the top as it was displaced by the rising column of solution. This displaced liquid amounted to about 16 tons; the first portion (10 tons) contained only a trace of copper and ammonia and was discarded; the last 6 tons contained some copper and ammonia, and this was sent to wash-solution storage. The first leach stood on the ore for about 12 hours without circulation, and at the end of this time the solution would be about three-fourths saturated with copper

(NH_3 : Cu = 1.3 : 1), which is about the practical limit for good extraction. A part of this liquid (59 tons in this example) was then pumped from the bottom of the tank to the rich solution storage. Sufficient strong ammonia (from the condensers plus new ammonia) and make-up solution to extract the rest of the copper was then pumped in on top, and this " second leach " solution was then circulated through the column for 36 to 48 hours. At the end of this time the liquid was pumped from the bottom of the tank to another tank of fresh ore, where it became the " first leach."

As the second leach was pumped off it was immediately followed by 20 to 30 tons of wash solution added at the top, and when the level of this wash solution was within a few feet of the bottom of the tank, live steam was admitted at the top and steaming was continued until the washing was completed. The first wash solutions from the tank contained the most copper and ammonia and went to make-up storage; as the steaming continued, the effluent liquid became leaner in copper and ammonia and was sent to wash solution storage. Steaming was continued until the NH_3 content of the effluent had been lowered to the proper amount, and the tailing was then excavated and sent to the dump.

Originally the steam was forced through the bed at 4 to 5 pounds pressure, but later a vacuum was used according to the practice at the Calumet and Hecla plant; this innovation shortened the time for the steam wash and reduced the steam consumption about 10 per cent. Steam washing is essential in the treatment of low-grade material in order to secure economical recovery of the ammonia; ammonia absorbs strongly on the surface of cold ore and is difficult to wash out with water. One ton of steam after the weak solution wash washes 20 tons of ore without the use of any other fresh water.

Recovery of the Solvent. The rich solution from storage went to the evaporators, where it was boiled with steam until the NH_3 and CO_2 were removed and the copper precipitated as CuO (Fig. 9). This was essentially a batch process also, as a given amount of rich solution placed in one of the evaporators remained there until it was completely " boiled out." The evaporators were arranged in a number of (one to four) " effects." (See Fig. 9 for a " three-effect " arrangement.)

This means that the rich solution from storage was first heated by vapor which had passed through two other evaporators; after a while the live steam was turned on the second tank, and the tank which had been on " third effect " became " second effect." After this the live steam was turned directly into the tank, giving the " first-effect " treatment.

Vapor from the third-effect tanks passed through a preheater where some of its heat was used to preheat the rich solution going to the evaporators, and then it passed to the condenser where it condensed as strong ammonia and passed back into the leaching circuit. The first gases to come off the third-effect tanks were largely CO_2, and these passed through the condenser to a scrubber which removed any NH_3. The CO_2 gas was then discharged into the atmosphere. The amount of CO_2 thus wasted corresponded to the amount of CO_2 picked up by the leaching of the copper carbonates.

Steaming was continued until the liquid on the first-effect tank contained only 0.01 per cent NH_3; by this time the copper had all been converted to CuO. The liquid was then forced out by steam pressure through a filter located below the evaporator; the CuO precipitate was dried by vacuum and shipped, and the barren solution passed through a sump to collect any suspended precipitate, and on to the discard.

The evaporators were 16-foot steel cylinders 10 feet in diameter with dome-shaped tops and 6-foot cones on the bottom. Below each evaporator was a filter which served to catch the precipitated CuO.

Extraction, Etc. The strength of the leach solutions was from 6 to 11 per cent NH_3 with corresponding copper percentages of 4.5 to 8.0. The Cu, NH_3, and CO_2 content of typical solutions is shown in Table 6, together with tonnages of these solutions. The plant had a capacity of 800 tons of concentrator tailing per day.

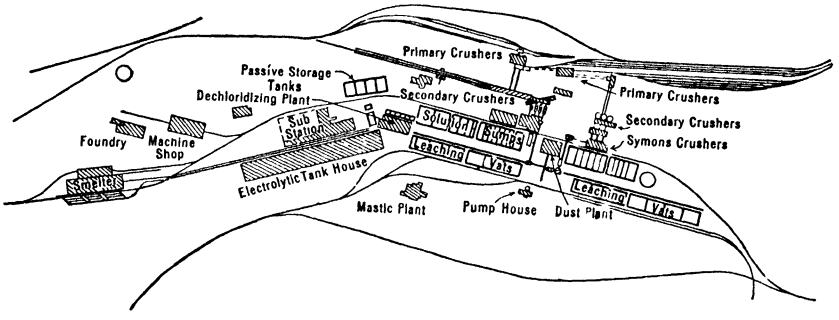
The precipitated black copper oxide contained about 75 per cent copper. Little ammonia was lost by volatilization to the atmosphere, and the total ammonia consumption amounted to 0.45 to 0.60 pound of NH_3 per ton of ore leached. Steam consumption was 210 to 230 pounds per ton of ore leached; 55 per cent of the steam was used for evaporation and 45 per cent for the steam wash. Recovery of copper ranged from 88 per cent to 76 per cent, the recovery being greatest in the finer sizes (Table 7).

TABLE 7

AVERAGE EXTRACTION OF COPPER, KENNECOTT LEACHING PLANT

Size of Ore Particles (mm)	Carbonate Copper in Heads (per cent)	Carbonate Copper in Tails (per cent)	Extraction (per cent)
13	0.90	0 22	75.9
11	0.90	0.18	80 4
9	0 90	0.14	84.8
7	0.90	0.11	88.1

Chuquicamata.[14] The leaching plant at Chuquicamata, Chile, is one of the largest plants in the world, having a capacity of 1,400,000



(Campbell, Am Inst Min. and Met Eng Trans, Vol 106, p 607, 1933)

FIG. 11 General Plan of Plant, Chuquicamata.

short tons of ore per month, which means a production of 20,000 to 28,000 tons of copper per month The following quotation is taken directly from Campbell's article.

> Copper is extracted from the Chuquicamata oxide ore by a hydrometallurgical process. The ore is crushed to ⅜-inch sizing, and leached with a sulfuric acid electrolyte. Chlorine is precipitated and the ferric iron reduced in the enriched electrolyte, after which the copper is recovered by electrolysis with insoluble Chilex and lead-antimony anodes, the spent electrolyte being returned to leaching. Cathodes are melted and refined in market furnaces and cast into commercial wire-bar and cake shapes. Sulfuric acid for the process is supplied by the brochantite in the ore. Water for washing the ore is advanced through the solution system and finally after cutting by electrolysis to from 6 to 16 grams per liter is completely stripped by the cuprous chloride method and run to waste. The cuprous chloride so obtained plus that resulting from precipitation of chlorine from strong solution is dissolved in ferrous chloride brine and the copper cemented on scrap iron. The cement so obtained is in part used to reduce ferric iron in electrolyte and as it is of exceptional purity is also furnace refined and cast into an exceptional quality of fire-refined copper. * * *
>
> The reduction plant is composed of seven divisions as follows: (1) crushing, (2) leaching, (3) tailings disposal, (4) dechloridizing, (5) sulfur dioxide treatment, (6) electrolytic tank house, (7) smelting and melting. * * *

Ore. Table 8 shows the average analysis of the ore and the amount of the various constituents extracted by the leaching process. The

[14] Campbell, T. C., A Brief Description of the Reduction Plant of the Chile Exploration Company at Chuquicamata, Chile, S. A : Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 559, 1933.

present ore (1933) contains 90 per cent oxide copper and 10 per cent sulfide copper; 98 per cent of the oxide copper and 40 per cent of the sulfide copper are extracted by the normal leach.

A moderate tonnage of "border-line mixed ore" is leached with large volumes of solutions containing ferric iron; these ores contain 60 per cent oxide and 40 per cent sulfide copper. As high as 70 per cent of the sulfide copper in this mixed ore can be extracted. When ferric sulfate is reduced by sulfides in the ore, an equivalent tonnage of scrap iron is saved in the dechloridizing operation.

TABLE 8

ORE ANALYSIS AND EXTRACTION AT CHUQUICAMATA

	Analysis		Extraction	
	Per Cent	Kilos per Metric Ton of Ore	Kilos Extracted per Metric Ton of Ore	Extraction, Per Cent
Copper	2.100	21.0	19 5	23.0
Iron	0.95	9 5	0.15	15 8
Chlorine	0 012	0.12	0.04	33.3
Arsenic	0.002	0.02	0 01	50 0
Antimony	0.001	0.01	0.004	40 0
Molybdenum	0.010	0.10	0.01	10 0
Nitric acid	0.015	0.15	0.08	53.3
Sodium	1.10	....	....	....
Potassium	5.20	. ..	...	....
Silica	68.0	..	.	....
Al_2O_3	16 0	. .	. ..	....

The oxide ore is a highly altered granite containing veinlets of brochantite with minor amounts of other oxide minerals; the sulfide minerals are chalcocite and pyrite, and very little of the pyrite is attacked by the leach solutions.

The ore is mined by open-cut methods and when delivered to the crushing plant contains pieces as large as 5 feet in diameter. This is crushed down to a −0.371-inch sizing by four-stage crushing. Two 60-inch Superior McCully gyratory breakers reduce the ore to 9-inch diameter. In the second stage the 9-inch material is reduced to 3-inch sizing in seven No. 10 McCully gyratories and one No. 7 cone crusher. The third and fourth stages of crushing are accomplished by fifty 48-inch disk crushers; 14 of these take the ore from 3-inch diameter down to 1-inch, and the remaining 36 disk crushers take the 1-inch material and turn out the final product of −0.371 inch. The crushed

ore is taken by conveyor belts to the loading bridges over the leaching tanks.

The brochantite supplies about 0.40 kilo of sulfuric acid per kilo of copper leached from the ore; this is sufficient acid to operate the plant, and no other acid source is required.

Leaching Equipment. The ore is leached in 13 leaching vats, each 150 feet long by 110 feet wide and 16½ to 18½ feet deep to the top of the filter bottom, with a net capacity of 11,500 tons of ore in each tank. The tanks, constructed of reinforced concrete, are arranged in blocks of three or four and are set on piers to facilitate inspection of their bottoms. The tanks have a 4-inch lining of a mastic sand mixture.

On this mastic floor a false bottom is laid composed of 6- by 6-inch pine 6 feet long laid end to end 18 inches apart. Across these are laid 2- by 6-inch pine planks spaced ¼ inch apart. Eight spaces 10 feet square are left in this false bottom for draining the tank; into these are inserted prebuilt filter units composed of 4- by 6-inch timbers laid 12 inches apart, across which are laid 2- by 6-inch planks set 3 inches apart. Over this is laid coco matting, and on the matting another layer of 2- by 6-inch planks ¾ inch apart is laid with the planks parallel to the closing movement of the excavating buckets. In excavating the tailings a small tonnage (800 tons) is left on the filter bottom to prevent injury to the filter. This filter bottom will drain 1500 cubic meters (400,000 gallons) of solution an hour through average ore and with occasional minor repairs will last about 8 years.

Leaching vats are arranged in two units, one of seven vats, and the other of six (Fig. 11). Each unit is served by one loading and two excavating bridges of the gantry type; the excavating bridges span the loading bridge. Two main loading conveyors run the length of the north side of the two vat units, and four tailings trains operate on the south side taking the discharge from the four excavating bridges.

The ore is loaded either into solution or a dry vat, depending upon the production cycle. Ore is not bedded but is loaded from bottom to top before the bridge is advanced. The loading bridge is advanced into the prevailing wind to prevent a layer of wind-blown fines from covering the exposed filter bottom, and curtains are suspended from the bridge to shield the ore from the wind as much as possible. After loading, the ore is leveled by hand and fines on the surface are turned in.

Tailings are excavated by means of clamshell buckets operated from the excavating bridges; these buckets have capacities of 8 to 12 tons. Two bridges operating together on a single vat can excavate 11,000

tons of tailings in 7 to 7½ hours. Tailings discharge into hoppers from which they are hauled in 12-cubic-yard dump cars in trains of 26 to the tailing dump.

There are 25 solution sumps for " active " solutions and four auxiliary storage (" passive storage ") sumps. These have a combined capacity of 75,000 cubic meters (20,000,000 gallons). The sumps are placed on higher ground than the leaching vats so that solution can be run into the vats by gravity. The sumps are used for transient storage of treatment advance and wash solutions and as buffer tanks for spent and strong electrolyte. Construction of the sumps is similar to that of the leaching vats but is somewhat lighter.

The leaching and electrolytic plants contain 68,865 feet of pipe, with 885 valves and 2090 elbows or tees, for transmitting solutions. Pipes are of 8-, 12-, 15-, and 24-inch diameter, depending upon the service, and all pipe is wood-stave pipe made of Oregon pine and Douglas fir. Pipe is made in 17-foot lengths, and sections are coupled with wood-stave couplings. Pipe fittings are of cast iron with mastic or hard lead linings. The average life of wood-stave pipe is 5½ years.

Nineteen 15-inch and four 9-inch vertical centrifugal pumps are employed to circulate the solutions. These have runners, casings, and boots all covered with hard lead, and the pump intakes are connected to mastic-lined sumps equipped with cast-lead screens. As high as 250,000 cubic meters (66,000,000 gallons) can be pumped daily against a 70-foot equivalent head.

Leaching Method. The method used for leaching is the batch percolation system in distinction to the countercurrent percolation system used elsewhere. By this treatment each tank is leached more or less independently of the others; the countercurrent system gives better recovery, but the batch system is more flexible.

Approximately 3500 cubic meters (925,000 gallons) of solution is required to submerge 10,000 metric tons of average ore; of this 750 cubic meters is absorbed and 2750 cubic meters is drainable.

The flow of the various solutions through the leaching and electrolytic cycle is shown in Figure 12. The flow is complex, and the details of leaching will vary from time to time, depending upon the grade of the ore and the production rate desired. In general, the purpose is to leach fresh ore with a partly spent solution to produce a strong (high copper) solution, which goes to the electrolytic plant. The partly leached ore is then treated with a strong acid solution to complete the removal of the copper; this solution when withdrawn then goes on another tank of fresh ore, where it picks up enough copper to

go out as strong solution. A certain amount of leach solution is discarded.

After a tank is charged and leveled the remainder of the treatment solution is run on through the bottom until the ore is submerged. The ore is then allowed to soak from 8 to 24 hours. Then the production of " first strong solution " is started from the bottom of the tank with a solution called " first advance " going on top at the same time; first strong solution is produced to a " cut-off " limit (i.e., solution is withdrawn until the copper content reaches a certain minimum value). The volume of first strong solution ranges from 3000 to 6000 cubic meters, depending upon the grade of the ore. Following the production of first strong solution, a second soaking period ensues of 24 to 72 hours, after which the production of " second strong solution " starts, with " second advance " solution going on top. Second strong solution is also produced to a cut-off limit, and the first strong solution from one tank is blended with the second strong solution from another tank to make the solution which goes to the electrolytic tank house.

After these two steps there are three more soaking periods and six washes, as follows:

At the end of the third soaking period, which is of variable duration, " first advance " solution is produced and " volume advance " solution and " spent electrolyte " go on top.

At the end of the fourth soaking period, which is also of variable duration, " second advance " solution is withdrawn, with spent electrolyte going on top.

At the end of the fifth and final soaking period the washing process starts. It continues until the ore is completely washed. Then the ore is drained for at least 4 hours and excavated.

The solutions going on top of the tanks after the fifth soaking are six washes of decreasing copper grade ranging from 9 grams to 1 gram per liter, followed by a water wash. The solutions drawn from the bottom of the tank during this period are determined by cut-off limits, and in order of their production are: " treatment " or " covering solution," " volume advance," the six wash solutions, and " volume discard." The " volume advance " solution is made in quantity sufficient to replace the volume loss of the leaching solution and is equal to the volume loss of primary spent electrolyte stripped and wasted plus the evaporation loss in the primary leaching system. The " volume discard " solution is the same as the " volume advance " solution. It is sent through the dechloridizing plant and to the discard.

The distinction between " volume advance " and " volume discard "

depends upon what use is made of the solution. No new water enters the *leaching system,* but some is lost by evaporation and discarding of electrolyte — this is made up by " volume advance " solution. In the *washing system,* however, new water enters the system in excess of the amount lost by evaporation and entrained in the tailings. This excess is the amount of " volume discard."

Table 9 gives the average composition and tonnages of the various solutions involved in leaching a vat of ore.

Ninety-six hours is the minimum cycle for good leaching. Leaching operations are scheduled on a time chart days in advance to prevent conflicts and to give a close control of operations.

Dechloridizing Plant. The dechloridizing plant is an essential part of the plant and it performs other functions besides the removal of chlorine from strong solution. The five important functions of the dechloridizing plant are:

1. Precipitation of chlorine from strong solution as cuprous chloride.
2. Reduction of ferric iron in strong solution.
3. Stripping of copper from electrolyte to be wasted.
4. Recovery of cement copper from cuprous chloride by redissolving in hot ferrous chloride brine and cementing on scrap iron.
5. Preparation of high-grade cement copper from which a high-grade fire-refined copper is made.

The precipitation of chlorine and reduction of ferric iron by cement copper is carried out by agitation of the strong solution with cement copper, and the reactions are the same as those given on page 328. Cuprous chloride precipitate is dissolved in $FeCl_2$ brine and the copper cemented out on scrap iron. Part of the precipitated copper is then returned for treatment of more strong solution, and the remainder goes to the melting furnaces.

Waste electrolyte can be stripped of its copper content quickly and efficiently by the action of cement copper and ferrous chloride. A small amount of $FeCl_2$ solution is added to the electrolyte and is agitated with cement copper; the reaction involved is

$$Cu + CuSO_4 + FeCl_2 \rightarrow 2CuCl + FeSO_4$$

The precipitate is settled out for treatment to recover the copper, and the liquid is then discarded. A slight excess of $FeCl_2$ and a large excess of cement copper is required to carry this reaction to completion in a short time.

Some chlorine is lost in discarded electrolyte and in washing operations, and as the chlorine content of the ore has diminished with the depletion of surface ores, the chlorine dissolved from the ore is no

TABLE 9

COMPOSITION AND TONNAGES OF SOLUTIONS, CHUQUICAMATA

	First Strong Solution	Second Strong Solution	First Advance	Second Advance	Covering or Treatment Solution	Spent Electrolyte	First Wash	Second Wash	Third Wash	Fourth Wash	Fifth Wash	Volume Discard or Advance	Sixth Wash	Water
Volume (cu m)	5000	5000	3500	3500	3500	8800	3000	2000	2000	2000	2000	300	3000	2350
Temperature, °C.	15°	22°	...		. .	. .	.....	.....	...	.....	....	.. ..	.....	.....
Copper, grams per liter	42 0	32.0	22.0	19 0	17 0	15 0	9 0	7.0	5 5	4.0	2.5	1.5	1.0	.....
H_2SO_4, grams per liter	25.0	32 0	. .	.		58 0	. ..	. .	.	.....	.. ...	.....	.....	.....
Iron, grams per liter	2.5	2.5	... .	.	.	2 5		. .	..	.....	.....	.....	.....	.....
Ferric iron, grams per liter	1.7	1.0	.. .	. . .	. .	2 0	. .	. . ..	.. .	.....	.....	.....	.....	.....
Ferrous iron, grams per liter	1.8	1.5	.... .	.. . .	.....	0 5	.....	.....	.....	....	. ....	.....	.....	.....
Nitric acid, grams per liter	1.5	1.5	.... .	. .	.. ...	1.5	.....	.....	... .	.....	.....	.....	.....	.....

longer sufficient to satisfy the needs of the dechloridizing plant. Accordingly, sodium chloride crystallized from nearby desert springs is added to make up the required chlorine. At present (1933) about 45 per cent of the required chlorine comes from the ore, 25 per cent from the wash water, and 30 per cent from NaCl. It will undoubtedly prove economical and desirable in the future to add NaCl, even though the chlorine content of the ore were to drop so low that dechloridizing of the strong solution would no longer be necessary.

Two principal advantages of the chlorine method of stripping waste solutions are (1) it is possible to produce a higher grade of cement copper than by direct precipitation on metallic iron, and (2) the consumption of scrap iron is only about half as much as would be required for direct precipitation. The CuCl is redissolved in ferrous chloride brine and precipitated on scrap iron, so the stripping of the solution is actually performed by scrap iron, although indirectly. In the electrolyte, however, the copper is in the cupric form, and twice as much iron is required per pound of copper precipitated as is required in precipitating the cuprous copper in ferrous chloride brine; thus:

$$CuSO_4 + Fe \rightarrow Cu + FeSO_4$$

$$2CuCl \text{ (in } FeCl_2 \text{ sol.)} + Fe \rightarrow 2Cu + FeCl_2$$

TABLE 10

DECHLORIDIZING PLANT DATA, CHUQUICAMATA

Dechloridizing capacity, cubic meters of strong solution per 24 hours	25,000
Tonnage capacity to cementation, short tons per 24 hours	140
Normal chlorine in entering strong solution, gram per liter	0.50
Normal chlorine in leaving strong solution, gram per liter	0.05
Scrap iron consumption per unit of cuprous copper	0 50
Grade of solution to stripping, grams per liter of copper	8 to 40
Grade of solution from stripping, gram per liter of copper	0.4

Sulfur Dioxide Plant. In 1930 a sulfur-burning plant with SO_2 absorption tower was installed. The plant burns a local volcanic sulfur ore to produce SO_2, and the SO_2 gas is absorbed by the electrolyte.

The purpose of this treatment is not to reduce ferric iron, for which purpose the process is employed elsewhere, but simply to dissolve SO_2 in the electrolyte to *stabilize* it. The contact of solution with SO_2 gas is just long enough to permit dissolution of some of the gas and is not prolonged enough to allow much reduction of ferric iron.

Previous to this installation operating difficulties were encountered in the tank house by the decomposition of nitric acid; this was catalyzed

by molybdenum in the solution when ore containing over 0.008 per cent molybdenum was treated. Once started, the reaction was self-catalyzed by nitrogen oxides and spread through the entire solution system of 100,000 cubic meters. Dechloridizing and stripping operations were hampered, and the chlorine content of the electrolyte and cuprous chloride in the cathodes increased greatly; current efficiency dropped from 90 to 60 per cent; and the anodes and pipe fittings were severely corroded.

Experimental work indicated that a small amount of sulfurous acid ($SO_2 + H_2O \rightarrow H_2SO_3$) in solution would inhibit the decomposition of nitric acid and would gradually dissipate the nitric acid without oxidation of anodes and fittings. Accordingly the SO_2 plant was constructed, and the flowsheet was arranged to keep SO_2 dissolved in the electrolyte by continually circulating a portion of the electrolyte through the SO_2 absorption plant.

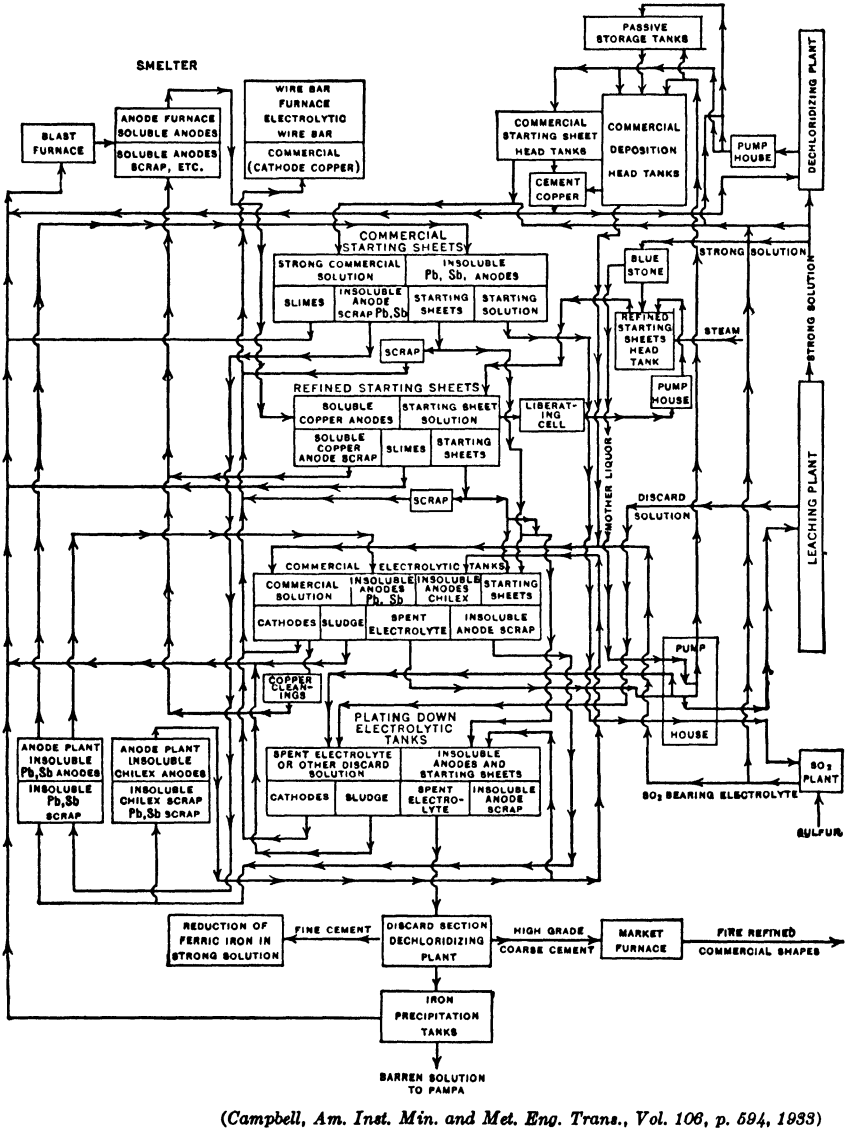
The plant burns 25 tons of fine sulfur per day producing about 50 tons of SO_2 in a gas of 14 per cent grade. The gassed electrolyte carries 0.7 gram to 2 0 grams of SO_2 per liter, and with electrolyte containing 0.2 to 0 5 gram of SO_2 per liter there is practically no odor of SO_2 in the tank house; escape of SO_2 is largely prevented by the oil blanket which covers the electrolyte in the cells. About 90 per cent of the absorbed SO_2 is converted to sulfuric acid by anodic oxidation in the cells.

Electrolysis. There are 1098 electrolytic tanks each measuring 19 feet 2 inches long, 3 feet 11 inches wide, and 4 feet 10 inches deep, inside dimensions. The tanks are of reinforced concrete and are lined with mastic. The deposition tanks rest on piers with ground footings constructed independently of the building proper, and the tank tops are 2 to 3 feet above floor level.

A *section* comprises sixteen or seventeen tanks arranged in a cascade, and four to eight sections in series make up an *electrical circuit.* Each circuit is powered by one or more rotary converters or motor-generator sets. One circuit and a variable number of tanks in another circuit are used for the deposition of starting sheets, and one or more circuits are always in use plating down solution which is to be discarded. The remainder of the tanks are used for commercial cathode deposition.

The anode plant adjoins the tank house, and here the copper silicide (*Chilex*) anodes and lead-antimony grid anodes are cast. Chilex anodes are 2 feet 9 inches by 5 feet 11 inches, are 1 inch thick, and are spaced on 3½- or 4-inch centers. Lead-antimony anodes are of the same width and length but are 0.5 to 0.6 inch in thickness and are spaced on 3- to 3½-inch centers. Each tank, therefore, carries 56

to 74 anodes and 55 to 73 cathodes, depending on the spacing. Chilex anodes are brittle, and the lead-antimony anode produces about 12



(Campbell, Am. Inst. Min. and Met. Eng. Trans., Vol. 106, p. 594, 1933)

FIG. 13. Flowsheet of Electrolytic Tank House, Chuquicamata, 1933.

per cent more copper per kilowatt day than the Chilex anode. The Chilex anode resists corrosion better than the lead-antimony anode, but with the low iron and nitric acid content of present-day electrolyte,

this is not such an important factor as it used to be, and lead-antimony anodes are gradually replacing the Chilex anodes. The tank house requires from 60,000 to 62,000 anodes.

Starting sheets are made from dechloridized strong solution using lead-antimony anodes. Equipment is also provided for making starting sheets from soluble anodes (made by fire refining cement copper) with an electrolyte made by dissolving bluestone. The method used for making starting sheets depends on the condition of the strong solution. If more than 0.2 gram per liter of chlorine is present the starting sheets are too brittle for use. The sheets are deposited to 12-pound weight and the submerged section measures 3 by 4 feet. Two loops cut from the starting sheets attach them to the cathode bar.

The outflowing solution from the stripper tanks is pumped to the SO_2 plant and then enters the commercial cells. The flow of the electrolyte is very fast in order to insure formation of hard cathodes and to decrease polarization. Each section takes a flow of 750 liters (198 gallons) per minute, and at times the flow may be as high as 1200 liters (317 gallons) per minute. The electrolyte is not heated except by the cell resistance, which causes a rise of about 10° C as the electrolyte passes through the cells. The temperature of the spent electrolyte will be 30° to 45° C, depending on atmospheric conditions. The average weight of a finished cathode will be about 150 pounds, production of which has required 5 to 15 days, depending on the current density.

TABLE 11

ELECTROLYTIC TANK HOUSE DATA, CHUQUICAMATA

Number of electrolytic tanks	1,098
Number of insoluble grid anodes to equip tanks	62,000
Current density, amperes per square foot of cathode area	7 to 18
Entering solution (Temp. 26–34° C), grams per liter:	
Copper	21 to 26
Ferrous iron	1.6 to 2.1
Total iron	2.5
Leaving solution (Temp. 31–43° C), grams per liter:	
Copper	14 to 16
Ferrous iron	0.5
Total iron	2.5
Current efficiency	85 to 92%
Pounds of copper per kilowatt-day	24 to 28
Capacity, kilowatt load	55,000

Current density ranges from 7 to 15 amperes per square foot of cathode in the stripper cells and from 7 to 18 amperes in the com-

mercial cells. Voltage drop per tank is about 1.9 to 2.0 volts for lead-antimony anodes and 2.1 to 2 3 volts for Chilex anodes.

Smelter. The smelter has three market furnaces (cathode furnaces) of 400 tons daily capacity each for melting cathodes and casting wire-bars, cakes, and other shapes. Each furnace is equipped with a 40-foot Clark casting wheel.

There is a market furnace (reverberatory furnace) of 150 tons capacity for the fire refining of cement copper; the technique employed is similar to the process used for smelting native copper. There is also a small blast furnace of 50 tons daily capacity for smelting refinery slags and miscellaneous secondaries. When soluble anodes are made, the black copper from the blast furnace is refined in the 150-ton reverberatory and cast into anodes.

Inspiration.[15] Practice at the Inspiration plant of the Inspiration Consolidated Copper Company at Inspiration, Arizona, differs from that at Chuquicamata in several important respects.

1. The ore is not suited for all-sand leaching, and part of it is treated by percolation and part by agitation.

2. The amount of sulfide copper is greater, and more of the sulfide copper is dissolved by ferric sulfate than at Chuquicamata.

3. It is not necessary to dechloridize the solution; and no effort is made to reduce ferric iron, as this is an effective leaching agent.

4. The ore does not supply sulfuric acid, so new acid must be continually added to the system.

The Ore. The copper content of the ore is about 1.3 per cent, of which about 0.7 per cent is sulfide copper (1931). The fluctuation of ore and tailing assays in the period 1927 to 1931 is shown in Figure 14.

Ore is crushed in gyratory crushers and Symons disk crushers which reduce mine-run ore to about 1½ inches. This is further crushed by coarse and fine rolls in closed circuit with a screen with ⅜-inch openings. Part of the undersize from the crushing plant (Fig. 15) goes to the washing plant, and the remainder goes directly to the sand leach.

The important oxidized copper minerals in the ore are chrysocolla, malachite, and azurite. Chalcocite is the principal sulfide mineral, and the ore contains very little soluble iron.

The plant has a yearly capacity of some 3,000,000 tons of ore.

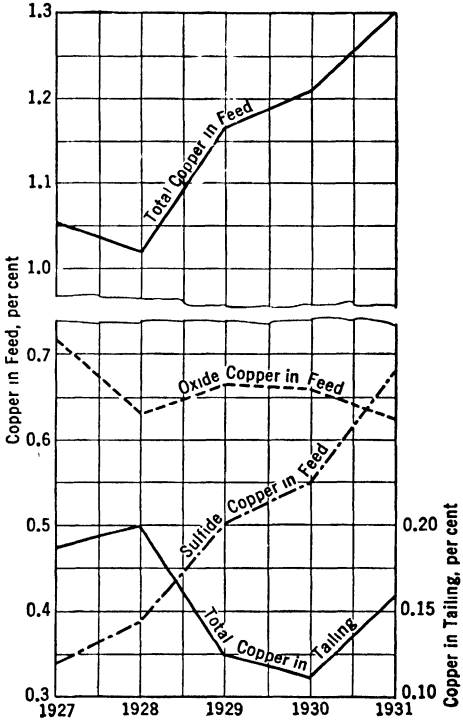
Washing Plant. The washing plant takes part of the ore from the crushing division (the undersize containing the "natural slimes" in the ore) and washes it in two 25-foot Dorr bowl classifiers. The sands from these classifiers join the rest of the crushed ore and go to

[15] Aldrich, H. W., and Scott, W. G., The Inspiration Leaching Plant: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 650, 1933.

the leaching tanks. The classifier slimes go to the flotation and slime-leaching divisions.

Taking 1931 as an average year, 5.75 per cent of the total ore mined was removed and sent to flotation and slime leaching; this material assayed 1.545 per cent total copper and 0.389 per cent sulfide copper. The classifier sands contained 3 3 per cent −200-mesh material, and the classifier overflow was 83 4 per cent −200 mesh. Water used per ton of slime amounted to 1045 gallons.

The wet classifier sands are mixed with the dry crushed ore and are sent to the leaching vats.



(*Aldrich and Scott, Am. Inst Min. and Met. Eng. Trans , Vol 106, p. 650, 1933*)

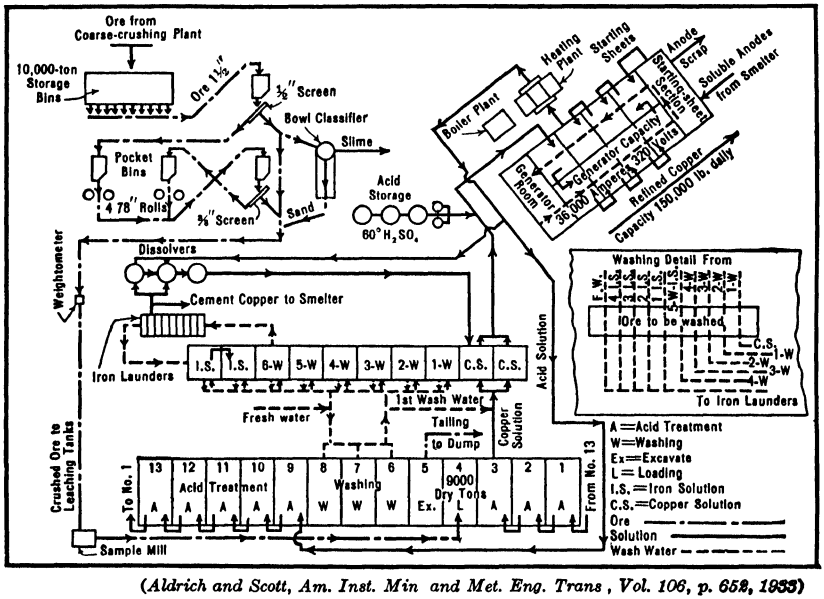
FIG. 14 Copper in Feed and Tailing, Inspiration Leaching Plant.

Sand Leaching Equipment. There are 13 concrete, lead-lined leaching tanks each 175 feet long, 67.5 feet wide, and 18 feet deep, with a capacity of 9000 tons of dry ore per tank. The lead on the side walls is protected by a covering of 2-inch planks held in place by vertical posts. The filter bottom is made of 2-inch boards having fifteen ⅜-inch holes per square foot of surface, each countersunk with a ¾-inch hole from beneath. The tank bottom slopes slightly toward the center as well as toward the end where the drain pipe is located. There is only one opening in the bottom of each tank — a 14-inch lead pipe burned to the lead lining, entering at the end opposite the overflow just above the tank bottom and below the filter bottom. All solution enters through this pipe and all drainage is taken out through it. Timbers 4 by 6 inches and laid on the 4-inch side are placed over the filter bottom to protect it, and a 6-inch layer of tailing is left when excavating.

The thirteen tanks are arranged in a single row and are served by one excavating bridge and a loading bridge. The loading bridge

contains a conveyor belt with an automatically reversing tripper which empties the load into the tank. At each reversal of the tripper the loading bridge moves forward 2½ feet until it reaches the end of the tank, when its motion is reversed. This lays the charge in the tank in a series of beds each about 3 feet thick. The excavating bridge uses an unloading bucket capable of lifting approximately 17 tons of wet tailing; two 8-hour shifts are required to unload a tank.

Leaching Method. The leaching method is simple, being a straight countercurrent system using upward percolation, followed by ten



(Aldrich and Scott, Am. Inst. Min and Met. Eng. Trans, Vol. 106, p. 658, 1933)

FIG. 15. Flowsheet of the Inspiration Leaching Plant.

washes. The complete cycle is 13 days, and at any one time there will be eight tanks on acid leach, three on washing, one being loaded, and one being excavated.

From 175,000 to 200,000 gallons of solution are required to cover a tank of ore. Each tank is provided with a vertical screw-type lead pump which takes the solution overflowing from the preceding tank and pumps it underneath the filter bottom and up through the ore. The spent electrolyte from the tank house plus new acid is added to the oldest ore on acid leach. The solution travels from tank to tank, being constantly reduced in solvent strength and increased in copper content, until it emerges from the vat containing the newest ore. From there it flows to the tank house.

Washing requires 3 days, and ten washes are used. The first five

are called regular washes and are systematically advanced, the first wash going to the main solution system, the second becoming the first wash on the next tank, and so on.

The solution for the fifth wash comes from the cementation solution stock, and after passing through the ore becomes the fourth wash on the next tank, and eventually works its way into the main solution circuit. The next four washes come from the cementation stock solution, and the tenth wash employs fresh water. The washings from the last four washes go to cementation. This liquid is passed over scrap iron, which precipitates copper, reduces ferric sulfate, neutralizes the acid present, and adds ferrous iron to the solution. This latter is the principal reason for the cementation process — this supplies ferrous iron to the leaching solution, which is necessary because there is not sufficient iron dissolved from the ore. This becomes oxidized to ferric iron in the tank house and thus provides the solvent for the sulfide copper.

The only solution discarded is the moisture in the tailings, and therefore the wash water and wash-water advances are carefully balanced (Table 12). Usually a batch wash is used, i.e., the wash liquor is added, circulated, and then drained before the next wash is added.

TABLE 12

VOLUME BALANCE (1931), INSPIRATION

	Gallons per Ton of Ore		Gallons per Ton of Ore
Entering moisture (in ore)	16 49	Moisture in tailing	24.73
Fresh water added in wash	15 87	Evaporation per ton per day	7.63
Total incoming water	32 36	Total water lost	32.36

The ferric sulfate content in the leach solution is held at 7.5 grams per liter with 10.0 as a maximum and 5.0 as a minimum. This is necessary to insure good leaching of the chalcocite. New acid is required in the amount of about 23 pounds of 60° Baumé acid per ton of ore leached.

During the four summer months the leach solution is not heated and the temperature averages 38° C. From October to May the solution is heated to about an average of 35° C (42° C on the oldest charge). This is important in the leaching of the sulfides, for with a cold solution (20° to 22° C) only 40 to 50 per cent of the sulfides dissolve, but at 35° C, the extraction rises to 75 per cent, other things

remaining equal. Metallurgical results for 1930 and 1931 are shown in Table 13.

TABLE 13

METALLURGICAL RESULTS OF SAND LEACHING AT INSPIRATION

(Per Cent)

Feed:	*1930*	*1931*
Oxide copper	0 658	0 625
Sulfide copper	0 550	0.681
Total copper	1.208	1.306
Tailing:		
Oxide copper	0 020	0 020
Water-soluble copper	Trace	Trace
Sulfide copper	0.092	0 142
Total copper	0 112	0.162
Extraction·		
Oxide copper	96 96	96.80
Sulfide copper	83 27	79 15
Total copper	90 73	87 60

Electrolysis. The commercial division contains 120 electrolytic tanks each 33 feet long, 4 feet wide, and 4 feet 3 inches deep. These are divided into 8 banks of 15 tanks each, the electrolyte flowing in series through the banks. Each bank has a solution circulation of about 1200 gallons per minute or 80 gallons per tank per minute. Each tank has 95 cathodes and 96 anodes spaced 4 inches from center to center of cathodes; this makes a total of 11,400 commercial cathodes and 11,520 anodes.

The anodes are made of a lead-antimony alloy containing 8 per cent antimony; the submerged section is 38 by 40 inches and ½ inch thick.

The stripper tanks constitute, in reality, a small refinery of 20 tanks. Each tank has a capacity of 95 cathode blanks and 96 anodes, making a total of 1900 blanks, capable of producing 3800 starting sheets per day.

Soluble anodes are used in the stripper tanks. These are cast from blister copper at the International smelter. Usually a special electrolyte is used for making starting sheets, because the commercial electrolyte is not suited for the purpose. Blanks are stripped every 24 hours; they weigh 11 to 12 pounds before the loops are attached. The cathode life varies with the current density but is about 5 days for maximum production; finished cathodes weigh 90 to 100 pounds each.

The entire leaching process is built around the oxidation of ferrous sulfate to ferric sulfate by oxidation at the anode. The resulting ferric

sulfate is the leaching agent for the sulfides in the ore. The " current efficiency " is comparatively low because of the corrosive action of ferric ions on the cathode deposit. Actually, the electrolytic cells are considered to have a double function — reduction of copper at the cathode and oxidation of ferrous ions at the anode — and instead of " current efficiency " as we have used it before, two values are reported, namely *cathode efficiency* and *anode efficiency*. The cathode efficiency is the ratio (in per cent) of the actual copper deposit to the theoretical deposit and is the same as " current efficiency " as reported at other plants. The anode efficiency is the ratio of the weight of ferrous sulfate oxidized to the weight of ferrous sulfate which could theoretically be oxidized (also expressed as per cent). The anode efficiency depends upon the condition of the anode surface, which must be cleaned at intervals to maintain the anode efficiency. Table 14 gives some of the tank house data for the years 1927 to 1931.

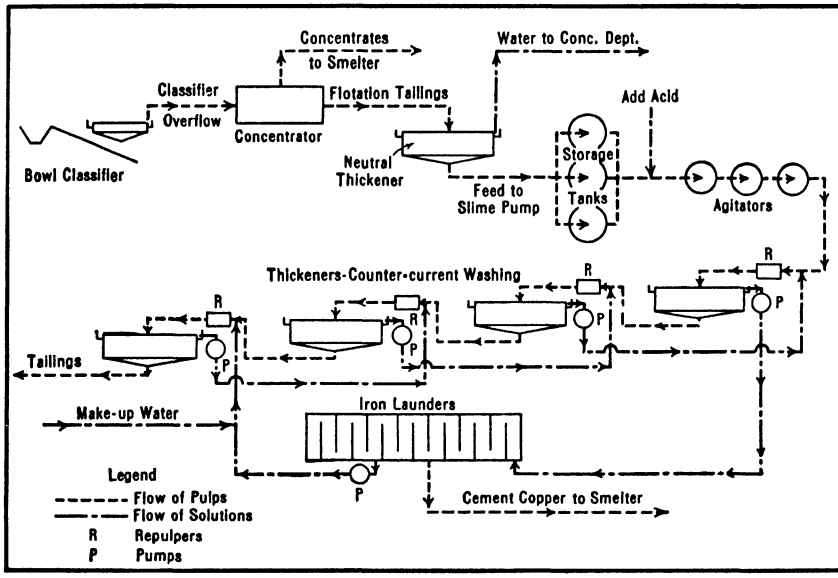
TABLE 14

TANK HOUSE RESULTS AT INSPIRATION

	1927	1928	1929	1930	1931
Current density, amp/sq ft cathode.	14 2	11 8	14 6	13.3	11.9
kw-hr per pound of copper.	1.641	1 540	1.695	1.615	1.431
Cathode efficiency, per cent.	61.4	64 7	61.8	64.1	67.9
Anode efficiency, per cent.	41.1	43.3	60.7	52.0	54.0
Electrolyte, in:					
Copper, grams/liter.	28 2	23 4	28 2	33.1	26.4
Total acid, grams/liter.	41.4	30.6	25.5	26.9	33.8
Ferric iron, grams/liter.	5.9	5.3	4.5	3.1	4 0
Electrolyte, out:					
Copper, grams/liter.	22 3	18 2	23 1	26 6	21 6
Total acid, grams/liter.	56 6	45 0	42 4	38 4	41 1
Ferric iron, grams/liter.	10 2	9 3	10 0	9.1	8 6
Total iron in electrolyte, grams/liter.	17.3	16 0	18 6	16 4	20.0

Cementation Launders. There are nine double-section cementation launders 60 feet long, 20 feet wide, and 5 feet deep charged with baled tin cans which serve as a precipitant. Wash waters from the leaching plant are treated here to precipitate the copper, and the tailing water is returned to the washing and leaching circuit. The function of the cementation plant is twofold: (1) to maintain the desired concentration of iron in the leaching solutions, and (2) to provide copper-free solution for washing the ore so that only the minimum amount of fresh water need be added to the system. No solution is discarded except that entrained in the tailings.

The amount of cement copper produced is about equal to the weight of blister copper anodes used for making the starting sheets and therefore amounts practically to an exchange of copper with the smelter. The amount of scrap iron consumed is 1.9 to 2.2 pounds per pound of cement copper; this high figure is due to the free acid and ferric sulfate in the wash solutions.



(Aldrich and Scott, Am. Inst. Min. and Met. Eng. Trans., Vol. 106, p 666, 1933)

FIG. 16 Flowsheet of the Slime Treatment Plant, Inspiration.

Slime-Treatment Division. The slimes from the washing plant are treated first by flotation to remove the sulfides, and the flotation tailings are then treated by agitation in acid solution to dissolve the oxide copper. The leached pulp is washed by countercurrent decantation in four thickeners, and the copper in solution is precipitated on scrap iron.

Figure 16 is a flowsheet of the slime-treatment division. The agitators consist of circular lead-lined wooden tanks, and the agitator blades are of rubber-covered steel. Four 150-foot Dorr traction thickeners are used for washing, the overflow from the first thickener contains 2.73 grams of copper per liter and goes to precipitation, the spigot product from the fourth thickener goes to waste, and the entrained solution carries 0.21 gram of copper per liter. Table 15 gives the combined recoveries for the entire plant — both the leaching division and slimes-treatment plant.

TABLE 15

COMBINED RESULTS FROM LEACHING AND SLIME PLANT AT INSPIRATION

		1930	*1931*
Original feed to leaching plant:			
Oxide copper	per cent	0.704	0.655
Sulfide copper	do	0.536	0.665
Total copper	do	1.240	1.320
Combined tailing from leaching plant and slime plant:			
Oxide copper	per cent	0.022	0.025
Sulfide copper	do	0.093	0.140
Total copper	do	0.115	0.165
Combined extraction:			
Oxide copper	per cent	96.875	96.183
Sulfide copper	do	82 649	78.947
Total copper	do	90 726	87 500
Copper recovered, lb/ton of ore		22.50	23.10

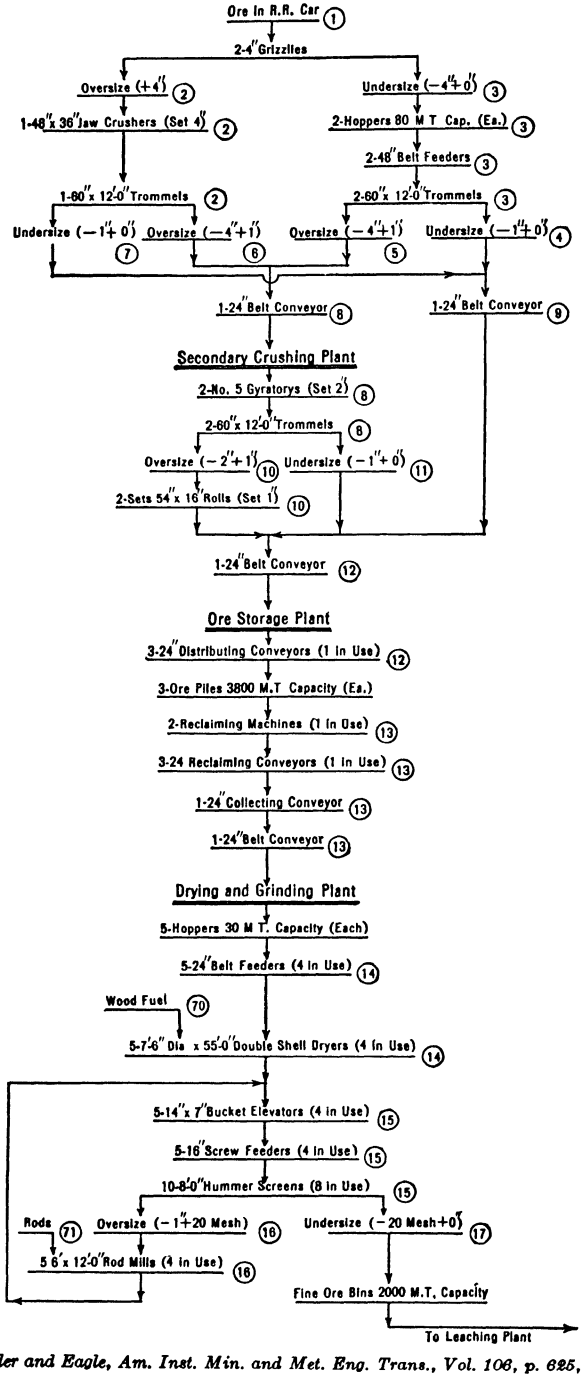
Katanga.[16] In our previous discussion of the metallurgy employed in the Province of Katanga, Belgian Congo, we mentioned the fact that leaching had been employed to treat some of the oxide ores of the Katanga district. The Panda leaching plant, which has a capacity of 30,000 metric tons of copper per year, differs from the plants we have considered so far in two important respects.

1. The leaching is carried on entirely by agitation. The ore contains fine slimes and large quantities of malachite, which effervesces strongly with acid. These two constituents would make it difficult to employ ordinary percolation leaching, so it was decided to use an all-agitation leach. Although the ore is ground finer than is customary at most leaching plants, we can hardly refer to this as an "all-slime" process, because there is plenty of coarse material in the ore as it is leached. In fact this coarse material made it necessary to modify the regular Pachuca tank to prevent segregation during agitation.

2. The ore is of a much higher grade than ores commonly treated by leaching — 6.5 to 7.0 per cent copper as against 0.9 to 1.5 per cent at other leaching plants.

The Ore. The ore is almost completely oxidized, with malachite as the predominating copper mineral. Minor amounts of azurite, chrysocolla, cuprite, and native copper are in evidence, together with traces of sulfides. The gangue is siliceous in character and consists of shales, sandstones, and quartzose rock.

[16] Wheeler, A. E., and Eagle, H. Y., Development of the Leaching Operations of the Union Minière du Haut Katanga: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 609, 1933.



(*Wheeler and Eagle, Am. Inst. Min. and Met. Eng. Trans., Vol. 106, p. 625, 1933*)

FIG. 17–*a*. Flowsheet of Crushing and Grinding Plant, Panda.

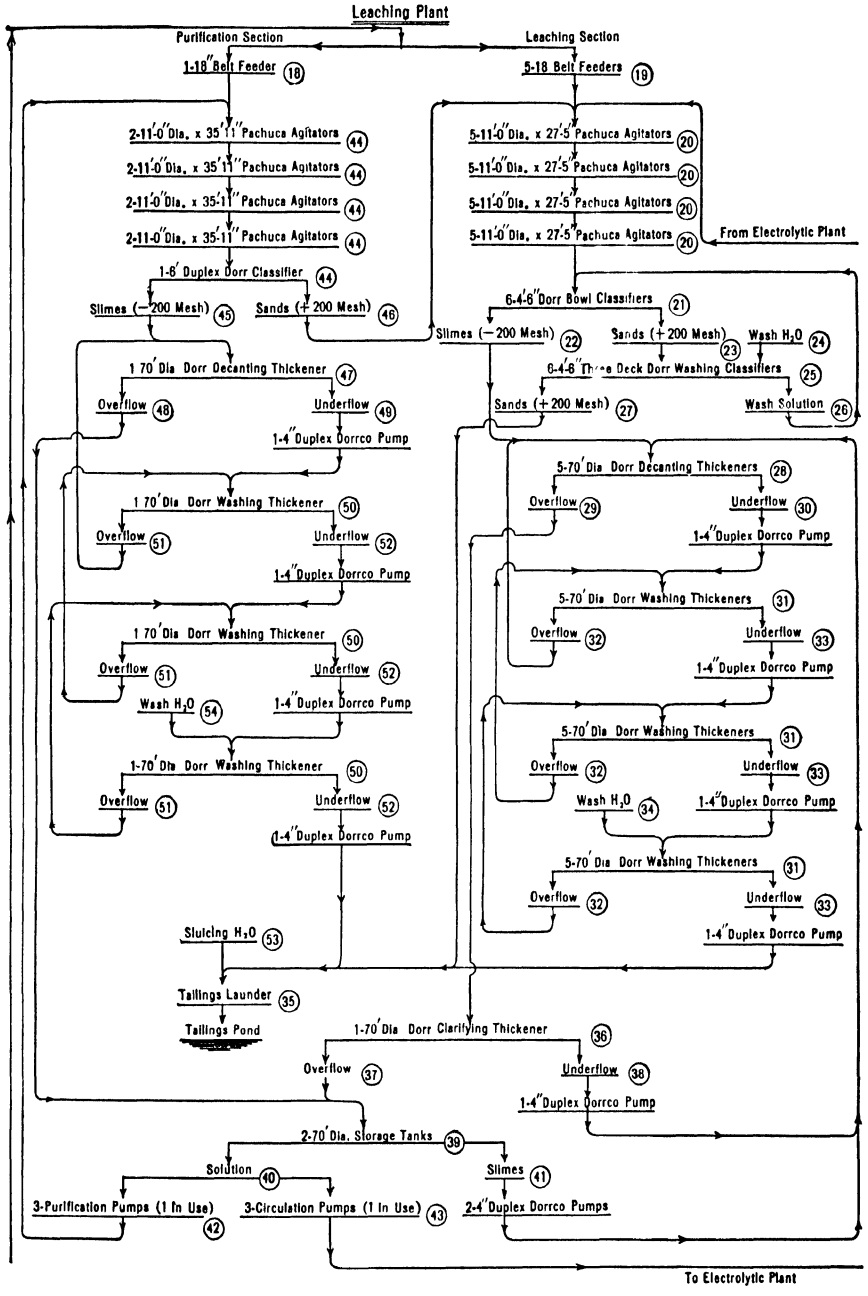


FIG. 17–b. Flowsheet of Leaching Plant, Panda.

The ore is crushed and ground to approximately −20 mesh before it goes to the leaching agitators. The crushing plant contains one primary jaw crusher, two No. 5 gyratories, and two sets of 54- by 16-inch rolls for secondary crushing. The roll product is dried and ground dry in 6- by 12-foot rod mills in closed circuit with a 20-mesh screen. Screen undersize passes to the leaching plant.

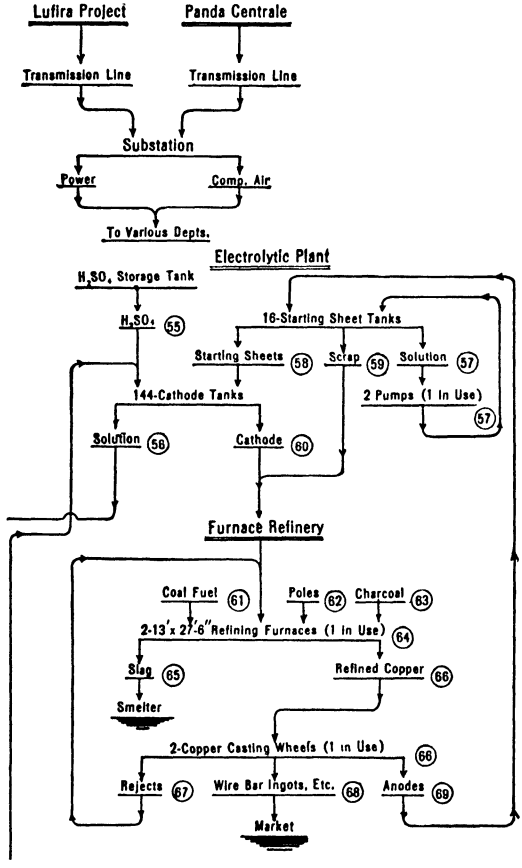


FIG. 17–c. Flowsheet of Electrolytic Plant, Panda.

Leaching Division. The leaching method employed at Katanga differs in several respects from percolation leaching. Some of the important differences are as follows:

1. Ore and leaching solution are agitated long enough to allow dissolution of the copper minerals.

2. Washing and separation of liquid and solids are carried out in

thickeners; simple draining such as is used in vat leaching is not applicable.

3. The process is continuous with respect to both ore and solution, and employs the countercurrent system of leaching and washing.

4. Purification of the solution is conducted in the leaching system by means of an " acid leach " and a " neutral leach."

Figure 17 shows the flowsheet of the leaching plant, and Figure 18 shows the general plant layout. The plant contains 28 agitators of the standard cone-bottomed Pachuca type built of steel and lined with 10-pound chemical lead sheet. They are equipped with a special discharge device to prevent coarse material from building up within the agitator and are provided with a supply of air at 30-pound pressure. Twenty of the agitators are arranged in five parallel sections each with four agitators in series; these constitute the five *acid leach sections.* The other eight agitators make up the *purification section,* which consists of two parallel groups of four tanks each arranged in series.

The bulk of the ore coming from storage is distributed by means of five conveyor belts to the five parallel groups of acid Pachucas. The spent electrolyte flows to the agitator buildings and is distributed to the five acid sections by means of a five-compartment weir box. The solution feed to each section joins the ore feed to that section in a mixing box immediately ahead of the first agitator in the series. The pulp then passes through the four agitators in series, and most of the copper goes into solution here.

After leaving the agitators the pulp goes to one of six 4-foot 6-inch Dorr bowl classifiers which classify the pulp into sands (+200 mesh) and slimes (−200 mesh) which are washed separately. The sands are washed in a three-deck washing classifier which is built integral with the bowl classifier. There are six of these bowl classifier-washing classifier units, one for each acid section and a sixth for a spare. Fresh wash water is added on the third deck of the washing classifier in amount equal to the entrained water carried out in the sand tailings. The washed sand tailings from the third deck of the washing classifier passes directly to the tailing dump.

The slimes from the bowl classifier are washed by countercurrent decantation in a series of four 70-foot Dorr thickeners. The overflow from the first thickener is the strong solution which passes through a clarifying thickener and on to the electrolytic tank house. Wash water is added to the last thickener, and the spigot product of the last thickener goes to the tailing dump. There are five sets of these thickeners, one for each acid circuit. Thus the acid circuit leaches the ore and washes the solution free from the solids. Spent electrolyte enters the

first agitator, and strong solution overflows the first slime washing thickener. The only other solution leaving the system is the water entrained in sand and slime tails. Wash water to replace this is added on the third deck of the sand-washing classifier and to the last of the slime-washing thickeners.

The only impurity in the ore which builds up enough to interfere with electrolysis is iron; some Al_2O_3 is dissolved also, but this is removed with the iron. The solution is purified to keep the iron content below about 5 grams per liter. To attain this result a certain amount of strong solution is circulated through the purification section.

In general the purification section resembles two sections of the acid leach section as far as equipment goes. The method of purification employed is to use an excess of ore to neutralize the free acid in the solution; aluminum and ferric salts hydrolyze in this neutral solution and precipitate as hydroxides In the presence of a large excess of ore or concentrate the sulfuric acid is soon used up and the iron and aluminum salts hydrolyze.

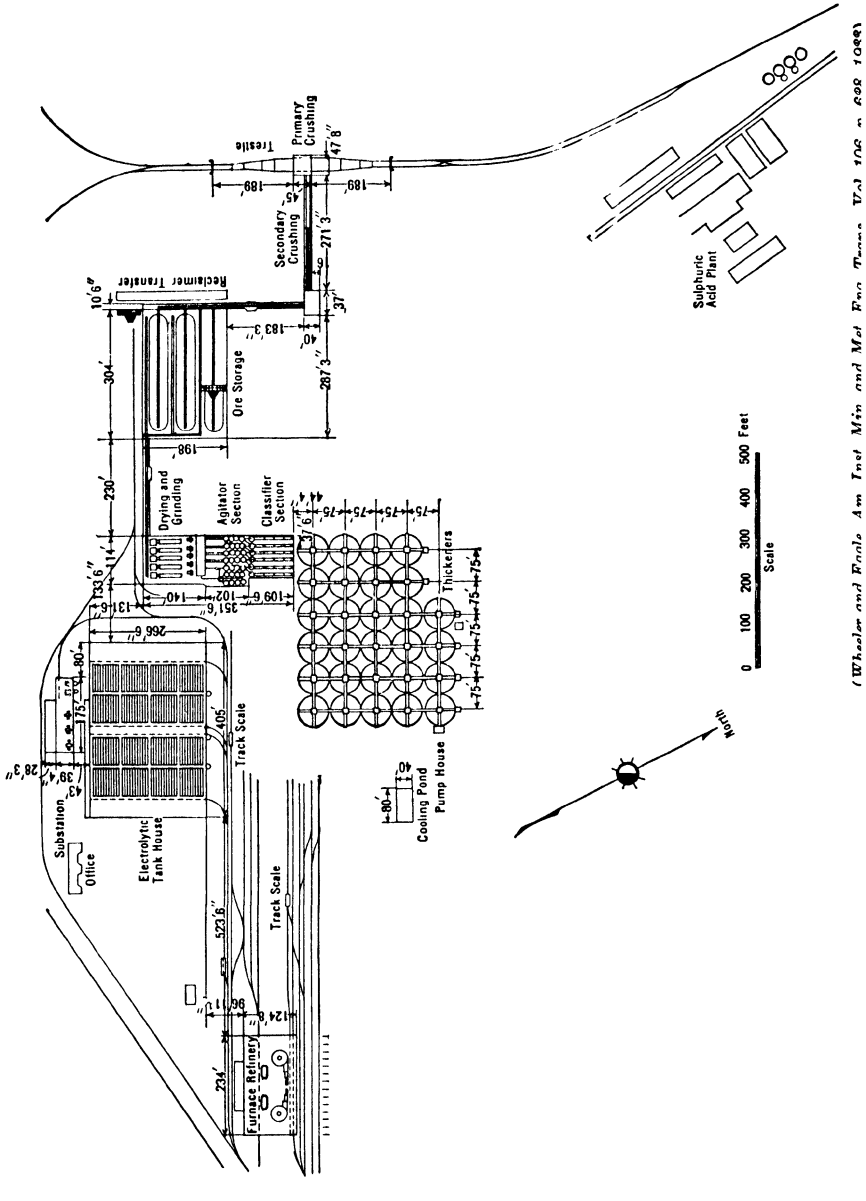
$$Al_2(SO_4)_3 + 3H_2O \rightarrow 3Al(OH)_3 + 3H_2SO_4$$

$$Fe_2(SO_4)_3 + 3H_2O \rightarrow 3Fe(OH)_3 + 3H_2SO_4$$

The acid formed is immediately consumed by the ore or concentrate, and more iron and aluminum are precipitated. Either ore or high-grade oxide concentrate is used for purification; the solution flowing through the system has all the free acid neutralized, drops most of its iron and aluminum, and becomes enriched in copper dissolved from the neutralizing agent.

This method of purification requires an excess of ore, which means that much undissolved copper is left in the "tailing." Also if the solids were sent back to the acid leach, the precipitated impurities would redissolve. The bulk of the undissolved copper is in the "sands" (+200 mesh), and most of the precipitated impurities are in the "slimes" (−200 mesh); so the overflow from the last of the neutral leach Pachucas is sent to a 6-foot Dorr duplex classifier which separates it into sands and slimes. The sands are sent to the head of the acid leach to join the new ore, the slimes are washed through four Dorr thickeners in a neutral circuit, and the spigot product from the last thickener goes to the tailing dump.

The leach solutions are so corrosive that the only materials which can be used in contact with them are lead, Duriron, rubber, asphalt mastic, glass, porcelain, and certain of the chrome-nickel-iron alloys. Thickener tanks have concrete bottoms and steel sides and are lined



(Wheeler and Eagle Am Inst Min and Met Eng Trans Vol 102 p 698 1933)

with lead. Blades in the rake classifiers are made of Duriron, and any steel which could come in contact with the solution is covered with sheet lead.

Electrolysis. The tank house contains 160 electrolytic tanks each 62 feet 6 inches long, 3 feet 2 inches wide, and 4 feet 2½ inches deep, inside dimensions — these are exceptionally long tanks. Tanks are of reinforced concrete lined with 2 inches of asphalt mastic. They are equipped with a feed pipe at one end, an overflow dam at the other, and a hard lead plug and seat in the bottom for draining and cleaning out. Conductor bars 2 by 6⅝ inches in cross-section are supported on wood insulating strips on the tank walls.

Anodes are of antimonial lead containing about 6 per cent antimony, and starting sheets are of the regular type made in stripper tanks using soluble anodes. The electrodes are arranged in three separate groups in each tank, the groups being in series and the electrodes in multiple. The entire tank house is laid out in two main electrical circuits, each taking normally 8000 amperes at 460 volts. Cathodes have a life of 10 to 14 days.

Sixteen of the electrolytic tanks are equipped so that they can be fed with a separate circulation of pure solution, and enough of these tanks are so used to produce the necessary starting sheets from soluble anodes.

Refinery. The furnace refinery is provided with two 130-ton refining furnaces each equipped with a 38-foot Clark casting wheel. The soluble anodes used in the stripper tanks are made in the furnace refinery.

Many of the significant data pertaining to the leaching and electrolysis are given in Tables 16 and 17. Note the effect of the purification cycle on the solution, also the heavy " cut " made by electrolysis reducing the dissolved copper from 30.5 to 16.3 grams per liter.

TABLE 16

SUMMARY OF PLANT OPERATIONS FOR DECEMBER 1929 AT PANDA LEACHING PLANT, KATANGA

Crushing and Drying	
Wet ore crushed	40,056 metric tons
Moisture in wet ore	13.20%
Cu in dry ore	6.57%
Wet ore to driers	39,984 metric tons
Moisture in dried ore	0.24%
Leaching Division	
Dry ore fed to leaching, weight	32,631 metric tons
Dry ore fed to leaching, copper assay	6.539%
Dry concentrates fed to purification, weight	1,058 metric tons
Dry concentrates fed to purification, copper assay	28.70%
Classifier sands:	
Copper assay (dry)	0.442%
Entrained solution	29.19%
Cu in entrained solution	11.84 g/l
Free H_2SO_4 in entrained solution	0.00 g/l
Acid slime tails:	
Copper assay (dry)	0.177%
Entrained solution	49 39%
Cu in entrained solution	9.52 g/l
Free H_2SO_4 in entrained solution	0.00 g/l
Purification slime tails:	
Copper assay (dry)	0.426%
Entrained solution	57.20%
Cu in entrained solution	11 33 g/l
Free H_2SO_4 in entrained solution	0.00 g/l
Tailing:	
Sand tails, % of total tailing	40.54%
Acid slime tails, % of total tailing	56.08%
Purification slime tails, % of total tailing	3 38%
Total weight of tails per metric ton of ore	0 869 metric ton
Total weight of tails per metric ton of concentrates	0 491 metric ton
Total extraction (% of total copper dissolved; 100% − chemical loss)	96.53%
Total recovery (% of total copper delivered to electrolysis; 100% − chemical loss − mechanical loss)	88.34%
Electrolytic Division	
Copper produced per kw-hr	0.471 kg (1.03 lb)
Ampere efficiency	78.53%
Volts per circuit	444.69 volts
Voltage across adjacent electrodes:	
Commercial tanks	1.97 volts
Stripper tanks	0.39 volt
Tanks in service, total	160
Commercial	148
Stripper	12

TABLE 17

AVERAGE SOLUTION ASSAYS, IN GRAMS PER LITER, AT PANDA LEACHING PLANT

	Tank House		Acid Agitation	Purification	
	Feed	Discharge		Feed	Discharge
Cu	30 51	16 26	30 53	30.17	44 98
Free H_2SO_4	5 50	34.35	12 22	11 17	0.00
Fe, total	5 63	5 63	6 65	5.81	1.99
Fe, ferric	5.43	3.97	6 34	4.98	1.42
Fe, ferrous	0 20	1.66	0 31	0 83	0.57
Al_2O_3	11.00	11 00	11 70	10 88	7.50

OTHER IMPURITIES ACCUMULATED IN SOLUTION

Co	Mn	MgO	SiO_2	P_2O_5	CaO
10.03	6.50	13 60	1.72	3.80	0.34

GRADE OF COPPER PRODUCED BY ELECTROWINNING

The cathode copper produced by leaching and electrolysis has about the same purity as electrolytically refined copper. Several typical analyses are given in Table 18, and for the sake of comparison some analyses of electrolytically refined copper are included.

TABLE 18

ANALYSES OF ELECTROLYTIC COPPER[a]

ELECTROWINNING

Source	Cu	Au	Ag	S	As	Sb
Andes; wirebars[b]	99 9610	Trace	0 019	0 0017	0 0005	0 0002
Inspiration; cathodes[c]	99 87	.....		0 045	Trace	0.0005
Chuquicamata; cathodes[d]	99 900	. ..	..	0 03	0 0002	0.0004
Chuquicamata; wirebars[d]	99 9600		..	0 0016	0 0002	0.0004

ELECTROREFINING

Montreal East; wirebars[e]	99 965	0 015	0 2	0 0013	0.0001	0 0001
Ontario; wirebars[f]	99 960		0 0012	0 0018	0 0005	0.0010
Raritan; wirebars[g]	99 95	0 003	0 0010	0 0020	0.0015	0 0015
Great Falls; wirebars[g]	99 955	.	0 0034	0 0019	0 0015	0 0009

ELECTROWINNING

Source	Fe	Co+Ni	O_2	Sc+Fe	Zn	Cl	Pb	Sn
Andes; wirebars[a]	0 0013	0 0001	0 0351	.....	.	.. .	.....	.....
Inspiration; cathodes[b]	0.021	0 0006	.....	.....	Trace	Trace	.....	.....
Chuquicamata; cathodes[c]	0.0050	.....	...	...	0 0003	0 005	0.0016	0 0011
Chuquicamata; wirebars[c]	0 0016		0 0320		Trace		0 0008	0 0006

ELECTROREFINING

Montreal East; wirebars[d]	0.0016	0.0002	0 035	0 0002	....		0.0007	.....
Ontario; wirebars[e]	0 0013	0 0016	0 0300	0 0032	.....	....	0.0003	.....
Raritan; wirebars[f]	0.0025	0 0015	0 035	. .	.....	.....	.....	.....
Great Falls; wirebars[f]	0.0026	0 0014	0.030	.....	.....	.....	.....	.....

[a] Au and Ag in ounces per ton, all others in percentage

[b] Callaway, L A , and Koepel, F. N , Metallurgical Plant of the Andes Copper Mining Co.: Am. Inst Min and Met Eng Trans., Vol. 106, p 726, 1933

[c] Aldrich, H. W , and Scott, W. A., The Inspiration Leaching Plant: Am. Inst. Min. and Met Eng. Trans , Vol. 106, p 650, 1933.

[d] Campbell, T C , A Brief Description of the Reduction Plant of the Chile Exploration Company at Chuquicamata, Chile, S. A : Am Inst Min and Met. Eng Trans , Vol 106, p. 559, 1933.

[e] McKnight, H. S., Montreal East Plant of Canadian Copper Refiners, Ltd · Am. Inst. Min and Met. Eng Trans , Vol. 106, p 352, 1933.

[f] Benard, Frederic, Electrolytic Copper Refinery of Ontario Refining Company, Ltd · Am Inst Min. and Met. Eng. Trans., Vol. 106, p. 369, 1933.

[g] Burns, W. T , Refining Anaconda Copper at Raritan and Great Falls· Eng. and Min. Jour , Vol. 128, No. 8, p. 306, 1929.

OTHER LEACHING METHODS

There have been many leaching operations utilized at one time or another in the metallurgy of copper, but we have confined our discussion principally to methods which are being used commercially to extract copper from its ores. To present commercial practice, the following statements apply:

1. The most common type of leaching is sulfuric acid leaching used on low-grade ores in large-scale operations.

2. Certain special ores (or tailings) containing either native copper or copper carbonates are treated by ammonia leaching.

3. Sulfides are not attacked by sulfuric acid alone but require an oxidizing agent in addition. The oxidation may be carried on as a separate operation (weathering, roasting) or the oxidizing agent may be dissolved in the leach solution (ferric salts).

4. Electrolytic precipitation is used with sulfuric acid leaching. The low-grade solutions from heap leaching and mine waters and the pregnant solution from an ammonia leach are not adapted for electrolytic precipitation.

5. Acid leaching has been applied to ores containing both oxides and sulfides (e.g., at Inspiration), but all-sulfide ores are still treated by milling followed by smelting of the concentrate.

We have already mentioned the question of using leaching methods for treating high-grade sulfide concentrates, and we shall conclude this chapter with a brief description of an experimental plant designed for this purpose. Up to the present, no full-scale commercial plant has been put into operation to treat copper sulfide concentrates by leaching.

Bagdad Copper Corporation.[17] The pilot plant at the Bagdad properties near Hillside, Arizona, treats two types of concentrates — (1) a chalcopyrite concentrate containing 25 per cent copper and (2) a chalcocite concentrate assaying as high as 45 per cent copper. These concentrates are first given a special roast which aims to put the copper in the form of CuO and the iron in the form of Fe_2O_3. Under these conditions the copper is soluble in sulfuric acid and the iron only slightly soluble.

Roasting, First Stage. The first stage is a low-temperature roast designed to remove all the sulfide sulfur and convert copper and iron to oxides and sulfates. The first oxidation of sulfur begins at 500° F (260° C) with the expulsion and burning of the free-atom sulfur in pyrite and chalcopyrite. Oxidation continues to the end of this stage,

[17] Baroch, C. T., Hydrometallurgy of Copper at the Bagdad Property: Am. Electrochem. Soc. Trans., Vol. 57, p. 205, 1930. From a paper presented before the 1930 meeting of the American Electrochemical Society, Inc.

at which point the roast is "dead," i.e., it shows no glowing particles or sparks when rabbled, and there are only traces of SO_2 in the furnace gases. The calcine consists of cuprous oxide, Cu_2O; ferrous oxide, FeO; a magnetic oxide, probably $FeO{\cdot}Fe_3O_4$ or $FeO{\cdot}Fe_2O_3$; and some cupric and ferrous sulfates. The calcine at the end of the first stage is black or gray, sometimes with a brownish tinge, and is so magnetic that almost the entire mass can be picked up with a magnet.

Temperature control determines the amount of sulfates formed. From 700° to 720° F (370° to 380° C) appears to be the temperature of maximum sulfate formation, and as much as 60 per cent of the copper may be present as sulfate at 700° F, but at 850° F (455° C) only 15 per cent of the copper will be present as the sulfate.

Although the calcine is strongly magnetic, it appears that the iron is not present as a true magnetite as long as the temperature remains below 850° F. Above this temperature a true magnetite forms, probably by the reaction:

$$FeS + 10Fe_2O_3 \rightarrow 7Fe_3O_4 + SO_2$$

This magnetite is difficult to reoxidize to Fe_2O_3.

The object of the first roasting stage, therefore, is to keep the temperature below 850° F until all the sulfides are decomposed; after the sulfides are gone there is no danger of reducing Fe_2O_3 to refractory magnetite.

Roasting, Second Stage. The second stage is an oxidizing and demagnetizing period, and its object is to produce the higher oxides of copper and iron.

$$2Cu_2O + O_2 \rightarrow 4CuO$$

$$4FeO + O_2 \rightarrow 2Fe_2O_3$$

$$4FeO{\cdot}Fe_2O_3 + O_2 \rightarrow 6Fe_2O_3$$

True crystalline magnetite, if present, does not readily oxidize to Fe_2O_3. Moreover, if sulfides and the concomitant SO_2 are present, some of the cupric oxide will be reduced back to Cu_2O, thus:

$$2CuO + SO_2 \rightarrow Cu_2O + SO_3$$

The presence of Cu_2O in the finished calcine is undesirable for leaching, as we shall see later.

Temperatures during the second stage are not critical, and the oxidation depends principally upon the amount of oxygen in the roaster atmosphere and the use of thorough rabbling to insure contact of the oxygen with the charge. The best temperature for the second roast is

about 980° F (530° C), but the temperature may range from 850° to 1000° F (455° to 540° C).

As the calcine progresses through the second stage the magnetic properties become less pronounced and finally disappear entirely, and the color gradually changes to the brilliant red of ferric oxide; in fact the color of the calcine can almost be used instead of control assays; the color comparisons must be made on cooled calcine, as all hot calcines are dull black.

Roasting, Third Stage. The third stage is essentially an extension of the second stage in which the temperature is raised to about 1040° F (560° C), and its purpose is to decompose the water-soluble sulfates of iron. Anhydrous ferric sulfate begins to decompose into ferric oxide and SO_3 at about 300° F and cannot exist above 716° F (380° C) as normal ferric sulfate. However, it forms a basic sulfate, probably $Fe_2O_3 \cdot 2SO_3$, which does not decompose completely below 1040° F (560° C). Much of the liberated SO_3 combines with CuO to form $CuSO_4$. A temperature of 1200° F (650° C) is required to decompose $CuSO_4$, and it is found that heating to this temperature invariably forms a black magnetic iron oxide which is fairly soluble in acid solutions.

The control of the entire process depends upon the roasting operation, and the most critical point in the roast is the transition point between the first and second stages. If the temperature is allowed to rise above 850° F before all the sulfide sulfur is removed the calcine will invariably show low copper solubility and high iron solubility. The principles involved in this roast are covered in U. S. Patent No. 1,674,491, issued to Herbert E. Wetherbee.

Table 19 gives the analyses of the calcines produced from the chalcocite and chalcopyrite concentrates.

The results given in Table 19 are from laboratory data, and although larger-scale tests were not quite as good, the results of all the tests seemed to indicate that extractions of 97 per cent could be made on a regular commercial scale.

Leaching and Electrolysis. The leaching and electrolysis of properly roasted calcine do not appear to present any difficulties over present commercial leaching practice. It is indicated that these high-grade concentrates can best be leached by agitation followed by thickening and filtration of the tailing. It should be noted that the tailing produced would amount to only about 50 to 60 per cent of the calcine because of the large amount of soluble material in it.

One of the principal sources of copper losses is the presence of Cu_2O in the calcines. This compound does not represent the highest stage

TABLE 19

ANALYSES OF ROASTED CHALCOCITE AND CHALCOPYRITE CONCENTRATES, BAGDAD, PER CENT

	Chalcocite		Chalcopyrite	
	Concentrates	Calcines	Concentrates	Calcines
Cu, total	37.50	30.30	26.10	25.00
Cu, acid soluble	.....	30.20	.....	24.70
Cu, water soluble	.....	21 00	.....	19.10
Fe, total	23 30	19 20	28.30	27.20
Fe, acid soluble	. ...	0.10	.....	0.44
Fe, water soluble	. .	Trace	.....	Trace
S, total	30.20	11 42	33.30	8 70
S, water soluble	.. .	11.22	.....	6.36
Insoluble	11 00	9 10	9.80	9.45

NOTE. In the case of the chalcocite concentrate, 99.7 per cent of Cu in the calcine is acid soluble and 69 3 per cent is water soluble, for chalcopyrite, 98 8 per cent of the Cu in the calcine is acid soluble and 76 4 per cent is water soluble

of oxidation of copper, and consequently only half of it will dissolve in sulfuric acid.

$$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + H_2O + Cu$$

The precipitated copper will not be dissolved except by long continued agitation with hot sulfuric acid or by the addition of some expensive or detrimental oxidizing agent (e.g., ferric sulfate).

The large amount of water-soluble copper ($CuSO_4$) in these calcines indicates that electrolysis of the leach solutions will produce an excess of free acid; where acid-consuming oxidized ore is present, this could be leached with this excess acid. Electrolytic precipitation should work successfully and should produce copper of standard " electrolytic " grade.

This process should be applicable to a wide variety of copper ores and concentrates, as the principal impurity, iron, is efficiently handled in the roasting; arsenic and antimony could also be controlled by the addition of a purification step following the leaching.

Recovery of Gold and Silver. The Bagdad ores contain only traces of gold and silver, so no effort was made to recover these metals. Laboratory experiments, however, seemed to indicate that the residual copper in well-washed tailing did not behave as a cyanicide, so that the cyanidation process might be employed where the concentrate contained gold. Chlorination methods might also be used for gold recovery.

For calcine tailings containing considerable silver, a chloridizing roast would probably be indicated, followed by a leach and precipitation on scrap iron, as in the Longmaid-Henderson process. This method would recover the residual copper in the tailings as well as the silver.

CHAPTER X

PROPERTIES OF COPPER[1]

PHYSICAL PROPERTIES

General. Copper and gold are the only two metals which are strongly colored. Copper has a reddish or rose color on a fresh surface, but old surfaces often have an orange tinge due to a film of cuprous oxide. Molten copper is light green, and very thin sheets of copper appear green by transmitted light because the green light passes through while other light rays are largely absorbed. Very finely divided copper is black, as are all finely divided metals.

Crystal faces, polished surfaces, and the surface of liquid copper display a metallic luster, but roughened surfaces, such as cathode deposits, and finely divided copper powder show no luster.

Crystallization. Copper crystallizes in the face-centered cubic lattice pattern,[2,3] and the side of the unit cube in the crystal lattice is 3 597 Angstrom units; the unit cube contains four atoms. Twenty other elements crystallize in the face-centered cubic pattern, including the following metals:

Silver	γ-Iron	Platinum
Aluminum	Iridium	Palladium
Gold	β-Nickel	Rhodium
α-Cobalt	Lead	

The face-centered cubic arrangement corresponds to one of the two possible patterns obtained by the closest packing of spheres (the other gives the "hexagonal close-packed" pattern). The metals in this class are usually rather ductile. The most ductile metals have the

[1] Data quoted in this chapter are from the following sources, with index numbers as follows:

[2] Wyckoff, R. W. G., The Structure of Crystals: Reinhold Publishing Corporation, New York, 1931.

[3] Handbook of Chemistry and Physics, 19th ed., Chemical Rubber Publishing Co., Cleveland, 1934

[4] Metals Handbook, 1936 ed., American Society for Metals, Cleveland.

[5] Eshbach, O. W., Handbook of Engineering Fundamentals: John Wiley and Sons, Inc., New York, 1936.

face-centered cubic crystal lattice (silver, copper, lead, aluminum, palladium, etc.).

Copper has no allotropic modifications, as do some other metals (e.g., iron, cobalt, nickel, chromium), and therefore has no "critical temperatures" at which changes take place in the crystal pattern. Many heat-treating operations used on metals and alloys depend upon allotropic changes, but these have no application to copper.

When copper is cold-worked it becomes harder, but the hardness can be removed by annealing. The softening effect is accompanied by the formation of a new crop of small equi-axed crystals replacing the elongated crystals of the cold-worked metal. The lowest temperature at which this phenomenon takes place is the *recrystallization* temperature, and the recrystallization temperature[4] for copper usually ranges from 200° to 400° C.

Highly purified copper will recrystallize at 100° C if annealed for a long time, but commercial copper contains impurities, notably silver, antimony, and arsenic, which raise the recrystallization temperature. Electrolytic copper begins to recrystallize at about 200° C (400° F), and Lake copper or other arsenic- or silver-bearing copper recrystallizes at about 350° C (550° F).

In spite of its high purity, the recrystallization temperature of oxygen-free copper is higher than that of ordinary tough-pitch electrolytic copper.

Rolled copper normally shows a small grain size (0.02 to 0.05 mm in diameter) and will not possess any directional properties; cold-rolled copper will have elongated or distorted grains, but these will be oriented at random as far as their crystal axes are concerned.

Density.[4] The density of commercial copper samples will range from 8.4 to 8.94 grams per cc. Cast tough-pitch copper contains about 3 to 5 per cent voids or gas holes, by volume, and such copper will have an apparent density of 8.4 to 8.7. The voids are closed up during rolling, and after working and annealing the density of tough-pitch copper will be 8.90 to 8.93, depending on the oxygen content; copper containing 0.03 per cent oxygen has a maximum density of 8.92.

Deoxidized and oxygen-free copper freezes without the voids and gas holes found in tough-pitch castings, and accordingly there are always deep pipes or shrinkage cavities in deoxidized or oxygen-free copper castings, caused by the volume shrinkage. The density of these coppers will range from 8.80 up to 8.90 for castings, and worked pieces will approach the maximum of 8.94. For commercial coppers containing over 99.85 per cent copper, the following formula employed by the

[4] Metals Handbook, 1936 ed., p. 1061, American Society for Metals, Cleveland.

American Brass Company gives the density at 20° C.

$$d = 8.933 - 0.44\ (100 - \%\text{Cu})$$

Liquid copper has a density of 7.93 at the melting point, and 7.53 at 1600° C.

Mechanical Properties. Copper is one of the most ductile of metals and is also rather malleable. Pure copper is not particularly strong or hard in the soft or annealed condition, but both strength and hardness are increased considerably by cold working.

Strength.[4] The tensile strength of pure copper (containing 0.015 per cent oxygen) in the form of an annealed rod ⅝ inch in diameter is 31,790 pounds per square inch. This may be taken as the strength of " pure " copper in the annealed condition. The tensile strength of other specimens will depend on the chemical composition, heat treatment, and mechanical treatment. For commercial copper, the tensile strength of the hot rolled or annealed metal is about 30,000 to 36,000 pounds per square inch.

Cold working increases the tensile strength to a maximum of about 70,000 pounds per square inch for severely cold-worked copper.

Hardness.[5] Copper is one of the softer metals. Soft copper in the annealed or hot-rolled condition will have a Brinell hardness number of about 42. Cold-rolled copper is harder and will have a hardness of about 103 Brinell.

Ductility. Annealed or hot-rolled copper is a very ductile metal and will show an elongation of about 50 per cent in length (2 inches) when pulled in a tensile machine. Cold working reduces the ductility, and severely cold-worked copper will show an elongation of only 5 per cent. Figure 2 shows the effect of cold working on tensile strength and ductility (the latter measured by both per cent elongation and per cent reduction in area of the specimens). Copper is also very malleable but there is no quantitative criterion for malleability.

Ductility specifically refers to the ability of metal to be drawn into wire, but the term is often used to mean the same as *formability,* which is a more general term and refers to that property of the metal which determines its response to all forms of mechanical working. The ductility is measured by the elongation and reduction of area of a tensile specimen as we have noted; other special tests are used to determine the formability — for example, the " cupping test " to measure the amenability of sheet metal for cold-drawing or stamping.

[4] Idem, p. 1065.

[5] Eshbach, O. W., Handbook of Engineering Fundamentals, p. 11–44: John Wiley and Sons, Inc., New York, 1936.

Oxygen-free copper is notably more ductile than tough-pitch copper and is used for "deep drawing," where the metal must undergo severe cold working.

Elastic Properties. Soft copper has very little elasticity or resilience, but both of these properties are increased if the copper is cold worked. Soft copper has an "elastic limit" or "yield point" of 5000 to 17,000 pounds per square inch, depending on the convention used in defining these terms; there is very little true elastic deformation, and even small loads produce some permanent deformation. Cold-rolled copper will have a yield point of 44,000 to 48,000 pounds per square inch. Young's modulus for hard copper is about 16,000,000 pounds per square inch.

Endurance Limit.[4] The endurance limit, which measures the maximum stress below which the metal will not fail from repeated stresses or "fatigue," is 10,000 pounds per square inch for soft copper. Cold-worked copper may have an endurance limit as high as 20,000 pounds per square inch, but 15,000 is probably a more conservative figure. These values are all for commercial tough-pitch copper.

Weldability, Etc. Copper can be silver soldered, brazed, or welded, and the welding may be done by either the arc or oxyacetylene method. For any welding operation where the copper is exposed to the action of reducing gases and high temperatures it is best to use deoxidized or oxygen-free copper. Even the small amount of oxygen in tough-pitch copper will cause embrittlement of the metal due to the segregation of cuprous oxide at the grain boundaries and reduction of the oxide by the gases.

Copper cannot be cut by the oxygen lance, as can iron and steel, because of its high thermal conductivity; heat is carried away so rapidly that it cannot be localized at the spot where the metal is to be cut.

"Hardening" and "Tempering" of Copper. We have been referring to hard and soft copper in the previous discussion, and in every case the term "hard" copper has meant copper hardened by cold working; there is no other way to harden pure copper.

The so-called lost art of "hardening" or "tempering" copper still comes in for its share of attention, although it has been pretty well demonstrated that the hardening of copper by heat treatment is impossible. The hardening of steel, for example, depends largely upon the fact that iron exists in several allotropic forms; copper, however, has no allotropic modifications. Moreover, it is doubtful if any pure metal can be hardened by quenching (or other heat treatment) even

[4] Metals Handbook, 1936 ed., p. 1071, American Society for Metals, Cleveland.

though it does possess allotropic modifications. Pure iron cannot be hardened by quenching, although steel (an iron-carbon alloy) can be so hardened.

Annealing is the only form of heat treatment applied to pure copper, and it is used to soften copper made hard by cold working. Certain copper alloys can be hardened by heat-treating methods, but these are fundamentally different from pure copper even though the amount of the alloying ingredient may be very small.

Thermal Properties. Table 1 lists the important thermal constants of copper. Copper is the second best heat conductor of all the metals, being surpassed in this respect only by silver. Comparative values[3] for thermal conductivity for different metals at room temperature are as follows:

	Heat Conductivity (cal/cm^2/cm/sec/° C)
Silver	1.006
Copper	0.918
Gold	0.705
Aluminum	0.480
Iron	0.161

TABLE 1

THERMAL PROPERTIES OF COPPER[4]

Melting point	1083 0° C (1981.4° F)
Boiling point	2325° C (4217° F)
Latent heat of fusion	50 46 cal/gram (90.83 Btu/lb)
Specific heat (25° C)[a]	0 0919 cal/gram/°C
Linear coefficient of expansion (20° C)[b]	16 42 $\times 10^{-6}$/°C
Thermal conductivity (20° C)[c]	0.923 cal/cm^2/cm/sec/°C

[a] A formula for specific heat which applies in the range 0° to 100° C is

$$c = 0\ 09088\ (1 + 0\ 0005341t - 0\ 00000048t^2)/\text{cal/gram/°C}$$

It will be noted that there are discrepancies in these different values, due principally to small variations in composition and condition of the samples investigated Such discrepancies will be found in published data for other properties of copper

[b] A formula for the linear coefficient of expansion which applies in the range 16° C to 300° C is given below L_o is the length of the specimen at 0° C, and L_t its length at t° C This formula was derived for hot-rolled copper rod containing 99.968% copper.

$$L_t = L_o\ (1 + 0\ 00001623t + 0.00000000483t^2,$$

[c] The thermal conductivity decreases as the temperature rises, and the following values apply in the range 0° C to 600° C.

°C	Thermal Conductivity	°C	Thermal Conductivity
0	0.912	300	0 879
20	0.910	400	0 867
100	0.901	500	0 856
200	0 890	600	0.845

[4] Metals Handbook, 1936 ed., p. 1060, American Society for Metals, Cleveland.

[3] Handbook of Chemistry and Physics, 19th ed., op. cit., p. 1263.

Electrical Properties. The high electrical conductivity of copper, more than anything else, accounts for its widespread use. Only one metal, silver, has a higher electrical conductivity than copper; aluminum is the principal rival of copper for certain types of electrical conductors, but in general copper is the best material available for carrying an electric current.

Pure copper of electrolytic grade or its equivalent is the best for electrical use; many impurities greatly decrease the conductivity of copper, and there are no alloying elements which will improve it. Following is a list of the electrical resistivities of a few metals for comparison:

Metal	*Resistivity, ohm/cm³ (18° to 20° C)*
Silver	1.629×10^{-6}
Copper (annealed)	1.724×10^{-6}
Gold	2.44×10^{-6}
Aluminum	2.828×10^{-6}
Iron	10.0×10^{-6}
Lead	22×10^{-6}

The property which measures the resistance of a metal to the flow of electricity may be expressed as *resistivity* or as *conductivity,* which is the reciprocal of resistivity. The unit of resistivity is the *ohm;* the unit of conductivity is the *reciprocal ohm* (*mho*). The *specific resistivity* is the resistance in ohms of a section of standard dimensions; generally, as in the listing above, this is a piece 1 centimeter long with a uniform cross-section of 1 square centimeter. But other dimensions may be used, as we shall see later. The resistance of a conductor increases directly with the length of the conductor, and inversely with its cross-section; thus the resistance of a copper bar 1 meter long and 2 square centimeters in cross-section would be:

$$\frac{1.724 \times 10^{-6}}{2} \times 100 = 0.862 \times 10^{-4} = 0.0000862 \text{ ohm}$$

The conductivity of the same piece would be

$$\frac{1}{0.0000862} = 13{,}550 \text{ mho}$$

and the *specific conductivity* of copper would be

$$\frac{1}{1.724 \times 10^{-6}} = \frac{10^6}{1.724} = 580{,}000 \text{ mho}$$

The conductivity of copper, however, is usually expressed in another fashion, namely as per cent of the resistance known as the *International*

Annealed Copper Standard. This value was adopted in 1913 to represent the average conductivity of high-grade commercial conductivity copper, and copper having the same conductivity is said to have 100 per cent conductivity. If a given sample of copper has a conductivity of 96.4 per cent, this means that its conductivity is 0.964 times that of the International Standard. Present day copper for conductivity purposes usually has a conductivity of 100 to 101 per cent, and occasional samples may run as high as 102 per cent.

The example we have given before (1.724×10^{-6} ohm per cm^3) is an example of *volume resistivity.* Resistivity and conductance may also be given in *mass units;* thus if we say that a sample of copper has a resistance of 0.15 ohm per meter-gram, we mean that 1 gram of the metal drawn into a uniform wire 1 meter long would have a resistance of 0.15 ohm. The density of commercial copper is subject to slight variations (as we have noted), and metal is bought by the pound rather than by the cubic foot; consequently the use of mass conductivity and resistivity is more common than the use of volume conductivity and resistivity.

There are many different ways of expressing conductivity and resistivity; Table 2 gives a number of different values — all these are equivalent to the International Annealed Copper Standard. In the parentheses the length of the conductor is given first; area or mass second.

TABLE 2[4,5]

EQUIVALENTS OF THE INTERNATIONAL ANNEALED COPPER STANDARD AT 20° C

Volume resistivity:

1.7241×10^{-6} ohm (cm, cm^2)
1.7241 microhm[a] (cm, cm^2)
0.67879 microhm (in , $in.^2$)
10.371 ohm (ft, mil)
0.017241 ohm (meter, mm^2)

Volume conductivity:

0.5800 megmho[b] (cm, cm^2)

Mass resistivity: (density = 8.89)

0.15328 ohm (meter, gram)
875.20 ohm (mile, pound)

[a] 1 microhm = 10^{-6} ohm.
[b] 1 megmho = 10^6 mho.

[4] Metals Handbook, 1936 ed., p. 1063, American Society for Metals, Cleveland.
[5] Eshbach, O. W., op. cit., p. 11-94.

The electrical resistivity of copper varies with temperature, and from room temperature to the melting point of copper the variation is almost linear. An expression[4] for the mass resistivity of copper in the range 0° to 150° C is

$$R_t = R_0(1 - 0.0041151t - 0.0000019988t^2)$$

At extremely low temperatures copper (and other metals) exhibits *super-conductivity*, i.e., its electrical resistance almost vanishes. Some of the values for conductivity at low temperatures are:[3]

Temperature	Resistivity, ohm (cm, cm^2)
20° C	1.7241×10^{-6}
−100° C	0.904×10^{-6}
−206.6° C	0.163×10^{-6}
−258.6° C	0.014×10^{-6}

Cold working increases the resistivity of copper, and the original conductivity is restored by annealing.

CHEMICAL PROPERTIES

Table 3 gives the chemical constants for the element copper.

TABLE 3[3,4]

CHEMICAL CONSTANTS FOR COPPER

Atomic weight	63.57
Atomic volume	7.11
Atomic number	29
Valence	1 or 2
Electrochemical equivalent,	Cu″ 0 32940 mg/coulomb
	Cu′ 0 65880 mg/coulomb

Symbol, Cu (Latin *Cuprum* from Latin *Cyprium*, the Island of Cyprus)
Position in periodic system—Group I, Series, 5, Period 3

[3] Handbook of Chemistry and Physics, 19th ed., Chemical Rubber Publishing Co., Cleveland, 1934.
[4] Metals Handbook, 1936 ed., American Society for Metals, Cleveland.

In the electromotive series copper lies below hydrogen and hence is not dissolved in dilute acids with the evolution of hydrogen. Iron, lead, tin, nickel, and zinc are all above copper in the series, and therefore can be used to displace or *cement* copper from solutions of its salts. Platinum, palladium, gold, silver, and mercury are below copper (more " noble ") and can be displaced from solution by metallic copper.

[4] Metals Handbook, 1936 ed., American Society for Metals, Cleveland.
[3] Handbook of Chemistry and Physics, 19th ed., op. cit., p. 1338.

The standard electrode potential for copper, as well as for a few of the common metals, is given in Table 4.

TABLE 4[3]

ELECTRODE POTENTIALS

[Metals Arranged in Order of Their Sequence in the Electromotive Force Series]

Element	Ion	Electrode Reaction	Electrode Potential (volts)
Na	Na^+	$Na \rightleftharpoons Na^+ + e$	+2 7146
Zn	Zn^{++}	$\frac{1}{2}Zn \rightleftharpoons \frac{1}{2}Zn^{++} + e$	+0 7618
Fe	Fe^{++}	$\frac{1}{2}Fe \rightleftharpoons \frac{1}{2}Fe^{++} + e$	+0 441
Ni	Ni^{++}	$\frac{1}{2}Ni \rightleftharpoons \frac{1}{2}Ni^{++} + e$	+0 231
H_2	H^+	$\frac{1}{2}H_2 \rightleftharpoons H^+ + e$	0.0000
Cu	Cu^{++}	$\frac{1}{2}Cu \rightleftharpoons \frac{1}{2}Cu^{++} + e$	−0.344
Cu	Cu^+	$Cu \rightleftharpoons Cu^+ + e$	−0 470
Ag	Ag^+	$Ag \rightleftharpoons Ag^+ + e$	−0 7978
Au	Au^{+++}	$\frac{1}{3}Au \rightleftharpoons \frac{1}{3}Au^{+++} + e$	−1 360

[3] Handbook of Chemistry and Physics, 19th ed., p 850, Chemical Rubber Publishing Co , Cleveland, 1934.

Although copper does not displace hydrogen from acids, it readily dissolves in oxidizing acids (such as strong nitric acid) or in acids plus an oxidizing agent (e.g., $H_2SO_4 + Fe_2(SO_4)_3$). Copper resists the action of the atmosphere and corrosive sea water and is widely employed for this reason. It does not usually give satisfactory service when exposed to acids, ammonia, or sulfur compounds. As we have noted, tough-pitch copper becomes embrittled when exposed to reducing gases at moderately high temperatures.

Copper exposed to the atmosphere for a long period of time develops a bright green protective surface coating or *patina* of basic copper carbonate. Artificial patinas can be developed on copper surfaces by the action of special reagents.

Gases in Copper.[6] Molten copper dissolves many of the common gases such as O_2, N_2, CO_2, CO, SO_2, H_2, and H_2O. Many of these undoubtedly react with the copper or with other compounds, thus dissolved oxygen is probably in equilibrium with Cu_2O:

$$4Cu + O_2 \rightleftharpoons 2Cu_2O$$

and reducing gases such as CO and H_2 react with any Cu_2O to form copper and CO_2 and H_2O.

[6] Ellis, O. W., A Review of Work on Gases in Copper: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 487, 1933.

The nature and amount of gas remaining in copper just before it solidifies has a marked effect on properties of the solid copper, as we have mentioned under "Fire Refining."

There are, however, no reliable data on the solubility of various gases in copper which can be quickly summarized. This is a rather complex and difficult problem to investigate for several reasons. (1) It is necessary to work at high temperatures, which makes it difficult to measure accurately small volumes of gas; (2) presence of even traces of impurities may have considerable effect on gas solubility; (3) many of the gases react with the copper so that it is not always a question of simple solubility. Commercial technique in copper converting and refining is based on more or less empirical rules, and a complete analysis of the effect of dissolved gases is still lacking.

Solvents for Copper. Copper will dissolve in most acids when aided by oxidizing action, to form soluble copper salts. Copper also forms complex salts with ammonium compounds and with cyanides, and as we have seen, metallic copper is soluble in oxygenated ammonium carbonate plus ammonia. The formula for cupric-ammonium carbonate we have given; other complex copper-ammonium salts are

$$Cu(NH_3)_4SO_4 \cdot H_2O, \text{ cupric ammonium sulfate}$$

$$Cu(NH_3)_6(OH)_2, \text{ cuprammonium hydroxide}$$

In these salts the copper is in the form of a complex cuprammonium ion which has a deep-blue color. Cupric ions impart a greenish-blue color to the solution; cuprous ions are colorless.

Examples of complex cyanides are the soluble sodium and potassium salts $NaCu(CN)_2$ and $KCu(CN)_2$. In these salts the copper is present in the negative ion $Cu(CN)_2^-$; these complex cyanides are used in electrolytes for electroplating copper.

Cupric chloride forms a soluble double chloride with ammonium chloride — $CuCl_2 \cdot 2(NH_4)Cl \cdot 2H_2O$. The insoluble cuprous chloride forms a similar compound with ferrous chloride, and this makes possible the dissolving of cuprous chloride in brines of ferrous chloride.

EFFECTS OF MECHANICAL WORK ON PHYSICAL PROPERTIES

In fabrication processes the wirebars, billets, or cakes are rolled down to rod or plates and these are further rolled into sheet (plates) or drawn into wire (rod). Other shapes are made by extruding metal through a die, by piercing billets to make seamless tubing, etc. All these processes are divided into two classes — hot working and cold working.

Hot Working. Copper may be worked extensively at any temperature up to about 1050° C. The higher the temperature the softer the metal and the less power required. The essential fact about hot working is that the temperature of the metal must be kept above the recrystallization temperature. When metal is deformed, the individual crystals are elongated and distorted, but if the temperature is high enough the atoms immediately reassemble to form new equi-axed grains. The size of the grains formed depends largely upon the temperature, and the higher the temperature the larger the crystal grains. The smallest grains will be formed just above the recrystallization temperature, and for this reason the *finishing temperature* of a hot-working operation should be around 400° or 500° C to avoid having an undesirable coarse grain in the finished object. Most hot-working operations begin with the metal at about 850° C.

Hot working refines the coarse grains found in cast copper and increases the density of the metal by closing up small pores and gas holes. Otherwise it has little effect on the physical properties — strength, ductility, electrical conductivity, hardness, thermal conductivity, etc., remain about the same regardless of the amount of hot working.

Cold Working. Cold working means the working of metal below the recrystallization temperature. Cold-worked copper is commonly known as "hard" copper, and cold working is the only method of hardening pure copper. The crystal grains in cold-worked copper are elongated, and the metal is harder and stronger than hot-worked or annealed copper. Cold working also decreases the electrical conductivity and ductility of copper.

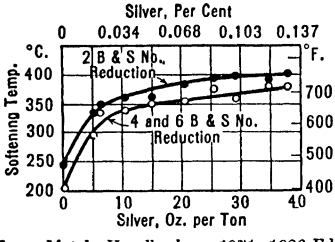
The effect of cold working on strength, hardness, and ductility is quite marked, as we have noted. The effect on electrical conductivity is less pronounced. The most severe cold working does not reduce the conductivity more than about 3 per cent.

Cold working is usually a finishing operation; in making cold-rolled sheet, for example, the rolling from the billet down almost to size would be done hot, and only the last few passes through the rolls would be made cold. The amount of hardening is determined by the per cent reduction of area of the piece during the cold rolling. Wire is made by cold drawing rod through a series of dies.

Stamping, spinning, and drawing are all cold-working operations by means of which sheet copper is formed into a number of shapes. When working is severe (heavy "draft"), oxygen-free copper is used because of its superior ductility.

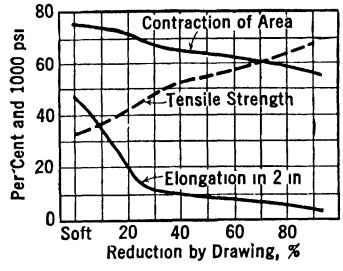
HEAT TREATMENT OF COPPER

Annealing is the only method of heat treatment used on pure copper, although other heat-treating processes may be used on some copper alloys. The purpose of annealing is to restore work-hardened copper to its original soft or ductile form.



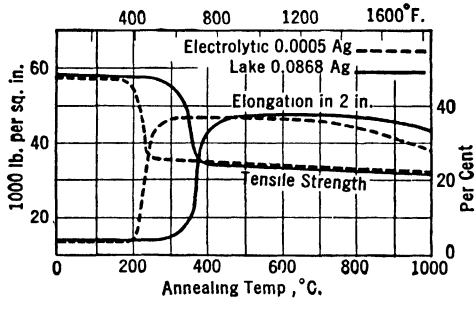
(*From Metals Handbook, p 1071, 1936 Ed.*)

FIG. 1. Effect of Silver on Annealing Temperature of Cold-Rolled Copper Sheet.



(*From Metals Handbook, p. 1070, 1936 Ed.*)

FIG. 2. Characteristic Drawing Curves of Tough-Pitch Copper.



(*From Metals Handbook, p. 1069, 1936 Ed.*)

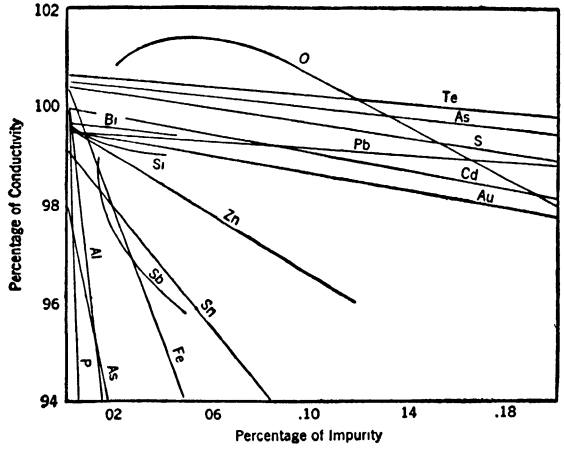
FIG. 3. Effect of Silver on Annealing of Copper (0.05-inch sheet).

The process of annealing involves the heating of the copper to the proper temperature, holding at this temperature for a certain period, and then allowing the metal to cool to room temperature. Most commercial annealing is done at 1100° F (590° C) which provides the necessary softening action without promoting undue grain growth. Theoretically it is only necessary to heat above the recrystallization temperature to obtain the full benefits of annealing, but practically it is necessary to use a somewhat higher temperature to make the process sufficiently rapid. Figure 3 shows the effect of various annealing temperatures on two specimens of work-hardened copper. Note that after a certain critical temperature is reached the tensile

strength drops and the ductility rises. Annealing at higher temperatures has no further effect on the tensile strength, but the ductility drops somewhat because of the increased grain size. This diagram also shows the effect of silver on the recrystallization or annealing temperature of copper.

For certain uses when slightly elevated temperatures are encountered in service such as engraver's plates, parts to be tinned or soldered, firebox plates and stays, etc., it is desirable that the part retain its work-hardened condition. Electrolytic copper would soften under these circumstances, so it is necessary to select a grade of copper with a high recrystallization temperature — Lake copper or a synthetic silver-, arsenic-, or antimony-bearing copper.

A *light anneal* is relatively short anneal designed principally to relieve mechanical strains in the cold-worked metal; it does not completely soften the metal. When the annealing is prolonged sufficiently to completely soften the metal, the operation is known as *dead annealing.*



(*Addicks in Metallurgy of Copper by Hofman and Hayward, McGraw-Hill Book Co., New York, 1924*)

FIG. 4. Effect of Impurities on the Conductivity of Copper.

IMPURITIES IN COPPER

Figure 4 shows the effect of some of the common impurities on the electrical conductivity of copper. Some elements show a pronounced lowering of the conductivity, whereas others have little effect. Oxygen in certain concentrations apparently increases the conductivity, but actually this is due to the fact that some of the harmful impurities are tied up as oxides and are not alloyed with the copper. Impurities affect

other properties of copper as well as the conductivity, and we shall briefly summarize the effects of the most common ones.[4]

Oxygen. Oxygen is present in all tough-pitch copper in the form of Cu_2O. In cast copper it appears as the Cu-Cu_2O eutectic at the grain boundaries, and in worked copper it exists as small globules of Cu_2O visible under the microscope. In the concentrations found in commercial copper it has little effect on the mechanical properties.

Sulfur, selenium, and **tellurium** are ordinarily regarded as harmful in copper, but they are actually dangerous only in tough-pitch copper unless their concentration exceeds 0.1 per cent. In the absence of oxygen these elements form the eutectics Cu-Cu_2S, Cu-Cu_2Se, and Cu-Cu_2Te, which are similar in behavior and effect to the Cu-Cu_2O eutectic.

Silver in varying amounts is one of the most common impurities found in copper. It has a pronounced effect on the recrystallization temperature (Figs. 1 and 3), but otherwise it has little effect on the properties, and in specifications it is common to count silver as copper in the analyses.

Bismuth is seldom encountered in detectable amounts in American coppers. When present in amounts over 0.001 per cent, however, it promotes brittleness of the metal and is very undesirable. Bismuth is not removed by fire refining alone but must be separated by electrolysis.

Antimony is sometimes added to copper to raise the recrystallization temperature. In amounts up to 0.5 per cent it hardens the copper slightly and decreases the ductility, but it cannot be considered a harmful impurity unless the highest conductivity is desired. Antimony is extremely harmful to brass, so antimony-bearing scrap copper is not suited for brass making.

Arsenic occurs naturally in Lake copper and is sometimes allowed to remain after refining in amounts up to 0.3 per cent or more. It has a small hardening and strengthening effect, and it raises the recrystallization temperature of the metal. It decreases the electrical conductivity considerably.

Iron is normally present in small amounts and is totally without effect on the mechanical properties of the metal; it does, however, lower the electrical conductivity.

Lead must not be present in amounts over 0.005 per cent if the copper is to be hot-rolled. Larger amounts, however, are without effect on the ductility at room temperature. The presence of oxygen decreases the harmful effect of lead.

[4] Metals Handbook, 1936 ed., p. 1072, American Society for Metals, Cleveland.

Cadmium is often added to copper in amounts of 0.7 to 1.0 per cent for the production of an alloy of high strength and good conductivity which is extensively used for trolley wire. In cold-drawn wire it is possible to obtain strengths as high as 92,000 pounds per square inch with a conductivity of 80 per cent International Annealed Copper Standard. Cadmium is rarely present in commercial copper.

Phosphorus is almost never found in commercial copper, but a certain residual amount remains in deoxidized coppers when phosphorus is used as the deoxidizing agent. Phosphorus has such a detrimental effect on electrical conductivity that phosphorized copper is not suitable for electrical uses.

COMMERCIAL CLASSES OF COPPER

There are several types of commercial copper graded principally according to their chemical composition and electrical conductivity. Accepted universally by the trade are the specifications of the American Society for Testing Materials, and we shall present excerpts from several of the American Society for Testing Materials standards to illustrate the nature of these specifications. The important classes sold in America are (1) electrolytic, (2) Lake, and (3) fire-refined copper other than Lake, or casting copper.

In addition to these there are other varieties such as Arsenical Lake, O F H C, and Deoxidized, which are used for special purposes. In England there is a class known as *Best Select* which is a fire-refined copper that corresponds to the American Casting Copper.

Electrolytic Cathode Copper.[7] Electrolytic cathode copper shall have a minimum purity of 99.90 per cent, silver being counted as copper. The copper shall have a resistivity not to exceed 0.15436 international ohms per meter-gram at 20° C (annealed). Cathodes shall be hard enough to stand ordinary handling without excessive breakage or excessive separation of nodules, and shall be substantially free from all foreign material, for example, copper sulfate, dirt, grease, and oil.

Electrolytic Copper Wirebars, Cakes, Slabs, Billets, Ingots, and Ingot Bars.[8] The copper in all shapes shall have a purity of at least 99.900 per cent, silver being counted as copper.

All wirebars shall have a resistivity not to exceed 0.15436 international ohms per meter-gram at 20° C (annealed); all ingots and ingot bars shall have a resistivity not to exceed 0.15694 international ohms per meter-gram at 20° C (annealed).

[7] A.S.T.M. Designation, B 115–38 T.

[8] A.S.T.M. Designation, B 5–27.

Cakes, slabs, and billets shall come under the ingot classification, except when specified for electrical use at time of purchase, in which case wirebar classification shall apply.

Wirebars, cakes, slabs, and billets shall be substantially free from shrink holes, cold sets, sloppy edges, concave tops, and similar defects in set or casting. This clause shall not apply to ingots or ingot bars, in which case physical defects are of no consequence.

Lake Copper Wirebars, Cakes, Slabs, Billets, Ingots, and Ingot Bars.[9] In order to be classed as Lake, copper must originate on the northern peninsula of Michigan, U. S. A.

Lake copper offered for electrical purposes, whether fire or electrolytically refined, shall be known as *Low Resistance Lake;* Lake copper having a resistivity greater than 0.15694 international ohms per meter-gram at 20° C shall be known as *High Resistance Lake.*

Low Resistance Lake. Wirebars shall have a resistivity not to exceed 0.15436 international ohms per meter-gram at 20° C (annealed). Ingots and ingot bars shall have a resistivity not to exceed 0.15694 international ohms per meter-gram at 20° C (annealed). Cakes, slabs, and billets shall come under the ingot classification except when specified for electrical use at time of purchase, in which case wirebar classification shall apply.

The purity shall be at least 99.900 per cent as determined by electrolytic assay, silver being counted as copper.

High Resistance Lake. The purity shall be at least 99.900 per cent, copper, silver, and arsenic being counted together. The arsenic content of High Resistance Lake copper, when required for special purposes, shall be the subject of agreement at time of purchase.

Fire-Refined Copper Other than Lake.[10] These specifications cover fire-refined copper other than Lake and not usually electrolytically refined. Fire-refined copper other than Lake is intended for use in rolling into sheets and shapes for mechanical purposes and is not intended for electrical purposes nor wrought alloys.

[9] A S T M. Designation, B 4–27.

[10] A.S.T.M. Designation, B 72–33.

The copper in all shapes shall conform to the following chemical composition:

	Per Cent
Copper plus silver, minimum	99.7000
Arsenic, maximum	0.1000
Antimony, do	0.0120
Bismuth, do	0.0020
Iron, do	0 0100
Lead, do	0.0100
Nickel, do	0.1000
Oxygen, do	0 0750
Selenium, do	0.0400
Tellurium, do	0.0140
Tin, do	0.0500

Copper Bars for Locomotive Staybolts.[11] Copper bars for locomotive staybolts will serve as an example of the specifications required for various types of fabricated and semi-fabricated copper objects.

These specifications cover two grades of copper bars for locomotive staybolts, namely, *Arsenical* and *Non-Arsenical*. The copper shall be fire-refined or electrolytic and shall be finished to dimensions by hot-rolling from suitable bars.

The copper shall conform to the following chemical composition:

Arsenical Copper shall contain 0.25 to 0.50 per cent arsenic and shall contain not more than 0.120 per cent of impurities exclusive of arsenic and silver.

Non-Arsenical Copper shall have a purity of at least 99.90 per cent, silver being counted as copper. The total of impurities other than silver shall not exceed 0.10 per cent.

The material shall conform to the following minimum requirements as to tensile properties:

	Arsenical	*Non-Arsenical*
Tensile strength, psi	31,000	30,000
Elongation in 8 inches, per cent	35	30

The test specimen shall stand being bent cold through 180° flat on itself without cracking on the outside of the bent portion. One tension and one bend test shall be made from each 5000 pounds or fraction thereof.

The bars shall be truly round within 0.01 inch and shall not vary more than 0.01 inch over nor more than 0.005 inch under the specified size.

[11] A.S.T.M. Designation, B 12–33.

CHAPTER XI

THE USES OF COPPER

INTRODUCTION

In this chapter we shall give a brief discussion of the various uses of metallic copper and copper alloys.

Table 1 gives the estimated use of copper in the United States for the period 1933–1937. This includes all copper produced, both primary and secondary (scrap), and includes all copper used, both as pure metal and as alloys. For 1937 the percentage for each classification is computed from the data in the preceding column. It is almost impossible to set up a table giving the " average " consumption of copper over a period of years, as consumption varies considerably from year to year as to both totals and distribution. Table 1 shows several examples of this.

1. The total consumption of copper in 1937 was more than twice the 1933 consumption.

2. Consumption of copper for electrical manufactures, telephones and telegraph, and light and power lines was also about twice as great in 1937 as in 1933.

3. Air conditioning showed a decided increase from 1934 to 1937, with no indicated consumption in 1933.

These and many other facts show that the consumption of copper depends upon general economic conditions and technological trends, but it will not be profitable to devote more space at this point to a further examination of consumption statistics.

Approximately 60 per cent of the copper consumed is used as metal; the remaining 40 per cent is used in alloys. About 38 per cent (Table 1) of the entire copper consumption is used for various electrical purposes, and this represents about 63 per cent of the total metallic copper used (excluding alloys).

Reasons for Using Copper. Copper is not used as pure metal because of its mechanical properties; pure copper is a relatively soft and weak metal and has a high specific gravity. Where strength is the principal requirement there are other metals and alloys which are much more suitable. This restriction of course, does not apply to copper alloys, many of which exhibit exceptional mechanical properties.

TABLE 1[a]

ESTIMATED USE OF COPPER IN THE UNITED STATES, 1933–1937, IN SHORT TONS

	1933	1934	1935	1936	1937	1937 (%)
Electrical manufactures[b]	90,000	101,000	128,000	164,000	213,000	24 8
Telephones and telegraphs	18,000	18,000	18,000	26,000	30,000	3 5
Light and power lines[c]	33,000	36,000	55,500	72,000	83,000	9 6
Wire cloth	5,000	4,600	5,600	6,500	6,600	0 8
Other rod and wire	46,000	40,000	48,000	90,000	112,000	13 0
Ammunition	10,500	13,500	13,700	11,900	14,100	1 6
Automobiles[d]	49,000	63,000	95,000	108,000	112,000	13 0
Buildings[e]	36,000	36,000	49,000	71,000	70,500	8 2
Castings, n.e.s[f]	36,000	36,000	36,000	39,000	40,000	4 6
Clocks and watches	2,800	2,200	2,400	3,400	3,200	0 4
Coinage	100	900	1,500	2,000	100	0 0
Copper-bearing steel	1,500	2,100	2,300	3,900	4,600	0 5
Fire-fighting apparatus	1,100	1,000	1,200	1,300	1,500	0 2
Radiators, heating	2,400	1,000	1,100	2,000	2,100	0 2
Radio receiving sets	11,500	12,500	16,000	24,000	23,100	2 7
Railway equipment[g]	800	2,100	1,800	4,000	7,100	0 8
Refrigerators[h]	11,400	15,700	15,400	15,000	13,500	1.6
Shipbuilding[h]	1,800	3,200	1,100	5,000	6,400	0 7
Washing machines[h]	1,000	1,400	1,300	1,500	1,500	0 2
Water heaters, household	1,500	1,500	1,500	1,500	1,500	0 2
Air conditioning[h,i]	0	3,800	4,800	6,400	7,200	0.8
Other uses	40,000	42,000	46,000	59,000	62,000	7.2
Manufactures for export	15,600	25,500	29,500	31,600	45,000	5 2
	415,000	463,000	574,000	749,000	860,000	99 8

[a] Minerals Yearbook, 1938, p 93, U. S Bur. Mines.
[b] Generators, motors, electric locomotives, switchboards, light bulbs, etc.
[c] Transmission and distribution wire and busbars, accounting only for the public utility companies
[d] Does not include starter, generator, and ignition equipment
[e] Excludes electrical work.
[f] Bearings, bushings, lubricators, valves, and fittings.
[g] Includes air conditioning
[h] Exclusive of electrical equipment.
[i] Other than railway.

The principal reasons for the widespread industrial use of metallic copper are (1) electrical conductivity, (2) heat conductivity, (3) ductility, (4) resistance to corrosion, and (5) decorative value.

The first of these is by far the most important, and more than anything else accounts for the importance of copper. The second is likewise very important and accounts for the use of copper in refrigerators, radiators, water heaters, air conditioning, etc., where the

rapid transfer of heat is essential. These two properties are peculiarly important because pure copper is exceeded in electrical and thermal conductivity only by the relatively expensive metal silver. Moreover, all alloying elements added to copper appear to lower both the electrical and thermal conductivity, and there seems to be small likelihood that any alloy or other material will be discovered which will be superior to copper in these two respects.

Copper is a very ductile metal and for that reason is suited for purposes which require extensive cold working — wire drawing, cold stamping, spinning, deep drawing, etc. Oxygen-free copper is even more ductile than tough-pitch copper and will stand more extensive cold working than any other metal or alloy with the exception of some of the precious metals.

The resistance of copper to corrosion by certain reagents is responsible for some of its uses, particularly in the manufacture of vessels for holding corrosive liquids, tubes for conveying corrosive liquids, and sheathing for boats. This use, however, is conditioned by two other factors. There are other metals and alloys which are superior to pure copper as corrosion resistant materials, and when copper is used it is because (1) it is cheaper than the other material, or (2) its superior ductility makes it easier to form the required shape. The latter consideration applies particularly to the manufacture and use of small-bore tubing. Of course there are some corrosive materials which readily attack copper and preclude its use in contact with them.

Finally there is the fact that the color and luster of copper make it desirable for its decorative effect. The green patina formed on copper exposed to the atmosphere gives an attractive color to copper roofing.

The reasons listed above, singly or in combination, account for practically all of the industrial uses made of commercially pure copper; the use of copper in alloys is dictated by many other considerations.

Temper. We shall have occasion in the discussion of copper and copper alloys to refer to the *temper* of a particular sample. As applied to non-ferrous metals and alloys, temper means the condition of the metal or alloy with respect to its previous mechanical and/or heat treatment. There is no standard method for designating temper, but the following examples will indicate some common usages:

1. Soft copper may be designated as *soft annealed, dead soft, dead annealed,* etc.

2. Cold-worked copper is known as *hard, cold drawn, cold rolled, hard drawn, full hard,* etc.

These terms generally refer to completely hardened copper; if the reduction in area has been only enough to partly harden the copper, then the metal is *medium hard, half hard, medium hard-drawn,* etc. In some coppers the amount of cold working is indicated; a designation which might be used for copper sheet is "0.0325 gauge, 3 numbers hard," which means that after the last anneal the metal was reduced by cold rolling 3 Brown and Sharpe gauge numbers to a thickness of 0.0325 inch.

A similar terminology applies to alloys, except that some alloys can be hardened by heat treatment, and the terms used must indicate whether the hard state was produced by cold working or by heat treatment.

ELECTRICAL CONDUCTORS

We have already considered the question of the electrical conductivity of copper, and at this point we shall briefly discuss the commercial shapes of copper used as conductors.

Busbars, Etc. For carrying heavy currents over short distances copper *busbars* or *busses* are used. These must have a cross-section large enough to carry the current required. Busses are made in different cross-sectional shapes; they may be rectangular, triangular, or cylindrical bars, I-beams, angles, or pipe. Generally busses are used bare, and the nature of the insulating supports will depend on the voltage drop between the bus and its surroundings.

Wire. Conductivity wire is made in a variety of sizes and conditions. Wires are usually circular in cross-section. They may be bare or covered with one of a number of insulating substances; a "wire" may be a single wire or it may be "stranded" or made up of a number of smaller wires. Large "cables" may consist of hundreds of small wires each insulated from the others, and some of these are sheathed in metallic lead over the insulation. A number of insulating materials may be used depending upon the use for which the wire is intended. These include special varnishes and enamels, fabrics, rubber, and asphalt.

In designating the sizes of individual wires, several special units are employed in addition to the common English and metric units.

Special Units. A common unit for the diameter of wire is the *mil,* which is one one-thousandth of an inch. A *square mil* is the area of a square 1 mil on a side, and a *circular mil* is the area of a circle 1 mil

in diameter. These may be converted to other units by the following relations:

1 inch = 1000 mils
1 millimeter = 39.37 mils
1 centimeter = 393.7 mils
1 square millimeter = 1973 circular mils
1 square centimeter = 1.973×10^5 circular mils
1 square inch = 1.273×10^6 circular mils
1 square mil = 1.2732 circular mils

Wires larger than ½ inch are usually designated by the wire diameter in mils or other units, but smaller wires have their size denoted by certain arbitrary "gauge numbers." The larger the gauge number the smaller the diameter of the wire. The principal wire gauge used in the United States is the *American*, or *Brown and Sharpe* gauge, which is abbreviated *A.W.G.* or *B. and S.*

The ratio of the diameter of any wire to the next smaller wire in the *B. and S* system is $\sqrt[39]{92}$ to 1 or approximately 1.1229 to 1. Thus No. 36 B. and S. wire has a diameter of 5 mils, and the diameter of the next larger wire (No. 35 B. and S.) is $5.0 \times 1.1229 = 5.61$ mils. The surd $\sqrt[39]{92}$ is approximately equal to $\sqrt[6]{2}$ (= 1.1225), and this makes it possible to have a group of wires of regular gauge size with an aggregate area approximately equal to that of another regular gauge size. Thus a reduction of three gauge numbers (say from No. 36 to No. 33 B. and S.) results in a new gauge number representing a diameter approximately $\sqrt{2}$ times that of the original gauge number or an area about twice as great. In other words the No. 33 wire has twice the cross-sectional area of the No. 36 wire.

From the definitions given above, the following approximate relations may be derived:

An increase of 1, 2, and 3 in the number increases the resistance 25, 60, and 100 per cent, respectively. An increase of 10 in the number increases the resistance 10 times. The cross-sectional area and weight per foot will vary inversely with the resistance, and by taking the constants for one wire, the approximate values for the other wires can be calculated. No. 10 B. and S. wire is convenient for a starting point. Its approximate characteristics are:

Ohms per 1000 feet = 1
Circular mils area = 10,000
Weight, pounds per 1000 feet = 32

Thus the resistance of No. 12 B. and S. wire would be $1 \times (1.0 + 0.60)$ = 1.6 ohms; the area would be $\frac{10{,}000}{1.6}$ = 6250 circular mils; the diameter $\sqrt{6250}$ = 79 mils; and the weight $\frac{32}{1.6}$ = 20 pounds per 1000 feet.

B. and S. numbers range from No. 0000 (diameter = 460 mils) to No. 40 (diameter = 3.1 mils).

Copper wire may be hard-drawn, medium hard-drawn, or annealed, and standard specifications for various size wires are shown in Tables 2, 3, 4, and 5.

TABLE 2[a]

WIRE TABLE, STANDARD ANNEALED COPPER AMERICAN WIRE GAGE (B. & S.). ENGLISH UNITS

Gauge No A W G	Diameter in Mils at 20° C	Cross-section at 20° C: Circular Mils	Cross-section at 20° C: Square Inches	Ohms per 1000 ft[b] at 20° C (= 68° F)	Pounds per 1000 ft	Feet per Pound	Feet per Ohm[c] at 20° C (= 68° F)	Ohms per Pound at 20° C (= 68° F)	Pounds per Ohm at 20° C (= 68° F)
0000	460 0	211 600	0 1662	0 049 01	640 5	1 561	20 400	0 000 076 52	13 070.
000	409 6	167 800.	1318	.061 80	507 9	1 968	16 180	000 1217	8219.
00	364 8	133 100	1045	.077 93	402 8	2 482	12 830	000 1935	5169.
0	324 9	105 500	082 89	098 27	319 5	3 130	10 180	000 3076	3251.
1	289 3	83 690	065 73	1239	253 3	3 947	8070	000 4891	2044.
2	257 6	66 370	052 13	1563	200 9	4 977	6400	000 7778	1286
3	229 4	52 640	041 34	1970	159 3	6 276	5075	001 237	808 6
4	204 3	41 740	032 78	2485	126 4	7 914	4025	001 966	508.5
5	181 9	33 100	026 00	3133	100 2	9 980	3192	003 127	319 8
6	162 0	26 250	020 62	3951	79 46	12 58	2531	004 972	201 1
7	144 3	20 820	016 35	4982	63 02	15 87	2007	007 905	126 5
8	128 5	16 510	012 97	6282	49 98	20 01	1592	012 57	79 55
9	114 4	13 090	010 28	7921	39 63	25 23	1262	019 99	50 03
10	101 9	10 380	008 155	9989	31 43	31 82	1001	031 78	31 47
11	90 74	8234	006 467	1 260	24 92	40 12	794 0	050 53	19 79
12	80 81	6530.	005 129	1 588	19 77	50 59	629 6	080 35	12 45
13	71 96	5178	004 067	2 003	15 68	63 80	499 3	1278	7 827
14	64 08	4107	003 225	2 525	12 43	80 44	396 0	2032	4 922
15	57 07	3257	002 558	3 184	9 858	101 4	314 0	3230	3 096
16	50 82	2583	002 028	4 016	7 818	127 9	249 0	5136	1 947
17	45 26	2048	001 609	5 064	6 200	161 3	197 5	8167	1 224
18	40 30	1624	001 276	6 385	4 917	203 4	156 6	1 299	0 7700
19	35 89	1288	001 012	8 051	3 899	256 5	124 2	2 065	4843
20	31 96	1022	000 802 3	10 15	3 092	323 4	98 50	3 283	3046
21	28 46	810 1	000 636 3	12 80	2 452	407 8	78 11	5 221	1915
22	25 35	642 4	000 504 6	16 14	1 945	514 2	61 95	8 301	1205
23	22 57	509 5	000 400 2	20 36	1 542	648 4	49 13	13 20	075 76
24	20 10	404 0	000 317 3	25 67	1 223	817 7	38 96	20 99	047 65
25	17 90	320 4	000 251 7	32 37	0 9699	1031	30 90	33 37	029 97
26	15 94	254 1	000 199 6	40 81	.7692	1300	24 50	53 06	018 85
27	14 20	201 5	000 158 3	51 47	6100	1639	19 43	84 37	011 85
28	12 64	159 8	000 125 5	64 90	4837	2067	15 41	134 2	007 454
29	11 26	126 7	000 099 53	81 83	3836	2607	12 22	213 3	004 688
30	10 03	100 5	000 078 94	103 2	.3042	3287	9 691	339 2	002 948
31	8 928	79 70	000 062 60	130 1	.2413	4145	7 685	539 3	.001 854
32	7 950	63 21	000 049 64	164 1	1913	5227	6 095	857 6	001 166
33	7 080	50 13	000 039 37	206 9	1517	6591	4 833	1364	000 7333
34	6 305	39 75	000 031 22	260 9	1203	8310	3 833	2168	000 4612
35	5 615	31 52	000 024 76	329 0	095 42	10 480	3 040	3448	000 2901
36	5 000	25 00	000 019 64	414 8	075 68	13 210	2 411	5482	000 1824
37	4 453	19 83	000 015 57	523 1	060 01	16 660	1 912	8717	000 1147
38	3 965	15 72	000 012 35	659 6	047 59	21 010	1 516	13 860	000 072 15
39	3 531	12 47	000 009 793	831 8	037 74	26 500	1 202	22 040	000 045 38
40	3 145	9 888	000 007 766	1049	029 93	33 410	0 9534	35 040	000 028 54

[a] Eshbach, W O, Handbook of Engineering Fundamentals, p 11–93, John Wiley & Sons, New York, 1936

[b] Resistance at the stated temperatures of a wire whose length is 1000 ft at 20 deg cent.

[c] Length at 20 deg cent of a wire whose resistance is 1 ohm at the stated temperatures

TABLE 3[a]

SPECIFICATIONS FOR HARD-DRAWN AND MEDIUM HARD-DRAWN COPPER WIRE

Diameter, in	Area, cir mils	Hard-drawn Copper Wire[b]		Medium Hard-drawn Copper Wire[c]		
		Tensile Strength, lb per sq in	Elongation, per cent in 60 in	Tensile Strength, lb per sq in		Elongation, per cent in 60 in
				Minimum	Maximum	
0 460	211,600	49,000	3 75[d]	42,000	49,000	3 75[d]
0 410	168,100	51,000	3 25[d]	43,000	50,000	3 6[d]
0 365	133,225	52,800	2 80[d]	44,000	51,000	3 25[d]
0 325	105,625	54,500	2 40[d]	45,000	52,000	3 0[d]
0 289	83,520	56,100	2 17[d]	46,000	53,000	2 75[d]
0 258	66,565	57,600	1 98[d]	47,000	54,000	2 5[d]
0 229	52,440	59,000	1 79[d]	48,000	55,000	2 25[d]
0 204	41,615	60,100	1 24	48,330	55,330	1 25
0 182	33,125	61,200	1.18	48,600	55,660	1 20
0 165	27,225	62,000	1 14		.	
0 162	26,245	62,100	1 14	49,000	56,000	1 15
0 144	20,735	63,000	1 09	49,330	56,330	1 11
0 134	17,956	63,400	1 07			.
0 128	16,385	63,700	1 06	49,660	56,660	1 08
0 114	12,995	64,300	1 02	50,000	57,000	1 06
0 104	10,815	64,800	1 00			
0 102	10,404	64,900	1 00	50,330	57,330	1 04
0 092	8,464	65,400	0 97			
0 091	8,281	65,400	0 97	50,660	57,660	1 02
0 081	6,561	65,700	0 95	51,000	58,000	1 00
0 080	6,400	65,700	0 94		.	
0 072	5,184	65,900	0 92	51,330	58,330	0 98
0 065	4,225	66,200	0 91		.	
0 064	4,096	66,200	0 90	51,660	58,660	0 96
0 057	3,249	66,400	0 89	52,000	59,000	0 94
0 051	2,601	66,600	0 87	52,330	59,330	0 92
0 045	2,025	66,800	0 86	52,660	59,660	0 90
0 040	1,600	67,000	0 85	53,000	60,000	0 88
		Maximum resistivity at 20° C for diameters 0 460 to 0 325 in , 900 77 lb per mile-ohm (10 674 ohms (mil, ft)), for diameters 0 324 to 0 040 in , 910 15 lb per mile-ohm (10 785 ohms (mil, ft))		Maximum resistivity at 20° C: for diameters 0 460 to 0 325 in , 896 15 lb per mile-ohm (10 619 ohms (mil, ft)); for diameters 0 324 to 0 040 in , 905 44 lb per mile-ohm (10 729 ohms (mil, ft)).		

[a] Eshbach, Handbook of Engineering Fundamentals, p 11-94, John Wiley & Sons, New York, 1936.
[b] A.S.T.M Standard B1-27, A.S.A. Standard H14-1929.
[c] A S T.M. Standard B2-27
[d] Elongation per cent in 10 in

TABLE 4[a]

SPECIFICATIONS FOR SOFT OR ANNEALED COPPER WIRE AND TINNED SOFT OR ANNEALED COPPER WIRE FOR RUBBER INSULATION

Diameter (in.)	Soft or Annealed Copper Wire[b]			Tinned Soft or Annealed Copper Wire for Rubber Insulation		
	Tensile Strength (lb/sq in.)	Elongation in 10 in (per cent)	Maximum Resistivity[d] (lb/mile-ohm)	Tensile Strength max (lb/sq in.)	Elongation in 10 in. min (per cent)	Maximum Resistivity[d] (lb/mile-ohm)
0.460 to 0.290	36,000	35	891.58	36,000	30	896.15
0.289 to 0.103	37,000	30	891.58	37,000	25	900.77
0.102 to 0.021	38,500	25	891.58	38,500	20	910.15
0.020 to 0.012	40,000	20	891.58	39,000	15	929.52
0.011 to 0.003	40,000	20	891.58	40,000	10	939.51

[a] Eshbach, O. W., Handbook of Engineering Fundamentals, p 11-95, John Wiley and Sons, Inc., New York, 1936

[b] A.S.T.M. Standard B3-27, A.S.A. Standard H4-1928 and C862-1928; A.I.E.E. Standards 60, 61-1928.

[c] A.S.T.M. Standard B33-21; A.S.A. Standard H16-1928 and C861-1928, A.I.E.E. Standards 60, 61-1928

[d] At 20° C (68° F).

TABLE 5[a]

ALLOWABLE CARRYING CAPACITIES OF COPPER WIRES[b]
(NATIONAL ELECTRICAL CODE)

Gauge No. A.W.G.	Diameter of Solid Wires (mils)	Area (cir mils)	Rubber Insulation (amp)	Varnished Cambric Insulation (amp)	Other Insulation (amp)
18	40.3	1,624	3	...	5[c]
16	50.8	2,583	6	...	10[c]
14	64.1	4,107	15	18	20
12	80.8	6,530	20	25	30
10	101.9	10,380	25	30	35
8	128 5	16,510	35	40	50
6	162.0	26,250	50	60	70
5	181.9	33,100	55	65	80
4	204.3	41,740	70	85	90
3	229.4	52,630	80	95	100
2	257.6	66,370	90	110	125
1	289.3	83,690	100	120	150
0	325.0	105,500	125	150	200
00	364.8	133,100	150	180	225
000	409.6	167,800	175	210	275
. .	....	200,000	200	240	300
0000	460.0	211,600	225	270	325
....	.....	250,000	250	300	350
. .	...	300,000	275	330	400
. ..		350,000	300	360	450
....	.. ..	400,000	325	390	500
....	.....	500,000	400	480	600
. .	... .	600,000	450	540	680
.	.	700,000	500	600	760
....	.....	750,000	525	630	800
....	.....	800,000	550	660	840
.	... .	900,000	600	720	920
. ..	.....	1,000,000	650	780	1,000
...	.....	1,100,000	690	830	1,080
. ..	.....	1,200,000	730	880	1,150
....	.....	1,300,000	770	920	1,220
..	.....	1,400,000	810	970	1,290
.	.....	1,500,000	850	1,020	1,360
.	. ...	1,600,000	890	1,070	1,430
....	.....	1,700,000	930	1,120	1,490
....	.....	1,800,000	970	1,160	1,500
....	.. ..	1,900,000	1,010	1,210	1,610
....	.....	2,000,000	1,050	1,260	1,670

[a] Eshbach, O. W., Handbook of Engineering Fundamentals, p. 11-95, John Wiley and Sons, Inc., New York, 1936.

[b] Copper wires and cables of 98 per cent conductivity. For aluminum wire the allowable carrying capacities shall be taken as 84 per cent of those given in the table for the respective sizes of copper wire with the same kind of covering.

[c] The allowable carrying capacities of No. 18 and No. 16 are 10 and 15 amp, respectively, when in cords for portable heaters, types HC and HPD.

Aluminum Conductors. Aluminum conductors compete with copper principally in large conductors where the saving in weight is of importance. The largest use for aluminum conductors is for power transmission through cables having a reinforcing core of high-strength steel wire. These composite cables are larger than copper cables of the same conductivity but are lighter in weight; at very high voltages, such as 100,000 volts, the greater diameter results in a lower corona loss. All-aluminum cables are used for railway feeders to carry heavy currents at low voltages, and aluminum busbars are used for both switchboards and general power transmission.

Hard-drawn aluminum wire has a conductivity of about 61 per cent, I.A.C.S. Thus the volume conductivity of aluminum is only about 61 per cent of that of copper. The mass conductivity, however, is about twice that of copper, as the specific gravity of aluminum is 2.7 and copper has a density of 8.89. For copper and aluminum wires of equal resistance per unit length, the following ratios apply:

	Copper	Aluminum
Cross-section	1	1.61
Diameter	1	1.27
Weight	1	0.488
Breaking strength	1	0.64

Thus we see that for equal conductivity per unit length, the aluminum conductor has only about one-half the weight of the copper; however, the aluminum wire is larger and has less strength.

Aluminum wire has been used for some motor windings, but these windings must occupy more space than copper windings if the same operating temperature is to be maintained (same total resistance).

OTHER WIRE AND ROD

Not all copper rod and wire are used in electrical work, but are used for other purposes, such as copper bars for locomotive staybolts (rod) and woven-wire screen or cloth.

COPPER SHEET AND STRIP

Copper sheet and strip is rolled from cakes of tough-pitch or oxygen-free copper. Copper sheets may be obtained in integral multiples of 1/16 of an inch up to 2 inches in thickness. The sheets thinner than about ½ inch may be designated by gauge numbers; the B. and S. wire gauge is most commonly used for this purpose, and the numbers have the same significance as in the case of wire; i.e., No. 0000 sheet would be 0.4600 inch thick. Table 6 gives the gauge numbers, thick-

TABLE 6[a]

AMERICAN WIRE GAUGE AND WEIGHTS OF COPPER, ALUMINUM, AND BRASS SHEETS AND PLATES

Gauge No.	Thickness		Approximate weight[b] lb/sq ft		
	Inch	mm	Copper	Aluminum	Commercial (high) brass
0000*	0 4600	11 68	21 27	6 49	20 27
000	0 4096	10 40	18 94	5.78	18 05
00	0 3648	9 266	16 87	5 14	16 07
0	0 3249	8 252	15 03	4 58	14 32
1	0 2893	7 348	13 38	4 08	12 75
2	0 2576	6 544	11 91	3 632	11 35
3	0 2294	5 827	10 61	3 234	10 11
4	0 2043	5 189	9 45	2 880	9 00
5	0 1819	4 621	8 41	2 565	8 01
6	0 1620	4 115	7 49	2 284	7 14
7	0 1443	3 665	6 67	2 034	6 36
8	0 1285	3 264	5 94	1 812	5 66
9	0 1144	2 906	5 29	1 613	5 04
10	0 1019	2 588	4 713	1 437	4 490
11	0 0907	2 305	4 195	1 279	3 996
12	0 0808	2 053	3 737	1 139	3 560
13	0 0720	1 828	3 330	1 015	3 172
14	0 0641	1 628	2 965	0 904	2 824
15	0 0571	1 450	2 641	0 805	2 516
16	0 0508	1 291	2 349	0 716	2 238
17	0 0453	1 150	2 095	0 639	1 996
18	0 0403	1 024	1 864	0 568	1 776
19	0 0359	0 9116	1 660	0 506	1 582
20	0 0320	0 8118	1 480	0 451	1.410
21	0 0285	0 7230	1 318	0 402	1 256
22	0 0253	0 6438	1.170	0 3567	1 115
23	0 0226	0 5733	1 045	0 3186	0 996
24	0 0201	0 5106	0 930	0 2834	0 886
25	0 0179	0 4547	0 828	0 2524	0 789
26	0 0159	0 4049	0 735	0 2242	0 701
27	0 0142	0 3606	0 657	0 2002	0 626
28	0 0126	0 3211	0 583	0 1776	0 555
29	0 0113	0 2859	0 523	0 1593	0 498
30	0 0100	0 2546	0 4625	0 1410	0 4406
31	0 00893	0 2268	0 4130	0 1259	0 3935
32	0 00795	0 2019	0 3677	0 1121	0 3503
33	0 00708	0 1798	0 3274	0 0998	0 3119
34	0 00630	0 1601	0 2914	0 0888	0 2776
35	0 00561	0 1426	0 2595	0 0791	0 2472
36	0 00500	0 1270	0 2312	0 0705	0 2203
37	0 00445	0 1131	0 2058	0 0627	0 1961
38	0 00397	0 1007	0 1836	0 0560	0 1749
39	0 00353	0 0897	0 1633	0 0498	0 1555
40	0 00314	0 0799	0 1452	0 0443	0 1383

[a] Eshbach, O. W., op. cit., p. 1–150.

[b] Assumed specific gravities or densities in grams per cubic centimeter: copper, 8.89; aluminum, 2.71; brass, 8.47.

nesses, and weights per square foot for the Brown and Sharpe series.

Copper sheet is used for producing fabricated objects by cold-working — stamping, spinning, etc.; also by welding, soldering, or brazing. The sheet may be used directly for roofing, sheathing of boats, flashings, drains, and numerous other purposes.

Copper is often used as a *refractory* material, for such purposes as tuyére jackets, furnace doors, and locomotive firebox plates. Copper is not particularly resistant to high temperatures, but its high thermal conductivity makes it valuable as a refractory — the heat is conducted through the copper so rapidly that its temperature never rises dangerously high. When copper is used in this way it must be cooled by circulating air or water. For moderately high temperatures when it is desired to retain the hardness of the copper, arsenic- or silver-bearing copper is used. For high-temperature service (furnace doors, for example) where the copper is exposed to reducing gases, oxygen-free copper must be used to avoid embrittlement.

TUBING AND PIPE

Copper pipe can be made by rolling copper sheet into a cylinder and welding the seam, or *seamless tubing* can be made by piercing billets and rolling them over a mandrel to give the proper size bore and wall thickness. Small tubes are commonly made by the piercing method; larger pipes are made from sheet copper.

Copper tubing is widely used in radiators, refrigerators, air conditioning equipment, and similar equipment where maximum heat transfer is desired.

SUMMARY

It has not been possible to enumerate all the detailed uses of copper, and we have indicated only the important general classifications. Practically all pure copper used commercially is in one of the three forms mentioned, with distribution about as follows:[1]

	Per Cent
Wire and rod	58
Sheet and strip	29
Tube	13

All the commercial uses we have mentioned, it will be noted, involve mechanically formed shapes. Pure copper does not make satisfactory

[1] Stoughton, B., and Butts, A., Engineering Metallurgy, 3d ed., p. 308, McGraw-Hill Book Co., New York, 1938.

castings and cannot be used to produce finished objects by casting. Brass, bronze, and other copper alloys can be used for castings, but not pure copper.

ELECTROPLATING AND ELECTROFORMING[2]

The object of *electroplating* is to deposit a layer of copper on the surface of another metal or alloy by electrolysis, and the purpose is to secure a composite object that will have the physical properties (or low cost) of the underlying metal or alloy plus the surface properties of pure copper. *Electroforming* is a process of making an electrodeposited shell to form a " negative " of some object.

Electroplating. In general the electroplating of copper resembles the electrolytic processes that we have already discussed. The object to be plated is immersed in the electrolyte and made the cathode; anodes may be either soluble or insoluble.

In electroplating, the deposit must be smooth and coherent, and this is best obtained when the deposit consists of very fine crystals. Thick deposits invariably become roughened because the crystals become larger as they grow away from the cathode (Fig. 8, p. 268). A number of factors influence the crystal size and coherence of the cathode deposit

1. Current density.
2. Concentration of metal ions in the electrolyte.
3. Concentration of other salts in the electrolyte.
4. " Throwing power " of the electrolyte.
5. Hydrogen-ion concentration.
6. Use of addition agents such as glue.
7. Nature of the base metal.
8. Conductivity of the solution.

The " throwing power " of an electrolyte refers to its ability to deposit an even layer of metal in holes and crevices of irregular objects; most conducting salts and substances that increase cathode polarization tend to improve throwing power.

In general the proper composition of electrolyte, current density, etc., is determined by experience in dealing with different metals. For copper plating, there are two types of " plating baths " or electrolytes in common use:

1. *Acid Sulfate Bath.* This bath consists of an aqueous solution of $CuSO_4$ and H_2SO_4, and the concentration of the two may vary between wide limits. The weight of bluestone ($CuSO_4 \cdot 5H_2O$) added

[2] Mantell, C. L., Industrial Electrochemistry, 2d ed., p. 187, McGraw-Hill Book Co., New York, 1940.

is usually held between 150 and 240 grams per liter. Temperature of the acid sulfate bath is maintained at 25° to 50° C, and a cathode density of 15 to 40 amperes per square foot is used.

2. *Cyanide Bath.* This is essentially a solution of the complex cyanide of sodium and copper which probably has the formula $Na_2Cu(CN)_3$, plus an excess of sodium cyanide. In some cases Rochelle salts (potassium sodium tartrate) are used in connection with the cyanide. The copper content of these solutions will range from 22 to 26 grams per liter, temperature from 35° to 40° C, and cathode current density from 3 to 14 amperes per square foot.

Plating baths having low concentrations of the metal ions are best for securing fine-grained deposits which are easily polished, and the low ionic concentration is produced not by using dilute solutions but (1) by the use of salts showing low ionization or by the addition of another salt having a common ion to depress the ionization of the metallic salt, or (2) by using a compound in which the metal ions are produced by secondary ionization. Sodium copper cyanide is an example of the latter; in water the principal ionization is of the type

$$Na_2Cu(CN)_3 \rightleftharpoons 2Na^+ + Cu(CN)_3^{--}$$

so that the bulk of the copper is tied up in the complex negative ion. There is a certain amount of secondary ionization of the type:

$$Cu(CN)_3^{--} \rightleftharpoons CuCN + 2CN^-$$

$$CuCN \rightleftharpoons Cu^+ + CN^-$$

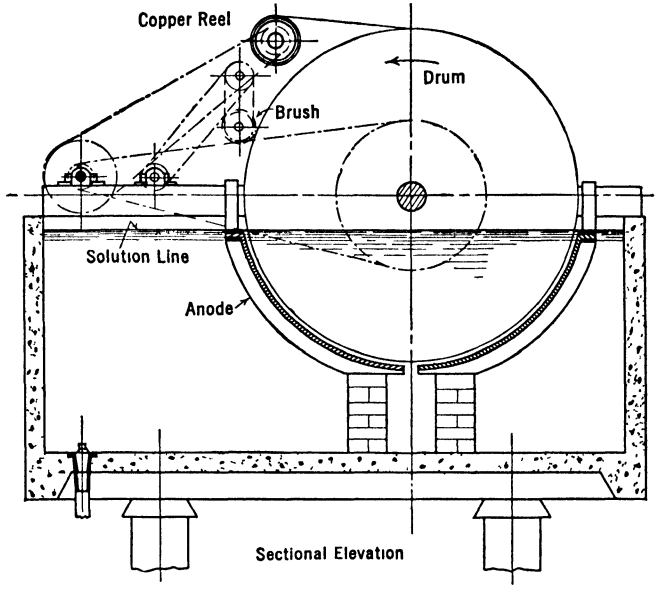
which produces the copper ions.

Cyanide baths are used for the formation of thin platings and as a foundation layer for thicker coats. Thick layers are generally plated from the acid sulfate bath.

Copper plating is widely used both to give a finished surface and as a foundation for the plating of other metals such as nickel. So-called "chrome plate" usually consists of a copper deposit followed by a nickel deposit with a thin deposit ("flash plating") of chromium over the layer of nickel.

Brass Plating. Brass (copper-zinc alloy) is the only alloy that is used for plating in commercial work on a large scale. It is plated from a solution of the double cyanides of copper and zinc, using a brass anode. Copper and zinc will precipitate together from such a solution because their deposition potentials are almost the same. In sulfate solutions, however, the deposition potentials are very far apart, and no zinc will deposit as long as there are copper ions in the solution.

Electroforming. Electrolytically deposited copper can be deposited on an object to form a shell which is a "negative" replica of the object. This method is used for reproducing a printer's set-up of type (*electrotyping*), engravings, and medals; for the reproduction of phonograph matrices; and for the manufacture of seamless tubes and sheets



(*Shakespeare, Am. Inst Min. and Met. Eng. Trans., Vol. 106, p 442, 1933*)

FIG. 1. Sectional Elevation of First Stage Machine Used in the Manufacture of Electro-Sheet Copper.

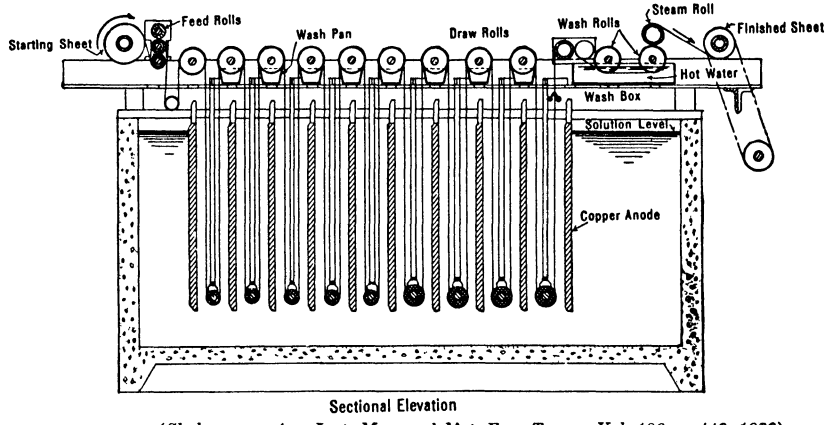
by electrodeposition. When it is desired to plate metal on a non-conducting object such as a wax phonograph record the surface is made conducting by giving it a light coat of graphite.

Seamless tubes are made by depositing a layer of copper on a rotating mandrel which serves as the cathode; the mandrel is coated with material which facilitates removal of the finished tube.

Very thin copper sheets have been formed by electrodeposition on a belt moving continuously through the solution, the product being taken off the belt where it passes out of the solution. A process developed at the Raritan copper plant[3] utilizes two stages (Figs. 1 and 2). In the first stage (Fig. 1) a slowly rotating lead-covered copper drum serves as the cathode, and insoluble lead anodes are used.

[3] Shakespeare, William M., Anaconda Electro-Sheet Copper: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p. 441, 1933.

The sheet produced measures 0.00135 inch thick and weighs about 1 ounce per square foot. This 1-ounce sheet is then sent through the second stage (Fig. 2), where it can be built up to any desired thickness.



Sectional Elevation

(Shakespeare, Am Inst Min. and Met Eng Trans., Vol 106, p 443, 1933)

FIG. 2. Sectional Elevation of Second Stage Machine for the Manufacture of Electro-Sheet Copper.

In the second stage the sheet is conducted through a series of depending loops spaced between standard refinery anodes. The sheet material produced is sound and uniform, both in physical properties and in gauge.

COPPER POWDER[4,5]

In recent years the use of powdered metals has become of considerable importance, and copper is included among the metals which are being produced commercially in the powdered form. Copper powder is a finely divided powder of pure metallic copper, its purity depending on the copper from which it is made.

Powdered copper is used to some extent as a pigment, but the most important use is in the manufacture of solid metals and alloys by various processes for compacting the powder into solid pieces. The technique of powder metallurgy has made it possible to produce solid compacts or " alloys " which could not be made by the standard method

[4] Noel, D. O, Shaw, J. D., and Gebert, E. B., Production and Some Testing Methods of Metal Powders: Am. Inst. Min. & Met. Eng. Tech. Paper 928 (Metals Technology), June 1938.

[5] Goetzel, C. G., Powder Metallurgy of Copper: Metals and Alloys, Vol. 12, Nos. 1 and 2, pp. 30, 154, 1940.

of melting and casting. Thus it is possible to make solid copper-graphite compacts by this method, but copper-carbon *alloys* cannot be made because carbon is insoluble in molten copper. Compacted alloys can also be made which have controlled porosity — "self-oiling" bronze bearings are an example. These are made by compacting copper and tin powders cold, and then sintering the section. Tin diffuses into the copper to form grains of alpha bronze, and between the grains are left the capillary pores through which the lubricating oil can flow.

Manufacture of Copper Powder. There are a number of methods for preparing metal and alloy powders; the following are applicable to copper.

1. *Machining.* Turnings, cuttings, filings, etc., produce a relatively coarse irregular powder which is useful for certain purposes. There is not much pure copper powder produced in this way because copper is too soft and tough to machine readily.

2. *Milling.* Copper and other ductile metals can be ground to powder in special ball mills or stamp mills. The metal is fed into the mill as small pieces of thin sheet, and a lubricant is used which prevents the particles from "welding" together. Powder produced in this way is flaky and has a low apparent density; it is especially suited for pigments because of the "leafing" characteristic of the powder flakes which give a good covering power. Copper flake is used extensively in the manufacture of motor brushes for commutator and collector rings, being compounded with carbon or graphite and occasionally smaller amounts of lead or tin. The flake type of copper powder has an advantage for this work owing to its tendency to laminate during molding.

3. *Reduction of Copper Oxide.* Copper powder can be produced by treating copper oxide powder in a reducing atmosphere at high temperatures (but below the melting point of either metal or oxide). Powders reduced from oxides have a granular spherical shape and a spongelike structure that makes them particularly adapted for molding work. Copper oxide scale formed in hot-rolling copper is the raw material commonly used for this method.

4. *Chemical Precipitation.* The "cement copper" produced by precipitating copper from its solutions is a type of copper powder, but it is generally too impure to be used directly.

5. *Electrolytic Deposition.* A large amount of copper powder is produced electrolytically, using essentially the same method as that employed in copper refining. Special conditions in the electrolyte cause the deposit to form as loosely adherent fine crystals which can be removed by scraping or tapping the cathode. The electrolyte con-

tains less copper and more acid than refinery electrolytes, and a higher current density is employed. Hydrogen evolution at the cathode, or the addition of certain colloidal materials to the electrolyte aids in the production of fine powders.[6] Electrolytic powder grains have a "fern-like" appearance under the microscope, a structure well adapted for molding work. The grain size of the particles is controlled by the electrolyte composition and current density used.

COPPER COMPOUNDS

A small amount of copper is consumed in the manufacture of chemicals, insecticides, preservatives, etc. Considerable quantities of "blue vitriol" or "bluestone" ($CuSO_4 \cdot 5H_2O$) are produced as a byproduct of electrolytic plants.

THE ALLOYS OF COPPER

Most of the "metals" used commercially are really alloys, and there probably would be some justification in considering some of the grades of commercial copper as alloys — tough-pitch copper as a copper-oxygen alloy; high-resistance Lake copper as an alloy of copper, silver, and arsenic. Certainly the elements present other than copper have a marked effect on the properties of the metal.

Copper is widely used in the unalloyed form for the following reasons:

1. Its high electrical and thermal conductivity makes it invaluable for many uses. Alloying invariably lowers both the electrical and thermal conductivity.

2. Its ductility makes it useful in many operations where severe cold-working is necessary.

3. It resists corrosion by certain corrosive agents; other materials, however, corrode copper quite rapidly.

Copper alloys are used because they are more satisfactory than copper for certain purposes, among which are the following:

1. Most copper alloys are harder and stronger than copper. Copper is rather soft and ductile in the annealed state as compared with annealed brass, bronze, or other copper alloys. Many of these alloys can be work-hardened to produce a much harder and stronger material than cold-worked copper.

2. Some copper alloys are used to make castings — brass and bronze valves, for example — which cannot be formed by any other method. Copper cannot be used to make satisfactory castings.

[6] Mantell, C. L., op. cit., p. 219.

3. Copper alloys are used to make objects which must be machined — cut, threaded, milled, etc. Copper is soft and tough and difficult to machine satisfactorily.

4. Many copper alloys show resistance to corrosion equal or superior to that of copper.

5. Alloys such as brass (copper-zinc) which contain a cheaper metal than copper, are equally satisfactory for many uses, and are less expensive.

6. Certain copper alloys can be hardened by heat-treating processes (notably the copper-beryllium alloys), but pure copper does not respond to this treatment.

7. Some copper alloys display marked elasticity; this is almost totally lacking in copper.

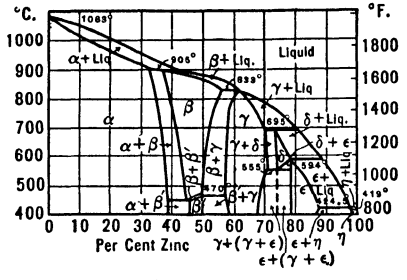
We shall divide the general subject into two parts: (1) *copper-base* alloys in which copper is the predominant metal, and (2) other alloys containing copper.

COPPER-BASE ALLOYS

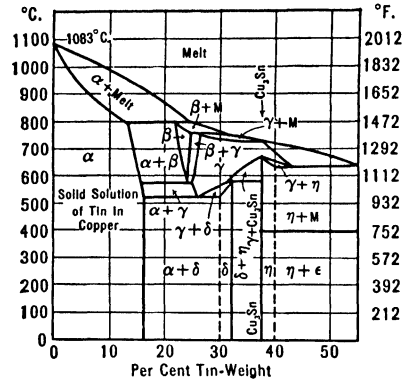
Brass and Bronze. Brasses and bronzes are the most important of the copper-base alloys. Originally the term *brass* was used to designate a copper-zinc alloy, and *bronze* for the copper-tin alloys, but commercial usage has modified this terminology, as may be seen from Tables 7 and 8. Many of the brasses and bronzes contain three or four alloying elements, and there are " bronzes " which contain no tin at all. The tendency is to call the reddish-colored alloys bronzes regardless of their chemical composition.

Constitutional diagrams of the copper-zinc and copper-tin alloy systems are given in Figure 3. Most commercial brasses contain less than 38 per cent zinc and hence consist entirely of the alpha solid solution of zinc in copper, or " alpha brass." A few alloys, such as Muntz metal, contain more than 38 per cent zinc, and these alloys are made up of alpha and beta brass. The beta constituent is brittle at room temperature and these alloys cannot be cold-worked. There are few commercial alloys which contain any of the other constituents shown on the diagram — these are all very brittle, and alloys containing them can be shaped only by casting.

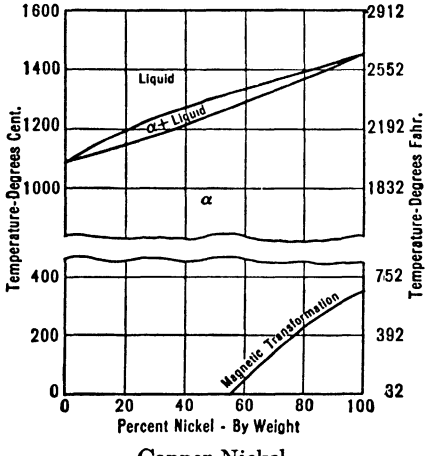
Alpha brass consists of homogeneous grains of the alpha solution of zinc in copper. It ranges in color from a copper red to a bright yellow. Brass containing relatively small amounts of zinc (5 to 20 per cent) is known by various names — *red brass, low brass, commercial bronze,* etc. Brass containing 30 to 40 per cent zinc is known as *common*



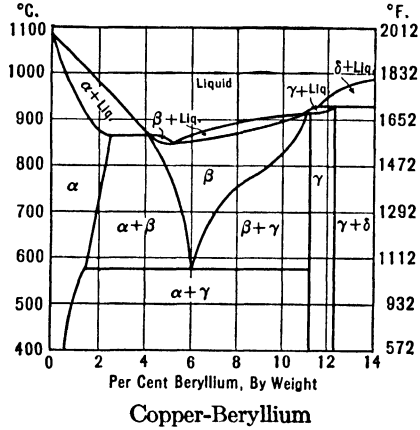
Copper-Zinc



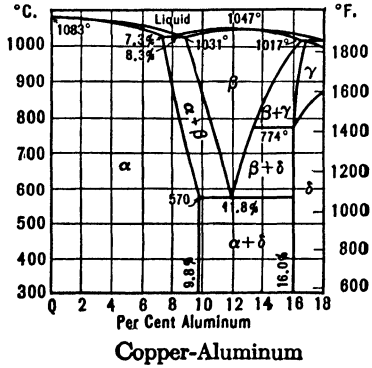
Copper-Tin



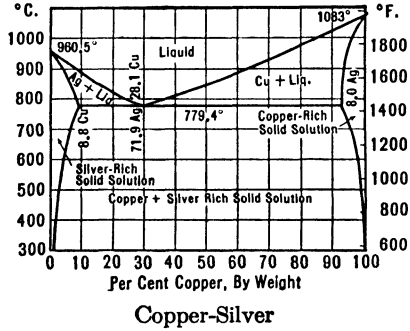
Copper-Nickel



Copper-Beryllium



Copper-Aluminum



Copper-Silver

(From Metals Handbook, Am. Society for Metals, 1936 Ed.)

FIG. 3. Equilibrium Diagrams for Some Copper Alloys.

yellow brass, high brass, cartridge brass, etc. In addition to copper and zinc, many brasses contain other metals (Tables 7, 8), added for various reasons. Lead is added to brass in small quantities to improve its machining qualities. Tin is added to some brasses to improve their mechanical properties.

Brass is an alloy that is cheaper, stronger, and harder than copper; it is less ductile but still retains excellent formability. It can be worked hot or cold and is made into sheet, tubes, pipe, stampings, and wire. The corrosion resistance of brass is comparable with that of copper for most uses. Brass is widely used for castings — gears, propellers, steam and pipe-fittings — a purpose for which copper cannot be used.

The tensile strength of brass increases with the zinc content, and annealed yellow brass will have a tensile strength of about 45,000 pounds per square inch (annealed copper = 32,500 psi). Cold-working may raise the tensile strength to 120,000 pounds per square inch (cold-worked copper = about 60,000 psi).

Brass can be softened by annealing after cold-working but cannot be hardened by heat-treatment. Rolled brass is subject to " season cracking," which is thought to be due to a combination of corrosion plus a readjustment of the strained crystals. Greater care in rolling and annealing will make season cracking less likely to occur.

Brasses for special purposes may contain iron, manganese, and aluminum, as well as the more common addition agents, lead and tin. The data in Tables 7 and 8 give the composition and properties of the most important of these alloys together with notes as to their common uses.

Bronze (Fig. 3) is a copper-tin alloy, and most commercial bronze consists entirely of the alpha solid solution (*alpha bronze*). True bronze is superior to brass in many respects, but tin is much more costly than zinc so bronze is not ordinarily used where brass will do. The recognized superiority of bronze probably explains the tendency to call copper-zinc alloys " bronze " when they have the characteristic reddish color that is associated with bronze. As in the case of brass, there are special bronzes which contain elements other than tin (Tables 7 and 8). Phosphor bronze is one of these special bronzes. Aluminum bronzes contain aluminum instead of tin.

Both brass and bronze are fairly good electrical conductors but far inferior to pure copper in this respect. Bronze is superior to brass in mechanical strength and corrosion resistance, and it makes sounder and denser castings.

Copper-Nickel Alloys. Copper and nickel are soluble in all proportions in the solid state (Fig. 3) and zinc can be dissolved in this solid solution. The cupro-nickels contain copper and nickel only; "nickel silver" is a ternary alloy of copper, nickel, and zinc (Table 8). In general these are white alloys and have the same general properties as brass and bronze; they are much more corrosion-resistant, however.

Beryllium Copper. Beryllium copper has come into prominence in the last 10 years or so, and is an example of an alloy which can be hardened by heat-treatment. Commercial beryllium copper contains about 2.25 per cent Be, and Figure 3 shows that the normal alloy consists of the alpha and gamma phases; the gamma phase is a hard compound of copper and beryllium. When the alloy is heated, the gamma phase goes back into solution, and if the alloy is quenched the gamma phase is retained in a supersaturated alpha solution. Heating the quenched alloy then causes the hard gamma phase to precipitate throughout the alpha grains and *key* the slip planes so that the alloy becomes much harder and stronger. This is the type of heat-treatment known as a *precipitation hardening* (*age-hardening*, if the precipitation in the quenched alloy takes place at room temperature).

OTHER COPPER ALLOYS

Copper is used in many other alloys — strong aluminum alloys, magnesium alloys, Monel metal, and copper-bearing steel.

Monel Metal. Monel metal is a widely used alloy containing about two-thirds nickel and one-third copper. It is about the equal of mild steel in mechanical properties, and is especially resistant to corrosion. Monel metal is a *natural alloy;* i.e., it is made by reducing copper-nickel mattes in which the nickel and copper ratio is about the same as in the alloy.

Copper-Bearing Steel. Steel for sheet and tubes is being manufactured which contains about 0.30 per cent copper. A considerable quantity is consumed for this purpose in spite of the small percentage of copper used in the alloy (Table 1). The principal advantage of copper-bearing steel is its increased resistance to atmospheric corrosion.

TABLE 7

SAND-CAST COPPER-BASE ALLOYS

Name	Analysis, per cent						Tension †			Reduction in Area, %	Compression		Brinell Hardness	Impact Strength, Izod, ft-lb	Remarks and Uses
	Cu	Al	Zn	Si	Mn	Fe	1000 lb per sq in. Yield Point	1000 lb per sq in. Ultimate Strength	Elongation in 2 in., %		Deformation Limit, 1000 lb per sq in.*	Reduction in Height, % Load = 100,000 lb per sq in.			
CAST COPPER															
Pure copper	99 6–99 9	..	..	..	.	..	...	20–25	20–25	75	...	...	40	...	Deoxidized with Si, B_2C_3 or carbon free Mn. Electrical uses, if pure.
HIGH TENSILE BRONZES AND BRASSES															
Aluminum bronze	90 6	9 4	..	..	..	..	21 7 46 6‡ 24 0*s*	67 85‡ 52 5*s*	36 9 5‡ 17 3*s*	47 20‡ 32*s*	...	...	...	. .	Aluminum-bronzes. These alloys should not be slowly cooled from a high temperature if they are to be stressed at ordinary temperatures. Resistant to cold dilute H_2SO_4, cold weak HCl, sea water, etc. Pipe fittings valves and other equipment for chemical industry.
Aluminum bronze	89	10	..		..	1	20–30 54‡	60–75 90‡	24 10‡	27 12‡	18–20	13–15	92–120 175‡	...	
Aluminum bronze	88	9	.	..	..	3	30–45 40‡	70–80 84‡	25–45 30‡	20–40 25‡	14–18	...	95–120 125‡	..	
Everdur	94 4	..	..	4 5	1 1	..	20–30	50–60	10–25	15–22	..	...	92	22	Everdur. Resistant to H_2SO_4, HCl (in absence of air), sea water, caustic soda, phenol, etc
Silicon brass	81.5	.	14	4.5	..	..	..	65–75	9–10	..	..	..	130–150	50	Silicon-brass, for hardness.
Manganese bronze	68 5	4	22	..	3.0	2 5	40–45	85–100	15–20	20–30	60–70	.	150–180	...	Manganese-bronze. For strength, toughness, and hardness.
Manganese bronze	58	..	39	..	0–1	0 75‡	30–45	65–75	20–40	..	12–16	...	90–110	...	Manganese-bronze. Propellers, engine frames, parts requiring strength and toughness. Resistant to sea water and acids.

See footnotes at end of table.

TABLE 7. SAND-CAST COPPER-BASE ALLOYS—*Continued*

Name	Analysis, per cent						Tension †			Reduction in Area, %	Compression		Brinell Hardness	Impact Strength, Izod, ft-lb	Remarks and Uses
							1000 lb per sq in.		Elongation in 2 in., %		Deformation Limit, 1000 lb per sq in *	Reduction in Height, % Load = 100,000 lb per sq in			
	Cu	Sn	Pb	Zn	Ni	Fe	Yield Point	Ultimate Strength							
Silicon brass	59 7		39 7	0 6				50–55	12–15					25	Silicon-brass
Nickel bronze	60		Ni, 30	.	Sn, 8	2		67	0				240		Nickel-bronze Valve facing for severe conditions Abrasion resistant For hardness
BRONZE AND RED BRASS FOR GENERAL ENGINEERING WORK ††															
	Cu	Sn	Pb	Zn	Ni	P									
Bronze	89	8	2	3	.	0 03‡	16–18	30–40	15–30	15–35	12 5–13	33–34	45–60		Bronze for valves and fittings for steam, gas, etc
Bronze	88	8	1 0‡	4	0 75‡	0 05‡	20–25	30–45	15–40	25–35			55–75		Bronze for water-tight castings, underwater fittings, machine parts Non-corrosive
Gear bronze	89	11				0 3‡	18–20	30–35	5–15	6–8	16	25–27	65–85		Gear bronze Very resistant to abrasion For heavy-duty gears and worm wheels.
Bronze	86	8	3	3		0 03‡		30–35	25–30	25–30			55–65		Steam fittings Machines well.
Bronze	86	13	1			Trace	20–35	30–45	1–8	.	16–22	.	85–120		Valve bodies subject to high pressure and vibration
Red brass	85	5	5	5			15–19	27–33	16–20	15–20	11 5–12	36	50–60		Red brass for pump bodies, valves, steam fittings, bearing backs, and metal patterns.

Semi-red brass	85	3	3	9		0 03‡		30–37	20–35	20–30			50–60		Semi-red brass Very resistant to atmospheric corrosion For overhead electrical fittings and for oil and water pumps
Bell metal	78	22					26–32	26–32	0		24–30		130–160		For hardness Difficult to machine
Red brass	75	5	10	10				25–30	10–15	10–15	19	32	50–55		Red brass For low-pressure valves and fittings (Radiator valves) Machines easily
Semi-red brass	76	2	6	16				25–30	20–30	20–30			43–48		Semi-red brass For air, gas, and water fittings Machines very easily
YELLOW BRASS															
Yellow brass	77		0 2‡	22			7–11	22–28	23–35	15–25			40–60		For oil feed cylinder top cover, etc., for automobiles
Yellow brass	69	1		30			10–20	30–40	20–40	25–35	6		45–60		For light castings, builders' hardware, ornamental work
Yellow brass	64	1	2	33		0 50	15	30–35	25–35	20–30			40–50		For common castings where cheapness and good machining properties are main considerations
Naval brass	62	1		37			25–30	35–50	15–30	20–30					"Naval brass" Miscellaneous work for strength
WHITE ALLOYS															
Ambrac	64 5	3 5	5 0	7 5	20 0		20–25	40–45	15–20						Ambrac Resistant to salt spray, dilute H_2SO_4, bleaching solution. Suitable for architectural trim
Benedict metal	55 0		12 5	20 0	12 5		15–20	30–35	15–20						Benedict nickel Resistant to atmospheric corrosion For architectural trim, bathroom and kitchen fittings, builders' hardware

* Load in pounds per square inch producing 0 001-in compression in a specimen 1 in long and 1 sq in. in cross-section † Proof stress is frequently taken as 75 per cent of yield point ‡ Quenched from 1472 deg fahr. § Slowly cooled from 1472 deg fahr *t* Maximum *tt* Should not contain over 0 25 per cent Fe.

Table reprinted by permission from Handbook of Engineering Fundamentals, by O W Eshbach, published by John Wiley and Sons, Inc , New York, 1936.

TABLE 8. CHEMICAL AND PHYSICAL PROPERTIES

(Variations must be

Material	Form	Approximate Composition, per cent					Tensile Strength, lb per sq in		Elongation in 2 in., per cent		Yield Point, (g) lb per sq in		Johnson's Elastic Limit, lb per sq in		Modulus of Elasticity, lb per sq in × 10⁻⁶, Hard*
		Copper	Zinc	Lead	Tin		Hard*	Soft	Hard*	Soft	Hard*	Soft	Hard*	Soft	
Copper	S	99 90+					51,000	32,500	4	37	48,000	12,000		5,000	16 0
	W	99 90+					60,000	38,000	3*e*	36*e*	39,000		36,500		
	R	99 90+					50,000	32,000	18	38	46,000	15,000	35,000		
Deoxidized copper	T	99 90+				Phosphorus present	50,000	35,000	10	35	48,000				
	S	99 90+				present	55,000	35,000	5	35	44,000	15,000			
	R	99 90+				present	58,000	35,000	5	38		20,000			16 0
	W	99 90+				present	60,000	35,000	2 6*e*	35					
Primer gilding	S	97 00	3 00				55,000	35,000	5	37	38,000				
Commercial bronze 95%	S	95 00	5 00				55,000	35,000	5	38	39,000	11,000			15 0
Commercial bronze 90%	S	90 00	10 00				67,000	37,000	3	40	53,000	11,000			15 0
Red brass 85%	S	85 00	15 00				75,000	42,000	4	43	71,000	18,000			15 0
	T	85 00	15 00				68,000	42,000	6	42	64,000	19,000	49,000		
Red brass 80%	S	80 00	20 00				85,000	43,000	4	50					15 0
	W	80 00	20 00				125,000	49,000	2*e*	43*e*					
Brazing brass	S	75 00	25 00				80,000	47,000	5	45					
Spring brass	S	72 00	28 00				76,000	47,000	4	55	38,000				14 0
Cartridge brass	S	70 00	30 00				86,000	45,000	4	50					
Cartridge brass	S	69 00	31 00				85,000	46,000	4	58					
Eyelet brass	S	68 00	32 00				78,000	46,000	5	58	55,000				
Drawing or spinning brass	S	66 67	33 33				76,000	46,000	5	52					
Commercial high brass	S	65 00	35 00				76,000	45,000	5	60			48,000	7,500	14 0
	R	65 00	35 00				70,000	45,000	15	50		12,500			
Brass wire	R	63 00	37 00				70,000	50,000	12	50					14 0
	S	63 00	37 00				84,000	48,000	4	50					
	W	63 00	37 00				125,000	50,000	2*e*	50*e*					

* For some alloys the figures given are for a temper slightly different from that commonly known as "Hard"

† Compared to water at 4 deg cent.

‡ Soft

R Rod

S Sheet

T Tube

W Wire

a Temper not known

b Determination

c Circular 73, U S Bureau of Standards

d Scientific Paper 410, U S Bureau of Standards

e Elongation of wire, per cent in 10 in.

f Corning Glass Works

g Yield point taken as the load producing an extension under stress of 0 75 per cent.

OF VARIOUS WROUGHT COPPER-BASE ALLOYS
expected in practice)

Shearing Strength, lb per sq in.		Brinell Hardness No 10-mm Ball, 500-kg Load		Rockwell Hardness No "B" 1/16-in Ball, 100 kg		Bend Test, deg		Melting Point, deg cent	Specific Gravity †	Density, lb per cu in.	Coefficient of Expansion $\times 10^6$ (y)	Electrical Properties at 20° C		Thermal Conductivity (u)	Uses—Remarks
Hard*	Soft	Hard*	Soft	Hard*	Soft	Hard*	Soft					Resistivity, ohms (mil, ft)	Conductivity, per cent I A C S		
	21,000	103	42	58	Too Soft	180 180 180	180 180 180	1083c	8 89	3217	177	10 371	100 0	0 9225	For electrical parts requiring high conductivity, also for rods, sheets, tubes and wire for commercial purposes
				58 61	Too Soft	180 180 180 180	180 180 180 180	1083b	8 93b	0 323	177				Copper pipe and tube Tougher than electrolytic copper and has better corrosion resistance Welding rod. May also be deoxidized with silicon, manganese, calcium boride, and other deoxidizers
		107	42	65	Too Soft	180	180	1075x	8 890d	0 321	177	15 62	66 40	0 59	Primer gilding
		110	43	68		180	180	1065x	8 866d	0 320	181	18 98	54 6	0 576	For jewelry trade and manufacturing where soft, pliable metal is required
	25,000	115	50	75	1	180	180	1045x	8 804d	0 318	182	25 36	40 90	0 446	For window screen wire and automobile radiators on account of resistance to corrosion and atmospheric action.
		135	52	82	10	180	180	1020x	8 745b	0 316	187	28 03	37 0	0 38	For architectural work on account of color and resistance to corrosion, also for hardware and pipe
43,000R	27,000	150	53	86	11	180 180	180 180	1000x	8 667d	0 313	191	31 95‡ 36 90y	32 5‡ 28 1y	0 335	For its color and resistance to corrosion and atmospheric action Fourdrinier wire
		157	53	87			180	980x	8 594d	0 310	196	34 6‡	30 0‡	0 31	For parts or articles to be brazed or silver soldered, etc.
		158	53	88	20		180	965x	8 553d	0 309	198	36 3	28 60	0 295	For turbine blades, best spring stock, brass rod, etc
		157	53	87			180	955x	8 528d	0 308	199	37 61	27 58	0 290	For primers, shot shells, cartridges, seamless tubes, etc.
		156	53	87	22		180	950x				37 55	27 60	0 290	For cartridges, etc.
		156	53	87	22		180	945x	8 50b	0 307		37 95	27 30	0 289	For eyelets, cartridges, drawn shells, etc
	30,000	153	52	86	20		180	938x	8 476d	0 306	201	40 12	25 85	0 287	For deep drawing, cartridges, etc
	28,000	153	52	85	30		180	930x	8 460d	0 306	202	38 68	26 8	0 285	For a large variety of articles, lamp fixtures, automobile radiators, and for ornamental purposes Not good for exposure to weather
							180	920x	8 437d	0 305	205	39 97	25 95	0 285	For rivets, pins, screws, and other heading operations.

h Jenkins and Hanson constitution diagram
j Average linear coefficient per deg cent from 25 to 300 deg cent Tests on rod Scientific Paper 410, U S Bureau of Standards
k At 18 1 deg cent
m Cold worked and heat-treated
n Guertler-Tammann constitution diagram
p Annealed, quenched, and heat-treated
r Smith constitution diagram
t Stockdale constitution diagram
u Gcal, per sec per sq cm per deg cent per cm at 20 deg cent
v Tafel constitution diagram
x Bauer and Hansen constitution diagram
y Hard at 25 deg cent
z Heycock-Neville constitution diagram

TABLE 8. CHEMICAL AND PHYSICAL PROPERTIES

(Variations must be

Material	Form	Approximate Composition, per cent					Tensile Strength, lb per sq in		Elongation in 2 in, per cent		Yield Point, (g) lb per sq in		Johnson's Elastic Limit, lb per sq in		Modulus of Elasticity, lb per sq in × 10⁻⁶, Hard*
		Copper	Zinc	Lead	Tin		Hard*	Soft	Hard*	Soft	Hard*	Soft	Hard*	Soft	
Muntz metal	S	60 00	40 00				80,000	57,000	9 5	48		20,000			12 8
Cap gilding	S	90 00	9 60	0 40			65,000	39,000	4	35					
Tube brass	S	67 50	32 00	0 50			85,000	43,000	3	46					
	T	67 50	32 00	0 50			50,000	44,000	5	45		17,000			14 0‡
Butt brass	S	64 00	35 00	1 00			80,000	45,000	5	60					
Leaded commercial bronze	R	88 50	10 00	1 50			60,000	35,000	3	30					15 0
Leaded red brass 80%	R	78 50	20 00	1 50			60,000	40,000	10	35					
Leaded brass	R	69 00	29 50	1 50			65,000	45,000	10	34	33,000				
Clock brass	S	61 50	37 00	1 50			80,000	45,000	4	40					
Forging brass	R	60 00	38 00	2 00			70,000	50,000	10	45	31,000	22,000			
Free-cutting rod	R	62 00	35 00	3 00			62,000	47,000	20	60	52,000	32,000			15 0
Oreide	S	87 25	11 50		1 25		80,000	45,000	4	40					
Admiralty	S	70 00	29 00		1 00		95,000	45,000	5	60					
	W	70 00	29 00		1 00		125,000	57,000	2e	42e					
	T	70 00	29 00		1 00			55,000		60					
Naval brass	R	60 00	39 25		0 75		62,000	54,000	25	40					
Tobin bronze	R	60 00	39 25		0 75		75,000	54,000	25	50	60,000	25,000			15 0
	S	60 00	39 25		0 75		90,000	54,000	4	40		25,000	72,500	16,000	
Fourdrinier wire	W	81 00	18 75		0 25			49,000		43e					
Special bronze	S	98 75			1 25		65,000	40,000	4	48					
Signal bronze	W	98 25			1 75		100,000	50,000	3e	33e			73,000		
Phosphor bronze, A	S	96 00			3 75	P 0 25	90,000	45,000	4	50		18,300	68,500	11,100	15 0
	S	95 00			5 00		100,000	50,000	3	55	87,000	23,000	74,000		15 0
Leaded phosphor bronze, B	R	94 00		1 00	5 00			50,000		40		20,000			
Phosphor bronze, C	S	92 00			8 00		110,000	55,000	3	70	85,000	25,000			14 0
Phosphor bronze, D	S	89 50			10 50		115,000	60,000	5	65	95,000	40,000	91,000		
Free-cutting phosphor bronze	R	88 00	4 00	4 00	4 00	Si	60,000		20		50,000				15 0
High-strength bronze	W	97 25			2 00	0 75	120,000	45,000	3e	36					

* For some alloys the figures given are for a temper slightly different from that commonly known as "Hard"

† Compared to water at 4 deg cent

‡ Soft

R Rod

S Sheet.

T Tube

W Wire.

a Temper not known

b Determination

c Circular 73, U S Bureau of Standards

d Scientific Paper 410, U S Bureau of Standards

e Elongation of wire, per cent in 10 in

f Corning Glass Works

g Yield point taken as the load producing an extension under stress of 0 75 per cent.

OF VARIOUS WROUGHT COPPER-BASE ALLOYS—*Continued*

expected in practice)

Shearing Strength, lb per sq in		Brinell Hardness No 10-mm Ball, 500-kg Load		Rockwell Hardness No "B" 1/16-in Ball, 100 kg		Bend Test, deg		Melting Point, deg cent	Specific Gravity †	Density, lb per cu in.	Coefficient of Expansion × 10⁶ (j)	Electrical Properties at 20° C		Thermal Conductivity (u)	Uses—Remarks
Hard*	Soft	Hard*	Soft	Hard*	Soft	Hard*	Soft					Resistivity, ohms (mil, ft)	Conductivity, per cent I A C S		
		155	80	87	42		180	905*z*	8 396	0 303	208	36 25	28 60	0 300	For bolts, nuts, sheathing, pin wire, etc
												24 63	42 10		For caps and electrical parts
		158	52	90	15				8 495*b*	0 307		38 68	26 8		Pipe and tube.
				85	15										For hinges, etc Also for threading and similar operations
35,000															For hardware, jewelry, etc.
		104		58					8 830*d*	0 319	183	25 61*y*	40 50*y*	0 432	Free cutting
.									8 698*d*	0 314	192	35 87*y*	28 91*y*		For rivets, etc. Free cutting.
									8 562*d*	0 309	200	37 65	27 55		For special shapes where high lead is detrimental to the bending or working of the stock.
		142	54	87	13										For clock and meter parts, pinions, and other articles where free milling is required.
		122	82				120		8 44*d*	0 305		39 10‡	26 5‡	0 258	For hot forging. Machines easily.
36,000	28,000	120	54	77	16	120	180	885*b*	8 489*d*	0 307	204	41 46	25 0	0 258	For automatic machine work. Drills and turns easily.
							180								
								935*b*	8 535*b*	0 308	202	42 07	24 65	0 263	For condenser tubes Resists action of sea water.
37,000	33,000						180				214				
45,000	33,000	100	89	75				885*b*	8 404*b*	0 304	211	41 60	24 93	0 279	For piston rods, propeller shafts, nuts, bolts, plates, etc Welding rod.
	33,000	165	90	93	55										
							180		8 712*d*	0 315			32 20	0 341	For Fourdrinier wire
.				71			180	1075*z*	8 89*h*	0 321		24 1	43 0	0 520	For flexible metal hose
.							180	1070*z*	8 89*b*	0 321		29 62	35 0	0 350	For electrical purposes.
54,000	33,000	175	60	90	30		180	1050*z*	8 88*b*	0 321	190	82 18‡	12 62‡	0 150	For springs, electric switches, etc.
		190	60	96	30		180	1050*z*	8 87*b*	0 320	178	56 46	18 37	0 195	For window weight chain. Bronze chain in general.
					75		180	.	8 929*b*	0 322	.	56 46	18 37	0 199	Phosphor bronze with good machining properties.
60,000		200	70	99	38		180	1025*z*	8 815*b*	0 318	182	79 8	13 00	0 150	For electric switches, contact fingers, diaphragms, radio parts, etc.
64,000		200	74	100	52		180	1000*z*	8 78*b*	0 317	183	98 10	10 6	0 121	For very stiff resilient springs (flat or coiled). Also for chain.
35,000	.	120		75					8 86*b*	0 320		.	.	12.2	0 133	For good machining properties.
							180	1022*b*				86 43	12 0		For electrical purposes

h Jenkins and Hanson constitution diagram
j Average linear coefficient per deg cent from 25 to 300 deg cent Tests on rod Scientific Paper 410, U S. Bureau of Standards.
k At 18 1 deg cent.
m Cold worked and heat-treated
n Guertler-Tammann constitution diagram.
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r Smith constitution diagram
t Stockdale constitution diagram
u G-cal, per sec per sq cm per deg cent per cm at 20 deg cent
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y Hard at 25 deg cent
z Heycock-Neville constitution diagram.

TABLE 8. CHEMICAL AND PHYSICAL PROPERTIES

(Variations must be

Material	Form	Approximate Composition, per cent						Tensile Strength, lb per sq in		Elongation in 2 in, per cent		Yield Point, (g) lb per sq in.		Johnson's Elastic Limit, lb per sq in		Modulus of Elasticity, lb per sq in $\times 10^{-6}$, Hard*
		Copper	Zinc	Nickel				Hard*	Soft	Hard*	Soft	Hard*	Soft	Hard*	Soft	
Super-nickel	T	70 00		30 00					65,000		30					
20% cupro-nickel	S	80 00		20.00				85,000	50,000	2	30					
15% cupro-nickel	S	85 00		15 00				70,000	45,000	3	30	51,000				
30% nickel silver	S	47 00	23 00	30 00				130,000	72,000	2	35					
	W	47 00	23 00	30 00				160,000	75,000	1*e*	35*e*					
Ambrac B	S	65 00	5 00	30 00				105,000	65,000	2	30					
	R	65 00	5 00	30 00				85,000	65,000	10	30					20 0
	W	65 00	5 00	30 00				130,000	65,000	2*e*	30					
25% nickel silver	S	55 00	20 00	25 00				110,000	72,000	4	30					
Ambrac A	S	75 00	5 00	20 00				85,000	50,000	5	35	77,000	23,000	57,000	10,000	
	R	75 00	5 00	20 00				80,000	55,000	10	50	70,000	18,000	52,000	13,000	19 0‡
	W	75 00	5 00	20 00				115,000	55,000	2*e*	30*e*					
18% nickel silver	S	65 00	17 00	18 00				90,000	58,000	3	40	83,000		72,000		18 0
18% nickel silver	S	56 00	26 00	18 00				100,000	60,000	2	40					
	W	56 00	26 00	18 00				143,000	60,000	1*e*	40*e*			103,000		14.1
15% nickel silver	S	64 00	21 00	15 00				93,000	58,000	5 5	40			75,000	22,000	
15% nickel silver	S	57 00	28 00	15 00				95,000	55,000	2	35					
Leaded nickel silver	S	61 00	25 00	12 50	Lead 1 50			90,000		5						
10% nickel silver	S	65 00	25 00	10 00				90,000	50,000	3	45		11,000			17 5‡
5% nickel silver	W	63 00	32 00	5 00				135,000		2*e*						
5% aluminum bronze	S	95 00			Al 5 00			105,000	52,000	5	70					
8% aluminum bronze	S	92 00			8 00			120,000	60,000	4	60	60,000				15 0
	R	92 00			8 00			100,000	60,000	4	60					
8% aluminum bronze with iron	R	89 50			8 00	Iron 2 50		125,000	72,000	5	50	80,000	35,000			
10% aluminum bronze	R	90 00			10 00			125,000 *m*	78,000	5*m*	36	67,000	41,000			
Avialite	R	90 00			9 50	0 50		88,000		35		43,000				

* For some alloys the figures given are for a temper slightly different from that commonly known as "hard"

† Compared to water at 4 deg cent.

‡ Soft

R Rod

S Sheet

T Tube

W Wire

a Temper not known

b Determination

c Circular 73, U S Bureau of Standards

d Scientific Paper 410, U S Bureau of Standards

e Elongation of wire, per cent in 10 in

f Corning Glass Works

g Yield point taken as the load producing an extension under stress of 0 75 per cent.

OF VARIOUS WROUGHT COPPER-BASE ALLOYS—*Continued*

expected in practice)

Shearing Strength, lb per sq in		Brinell Hardness No 10-mm Ball, 500-kg Load		Rockwell Hardness No "B" 1/16-in Ball, 100 kg		Bend Test, deg		Melting Point, deg cent	Specific Gravity †	Density, lb per cu in	Coefficient of Expansion $\times 10^6$ (*j*)	Electrical Properties at 20° C		Thermal Conductivity (*u*)	Uses—Remarks
												Resistivity, ohms (mil, ft)	Conductivity, per cent I A C S		
Hard*	Soft	Hard*	Soft	Hard*	Soft	Hard*	Soft								
				85	37 5		180	1225*n* 1200*n*	8 950	0 323	162*f*	218 4 160 2	4 75 6 47	0 069 0 087	For condenser tubes For turbine blades and parts where resistance to corrosion and erosion is required
							180	1175*n*	8 95*b*	0 323		127 0	8 17	0 112	For bullet jackets
					61		180	1140*v*	8 74*b*	0 316		290 0	3 58		Has comparatively high electrical resistance Used in electrical instruments
55,000		195	63	96	32		180	1220*b*	8 86*b*	0 320	162*f*	231 8*a*	4 47*a*	0 068	For resistance to corrosion and atmospheric action, also for ornamental purposes
		208	89		60		180	1135*v*	8 72*b*	0 315		259 0*a*	4 00*a*		For tableware, plated and unplated
50,000	33,000	160	58	88	25		180	1150*b*	8 860	0 320	164*f*	172 0	6 2	0 092	For resistance to corrosion and atmospheric action, also for ornamental purposes.
		170	70	91	40		180	1110*v*	8 752*b*	0 316		175 0	5 91	0 080	For silver-plated forks, spoons, knives, hollow ware, etc
65,000		190	70	95	40	180	180	1055*v*	8 68*b*	0 314		186 5‡ 185 0	5 56‡ 5 61	0 071 0 071	Similar to 30% nickel silver but of lower resistance
			73	92	33		180	1075*v*	8 691*b*	0 314		165 6	6 26	0 081	For silver-plated ware, spinning, drawing, and for work where a low percentage of nickel is required
			7-				180	1030*b*	8 631*b*	0 312					For white metal tubes, sheets, wire, etc Also in plumbing and decorations.
		166		88			180								For watch parts, etc Free cutting
	34,000			82	32			1010 960*v*	8 675*b*	0 313		125 5 86 5	8 27 11 99	0 110 0 140	For cheaper grades of silver-plated ware.
		176	67	93	20			1060*t*	8 176*b*	0 295		58 61	17 69	0 198	For diaphragms to withstand pressure, also for its color
		185	60	99	30			1040*t*	7 80*b*	0 281	179	70 08*k*	14 80*k*	0 173	For diaphragms to withstand pressure, also for resistance to ordinary corrosion and wear
		190	70	100	52				7 74*b*	0 280		95 10	10 9		For strength and resistance to ordinary corrosion and wear
		190	100	100	65			1040*t*	7 57*b*	0 273		76 80	13 5	0 157	For strength and resistance to ordinary corrosion and wear
45,000		140						1042*b*	7 585*b*	0 274	169	82 25	12 61	0 144	For valve seats in airplane engines and at elevated temperatures

h Jenkins and Hanson constitution diagram
j Average linear coefficient per deg cent from 25 to 300 deg cent Tests on rod Scientific Paper 410, U S Bureau of Standards.
k At 18 1 deg cent
m Cold worked and heat-treated
n Guertler-Tammann constitution diagram
p Annealed, quenched, and heat-treated
r Smith constitution diagram
t Stockdale constitution diagram
u G-cal per sec per sq cm per deg cent per cm at 20 deg cent
v Tafel constitution diagram
x Bauer and Hansen constitution diagram
y Hard at 25 deg cent
z Heycock-Neville constitution diagram

TABLE 8. CHEMICAL AND PHYSICAL PROPERTIES

(Variations must be

Material	Form	Approximate Composition, per cent						Tensile Strength, lb per sq in		Elongation in 2 in., per cent		Yield Point, (g) lb per sq in.		Johnson's Elastic Limit, lb per sq in		Modulus of Elasticity, lb per sq in $\times 10^6$, Hard*
		Copper	Zinc	Nickel				Hard*	Soft	Hard*	Soft	Hard*	Soft	Hard*	Soft	
Calsun bronze	W	95 50		Manganese 0 10	Al 2 50	Iron 1 45	Tin 2 00	135,000	50,000	4*e*	35*e*			81,000		
Manganese bronze	R	57 00	40 00				1 45	90,000	65,000	15	45					
Manganese bronze	R	59 00	39 00	0 50		0 80	0 70	85,000	60,000	20	45					
Everdur (A) 1010	S	96 00		1 00	Si 3 00			113,000	55,000	5	48	75,000	20,000	72,000	9,300	
	R	96 00		1 00	3 00			95,000	55,000	15	85	75,000	20,000	67,000		15 0
	W	96 00		1 00	3 00			145,000	59,000	5*e*	50*e*	95,000	25 000	90,000		
Everdur (B) 1015	T	98 25		0 25	1 50			65,000	40,000	15	60	60,000	10,000			
	R	98 25		0 25	1 50			70,000	40,000	6	60		10,000			
	S	98 25		0 25	1 50			70,000	40,000	6	46	65,000	10,000	38,000		
Hitenso A	W	99 35			Cadmium 0 65			75,000		3*c*		47,000		45,000		15 6
	S	99 35			0 65			54,000		5						
Hitenso BB	S	99 00			1 00			60,000	35,000	3	50			36,000		
	W	99 00			1 00			92,000	35,000	3*e*	50*e*			55,000		
Hitenso C	S	98 60			0 80		0 60		36,000		50		15,000			
	W	98 60			0 80		0 60	99,000	40,000	4*e*	45*e*			59,000		
Tempaloy 917	R	81 90	Iron 2 50	Ni 5 00	Al 9 60	Mn 1 00		100,000		10		50,000	.			
Extruded architectural bronze shapes		57 00	Zinc 40 00	Lead 2 50	Tin 0 34	Iron 0 16		70,000	50,000	10	20					
Beryllium copper	S	97 40	.	Be 2 25 Ni 0 35				118,000	70,000	4 3	45	105,000	31,000	79,000	18,000	17 2
	S	97 40		Ni 2 25 Ni 0 35				192,000 *m*	175,000 *p*	2 *m*	6 3*p*	138,000 *m*	114,000 *p*	130,000 *m*	87,000 *p*	18 4 *m*

* For some alloys the figures given are for a temper slightly different from that commonly known as "hard"

† Compared to water at 4 deg cent.

‡ Soft

R Rod

S Sheet

T Tube

W Wire

a Temper not known

b Determination

c Circular 73, U S Bureau of Standards

d Scientific Paper 410, U S Bureau of Standards

e Elongation of wire, per cent in 10 in.

f Corning Glass Works

g Yield point taken as the load producing an extension under stress of 0 75 per cent

OF VARIOUS WROUGHT COPPER-BASE ALLOYS—*Continued*
expected in practice)

Shearing Strength, lb per sq in		Brinell Hardness No 10-mm Ball, 500-kg Load		Rockwell Hardness No "B" 1/16-in Ball, 100 kg		Bend Test, deg		Melting Point, deg cent	Specific Gravity †	Density, lb per cu in	Coefficient of Expansion $\times 10^6$ (*y*)	Electrical Properties at 70° C		Thermal Conductivity (*u*)	Uses—Remarks
Hard*	Soft	Hard*	Soft	Hard*	Soft	Hard*	Soft					Resistivity, ohms (mil, ft)	Conductivity, per cent I A C S		
..								1054*b*	8 540*b*	0 308		61 0	17 0		For electrical uses where corrosion resistance is important
.		170													For structural work due to strength and resistance to corrosion
.				90					8 370*b*	0 302		42 15	24 6	0 241	For structural work due to strength and resistance to corrosion
		200	70	95	40		180	1019*b*	8 539*b*	0 308	180	155	6 7	0 078	For strength and resistance to corrosion Has strength of mild steel and corrosion resistance of copper Welding rod
56,000	33,000	190	60												
75,000	35,000														
				75	20		180	1055*r*	8 740*b*	0 316					For strength and resistance to corrosion, bolt stock, and sheet metal requiring high ductility
							180					86 4	12 0	0 129	
				80	3		180								
							180	1080*h*	8 89*b*	0 3212		12 20	85 0		For electrical wire and cable, etc
		95		62											
		98		65			180	1076*h*	8 89*b*	0 3212		12 95*y*	80 0*y*	0 824	For electrical wire and cables, contact fingers, commutator segments, etc.
												12 95*y*	80 0*y*		
							180	1070*b*	8 89*b*	0 3212		18 85*y*	55 0*y*	0 556	For electrical wire and cables, etc
												18 85*y*	55 0*y*		
								1054*b*	7 569	0 273					For strength and resistance to corrosion
								884*b*	8 432*b*	0 305					For architectural shapes.
.				102	65 to 73			955*b*		0 297 ± 01	170		17 ± *p*		For springs, diaphragms, low duty bushings and bearings, and Bourdon tubes
.				114	112 5					0 297			18 to 25 *m*	0 25 *p*	High resistance to fatigue.
		m	*p*	*m*	*p*					± 01				0 20 *m*	

h Jenkins and Hanson constitution diagram
j Average linear coefficient per deg cent from 25 to 300 deg cent Tests on rod Scientific Paper 110, U S Bureau of Standards
k At 18 1 deg cent
m Cold worked and heat-treated
n Guertler-Tammann constitution diagram.
p Annealed, quenched, and heat-treated.
r Smith constitution diagram
t Stockdale constitution diagram
u G-cal per sec per sq cm per deg cent per cm at 20 deg cent
v Tafel constitution diagram
x Bauer and Hansen constitution diagram
y Hard at 25 deg cent
z Heycock-Neville constitution diagram

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CHAPTER XII

PRODUCTION OF COPPER

INTRODUCTION

In this chapter we shall give a brief analysis of the production of copper throughout the world. Copper and copper alloys were known to man long before there was any written history, but until 200 to 300 years ago the supply of copper (and other metals) available for man's use was insignificant when compared with the amounts in use today. Kings, nobles, and other wealthy people possessed most of the metal, and copper was classed with the precious metals in value. Mining was confined to rich ores found near the surface, and metal production was limited. As far as any considerable production of copper is concerned, history does not begin until about 1800.

With respect to the world production of copper in 1800, Julihn[1] makes the following statement:

> In 1800 there was as yet no established production from North America, Africa or Australasia, but Europe produced an average of about 12,400 tons a year, including about 7,300 tons from Great Britain, 3,300 tons from Russia, and 1,700 tons from Sweden, Norway, and Germany. Japan produced about 3,100 tons a year and South America about 2,600 tons a year — 1,700 tons from Chile and 900 tons from Venezuela. All other production appears to have been casual in character and slight in quantity.

Comparing the world production in 1800 (18,100 tons) with the 1937 production (2,343,156 metric tons)[2] we find that the yearly production has increased over 130-fold in a period of 137 years. Some of the oldest known deposits are still producing; in 1938 Spain produced about 30,000 metric tons of copper, and the island of Cyprus 29,780 tons. Copper has been mined in both of these places since the earliest times, in fact our word "copper" is derived through Greek and Roman sources from the name Cyprus. It is interesting to note that although the present production from Spain and Cyprus is each only a little

[1] Julihn, C. E., Summarized Data of Copper Production: U. S. Bur. Mines Econ. Paper 1, p. 30, 1928.

[2] Minerals Yearbook, 1939, p. 115, U. S. Bur. Mines.

over 1 per cent of the world production, yet either of these is now producing more copper than the entire world production in 1800.

The present large production of copper is the result of the great demand for the metal which followed the industrial revolution in the nineteenth century. Two primary factors are responsible for the large increase in production — the discovery of immense new ore deposits in Africa and the Americas, and the development of techniques for winning copper from low-grade ores

COMPARISON WITH OTHER METALS

Copper ranks second in tonnage of all metals produced; iron exceeds it both in tonnage and in value, and in recent years the value of gold produced has exceeded that of copper. Statistics of world production of the nine most important metals are given in Table 1.

Although the amount of metal produced in the world depends on many economic, political, and military factors, so that the production fluctuates from year to year, there are certain generalizations which apply to the position of copper in relation to other metals, most of the points listed below are illustrated by the statistics in Table 1.

1. Copper is the most important non-ferrous base metal, both with respect to the tonnage produced and to its value. It has maintained this position for many years and probably will maintain it for many years to come.

2. In recent years the higher price of gold has stimulated production, and now the value of gold produced greatly exceeds that of copper. In 1929, however, the value of the copper produced was almost twice that of gold.

3 From the tonnage standpoint, there is from 40 to 50 times as much pig iron produced as copper Copper, however, is worth from 10 to 20 times as much as pig iron, so that the ratio of the total value of these metals is much smaller than the tonnage ratio

4. Lead and zinc are produced in tonnages only slightly less than that of copper (Table 1), but the prices of both these metals are consistently much lower than the copper price.

5. In recent years the production of both aluminum and nickel has increased rapidly; aluminum rose from eighth place in 1929 to fourth in 1938 (Table 1). In the same period the tonnage of nickel produced was doubled Aluminum tonnage is still well below the tonnage of copper, lead, or zinc, but in value the aluminum ranks next to copper (1938).

TABLE 1[a]

WORLD PRODUCTION OF METALS FOR 1929, 1936, AND 1938

Metal, Ranked According to Value	Production (short tons)	Price	Value
1929			
1. Pig iron	107,408,000	$20 00/long ton	$1,918,000,000
2. Copper	2,104,110	18 107 cents/pound	757,479,600
3. Gold[b]	670	$20.67/troy ounce	403,366,000
4 Lead	1,935,110	6 833 cents/pound	264,300,000
5. Zinc	1,621,230	6.512 cents/pound	211,100,000
6. Tin	213,143	45 19 cents/pound	192,700,000
7. Silver[c]	9,000	53.3 cents/troy ounce	147,212,439
8. Aluminum	298,000	24 0 cents/pound	143,000,000
9 Nickel	62,300	35 0 cents/pound	43,610,000
1936			
1 Pig iron	100,578,240	$18 90/long ton	1,700,000,000
2. Gold[b]	1,219	$35 00/troy ounce	1,233,312,825
3. Copper	1,836,480	9 474 cents/pound	350,000,000
4 Tin	199,034	46 42 cents/pound	185,000,000
5. Aluminum	394,700	20 5 cents/pound	161,800,000
6. Zinc	1,646,786	4 901 cents/pound	161,400,000
7. Lead	1,642,726	4 710 cents/pound	158,500,000
8. Silver[c]	8,557	45 399 cents/troy ounce	114,007,000
9. Nickel	98,400	35 0 cents/pound	68,880,000
1938			
1. Pig iron	90,000,000	$21 67/long ton	1,745,000,000
2. Gold[b]	1,263	$35 00/troy ounce	1,289,785,000
3. Copper	2,185,000	10 00 cents/pound	437,000,000
4. Aluminum	648,000	20 0 cents/pound	259,200,000
5. Lead	2,070,000	4 74 cents/pound	196,300,000
6. Zinc	1,750,000	4 610 cents/pound	161,200,000
7. Tin	165,000	42 26 cents/pound	124,500,000
8. Silver[c]	9,050	42 944 cents/troy ounce	113,496,269
9. Nickel	123,500	35 0 cents/pound	86,450,000

[a] Mineral Industry, 1929, 1936, and 1938, McGraw-Hill Book Co , New York The world price of silver is used, in other cases the price is the average United States price for the year

[b] Production of gold in troy ounces 19,500,000 in 1929, 35,500,000 in 1936, and 36,851,000 in 1938

[c] Production of silver in troy ounces 262,000,000 in 1929, 250,000,000 in 1936, and 264,289,000 in 1938

WORLD PRODUCTION OF COPPER

The data in Table 2 show the total world production of new copper from 1800 to 1940, taken by decades, and these data are plotted in Figure 1. Considering the production data in this way gives a better picture of the general trend than a direct plot of annual production (Fig. 2) because the irregularities are smoothed out. A curve drawn through the extremities of the ordinates in Figure 1 shows the general characteristics of world production. The total production in the decade 1931–1940 is almost 100 times the 1801–1810 production, and the most rapid increase in production took place from 1881 to 1920. For the hundred years 1821 to 1920 the average increase was 52.8 per cent per decade. Since 1920 the curve has been rising less steeply but still does not appear to have "flattened out."

TABLE 2[a]

WORLD PRODUCTION OF COPPER BY DECADES

Decade	Production (short tons)	Increase (per cent)	Decade	Production (short tons)	Increase (per cent)
1801–1810	182,000	. . .	1871–1880	1,423,744	23 9
1811–1820	188,496	3 6	1881–1890	2,488,591	74.8
1821–1830	273,504	45 1	1891–1900	4,149,353	66.7
1831–1840	364,448	33 3	1901–1910	7,628,334	83 8
1841–1850	493,808	35 5	1911–1920	12,187,341	59 8
1851–1860	759,079	53 7	1921–1930[b]	15,198,926	24 9
1861–1870	1,149,344	51 4	1931–1940[c]	17,000,000	11 8

[a] U S Bur Mines Econ Paper No 1, 1928
[b] Mineral Industry for 1938, McGraw-Hill Book Co , New York
[c] Estimated

Figure 2 shows the yearly world production in the period 1881–1938. Since 1910 the production curve has shown a series of violent fluctuations, although the general trend is the same as that noticeable in Figure 1. In 1937 the world production reached an all-time high of about 2½ million short tons; previous records were 1.5 million tons in 1919 and 2.1 million tons in 1929.

It is very difficult to predict what the future world production of copper will be because there are many unknown factors which will affect it. It is possible to extrapolate the production curve into the future by drawing "average" curves or "trend lines," and these, of course, indicate that copper production will increase rapidly according to the sharp rise of the production curve during the last 50 years (Figs. 1 and 2). Such predictions indicate an annual production of

7 to 8 million tons in the early part of the twenty-first century — three times the 1937 production. An increased demand such as this would require the discovery of new ore deposits much greater than the reserves

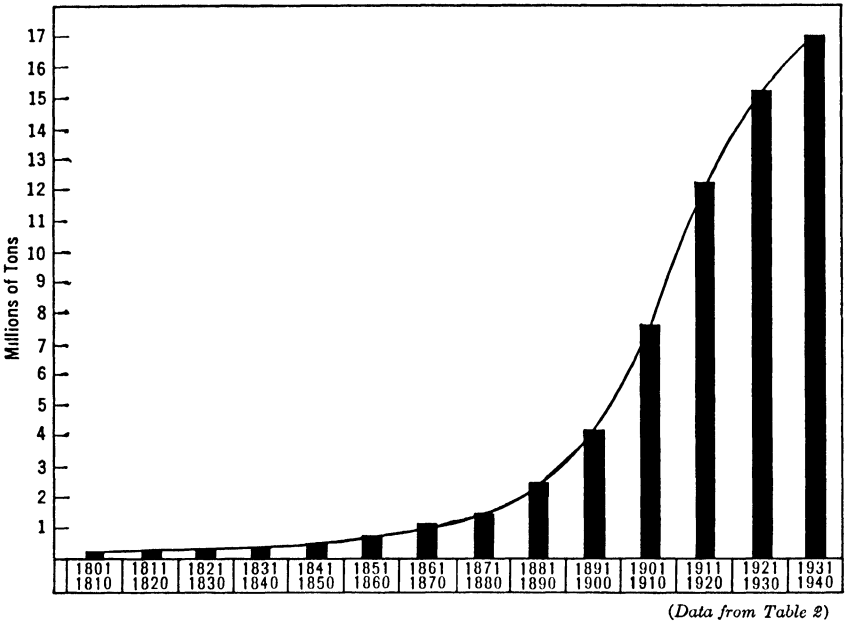


FIG. 1 World Production of Copper by Decades

we have today, and also the mining, milling, and smelting methods would have to be completely revolutionized in order to exploit low-grade and complex ores.

There are many other factors which must be considered which cast some doubt on the accuracy of a simple extrapolation of the trend line to determine future production.

1. An increasing demand in the next century corresponding to the increase in the past 50 or 60 years will follow only if there is a corresponding increase in industrialization throughout the world. If China, India, and other countries were to develop an industrial plant comparable to that of the United States, Great Britain, or Germany, then the copper production would probably exceed the predictions of the most optimistic statistician. Some such development seems likely, but its nature and extent cannot be predicted.

2. The figures we have quoted thus far refer to *primary copper* or copper obtained from newly mined ores. Much of the world's consumption, however, is *secondary* or *scrap* copper. Up to the end of

1938 the total world production of primary copper was about 60 million short tons and at present the world is adding to this stock at the rate of about 2 million tons yearly. Copper is an "indestructible" metal, and much of the copper used commercially can be reclaimed and used over and over again. This rapidly growing supply of copper is found to decrease the demand for newly mined copper, and the time may come when the production of primary copper will be just sufficient to replace the unavoidable loss or wastage in the circulating

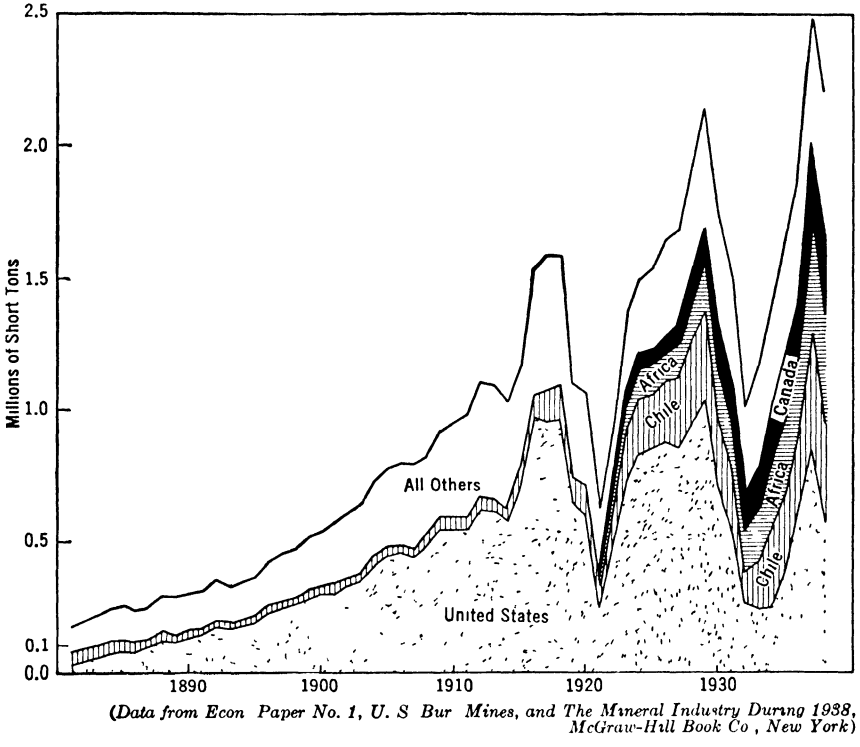


FIG. 2. World Annual Production of Copper.

supply of metal. Secondary copper is already an important factor in world markets, and we shall have more to say on this subject in another section.

3. For certain uses other materials are being substituted for copper — aluminum, nickel, and some non-metallic substances. This may eventually prove to be an important factor; but, as we have noted, it is unlikely that a substitute can be found for copper where the material must have high electrical and thermal conductivity.

TABLE 3[a]

WORLD PRODUCTION OF COPPER BY CONTINENTS FOR VARIOUS PERIODS SINCE 1801

Continent	1801–1900 (100 years)		1901–1925 (25 years)		1926–1937 (12 years)		1938 (1 year)	
	Short Tons	Per Cent	Short Tons	Per Cent	Short Tons	Per Cent	Short Tons	Per Cent
North America	3,795,858	33 09	16,920,711	65 77	10,060,000	50 4	910,000	41.7
South America	2,358,303	20 56	2,845,801	11 07	3,830,000	19 2	430,000	19.7
Europe	3,910,565	34 08	2,658,096	10 33	2,220,000	11 1	282,000	12 9
Asia	684,561	5 97	1,641,342	6 38	1,140,000	5 7	144,000	6.6
Africa	200,623	1 75	779,620	3 03	2,530,000	12 6	396,000	18 1
Australasia	522,457	4 55	880,836	3 42	194,000	1 0	21,800	1.0
World Total	11,472,367	100 00	25,726,406	100 00	19,974,000	100 00	2,183,800	100 00

[a] Data from U. S. Bur. Mines Econ. Paper No. 1, and Mineral Industry, 1933 and 1938, Vols. 42 and 47.

4. Although the future may create greater demands for copper, it is possible that present reserves may become exhausted and that new discoveries of copper ore may not keep pace with the demand. In such a case the price of copper would rise, and pressure of this sort would result in a greater use of copper scrap and more intensive development of substitutes for copper.

Table 3 lists the copper production of the continents for various periods from 1800 to 1938, these data are plotted in Figure 3. From

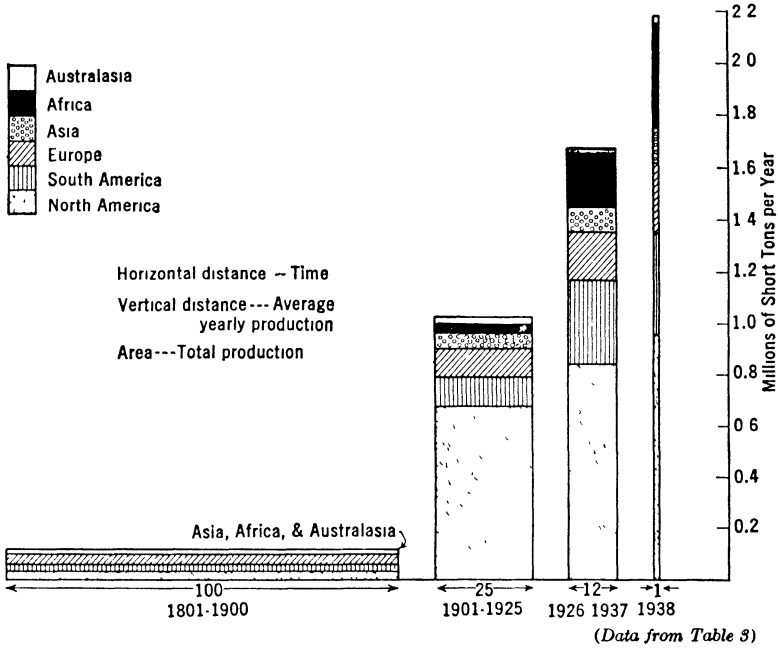


FIG. 3. World Production of Copper Since 1800.

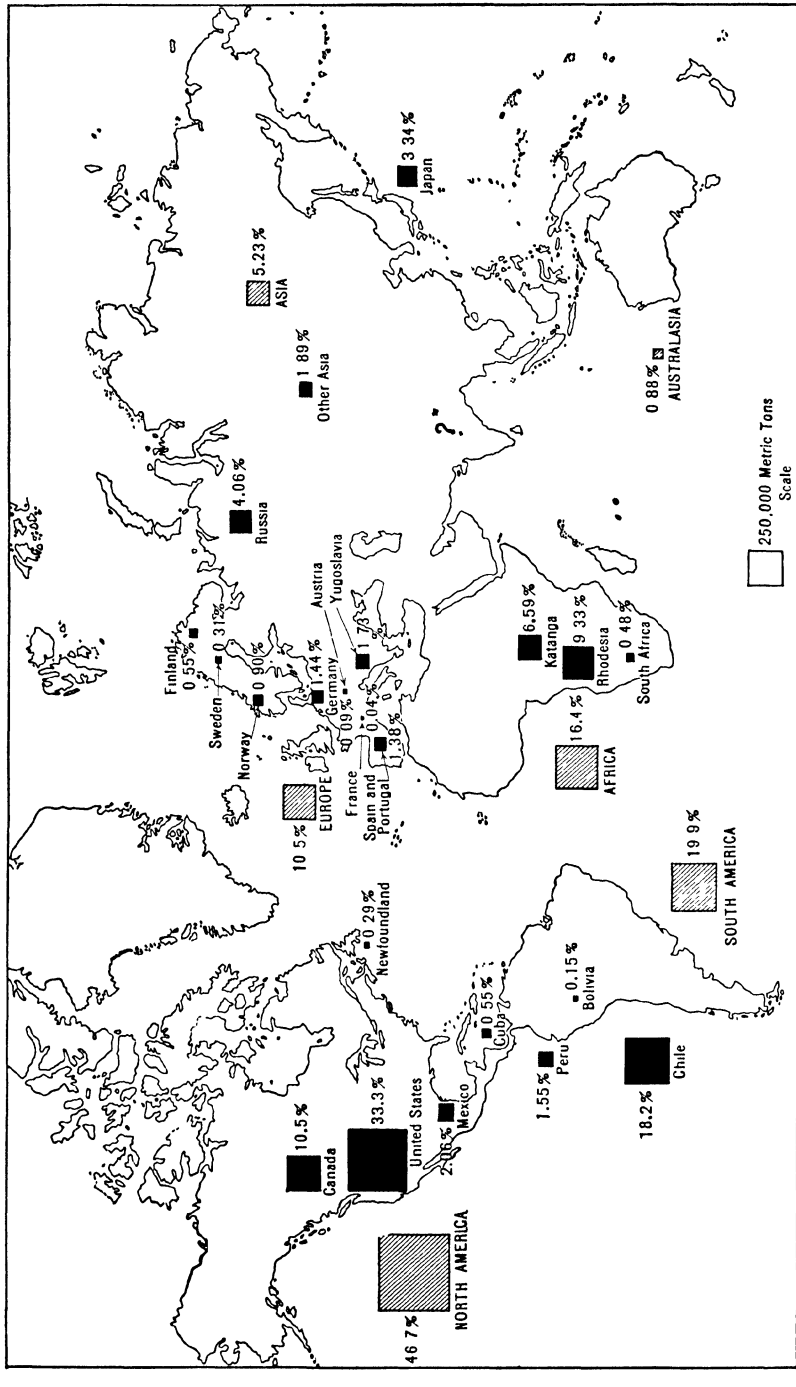
these figures we can compare the relative amounts of metal produced throughout the world and also the relative importance of the continents as producers of copper.

The total world production of copper in the half century from 1801 to 1850 is given in Table 4. The figures in this table show several facts which may be contrasted with present day figures

1 England was the most important copper producing country; today the amount of primary copper produced in England is negligible.

2. Europe was the largest producer of all the continents.

3. No production whatever was shown for Africa, and the bulk of the North American production came from Cuba. All the production



(*Data from The Mineral Industry During 1938, McGraw-Hill Book Co., New York*)

FIG. 4. World Production of Copper in 1937.

TABLE 4[a]

WORLD COPPER PRODUCTION, 1801–1850

Europe									
	England	Russia	Sweden	Germany	Norway	Austria-Hungary	Spain and Portugal	Italy	Total Europe
Production, short tons	594,160	216,048	49,056	31,808	25,872	17,422	8,137	7,056	949,559
Yearly average, short tons	11,883	4,321	981	636	517	348	163	141	18,991
Per cent of European total	62 5	22 8	5 2	3 4	2 7	1 8	0 9	0 7	100 0
Per cent of world total	39 55	14 38	3 27	2 12	1 72	1 16	0 54	0 47	63 21

South America				Asia	
	Chile	Venezuela	Total South America		Japan
Production, short tons	212,912	47,600	260,512	Production, short tons	197,120
Yearly average, short tons	4,258	952	5,210	Yearly average, short tons	3,942
Per cent of South American total	81 7	18 3	100 0	Per cent of Asiatic total	100 0
Per cent of world total	14 17	3 17	17 34	Per cent of world total	13 12

Australasia		North America				Total World (short tons)	
	Total Australasia		Cuba	United States	Total North America		
Production, short tons	17,584	Production, short tons	74,794	2,688	77,482	Production	1,502,256
Yearly average, short tons	352	Yearly average, short tons	1,496	54	1,550	Yearly average production	30,045
Per cent of world total	1 17	Per cent of North American total	96 5	3 5	100 0		
		Per cent of world total	4 98	0 18	5 16		

[a] U S Bur Mines Econ. Paper No 1.

credited to the United States came in the decade 1841–1850, but Cuba had been producing copper since before 1830.

4. South America accounted for a good share of the world's production, and the bulk of the South American copper came from Chile since 1800. Chile has always produced a considerable share of the world's copper (Fig. 2).

5. The average annual production was small when compared to today's figures, and the total world production in the 50 years from 1801 to 1850 was only about 60 per cent of the world production in the single year of 1937.

EUROPE

Until 1800, Europe was far and away the leading producer of copper in the world, and in the first half of the nineteenth century (1801–1850) it accounted for 63 per cent of the world's copper. Since that time the relative importance of European copper has steadily declined; the yearly tonnage has increased, but Europe's share of the world total has dropped to 8 or 10 per cent because of the great increase in production in other parts of the world.

Spain and Portugal. The main producing districts in Spain are Rio Tinto and Tharsis, and most of the Portuguese production comes from the Mason and Barry mines. From 1801 to 1927 inclusive, Spain and Portugal constituted the leading European producer of copper and in that period accounted for 6 97 per cent of the world's production.[3] Table 5 gives the copper production of Spain and Portugal for various periods; note that in recent years its importance has declined both with respect to European and world production. There has been relatively little fluctuation in the yearly tonnage produced.

Germany. The copper production of Germany is shown in Table 6 for the same periods as those shown in Table 5. During the periods shown, Germany has generally accounted for one-fifth to one-fourth of the European production, and the yearly tonnage has shown a steady increase up to 1937.

The most important deposits in Germany are the low-grade copper-bearing shales of Mansfeld in central Germany; these account for practically all the present German production.

Russia. Table 7 gives the copper production of Russia during periods comparable with those in Tables 5 and 6. Note particularly the rapid increase in tonnage in the last few years; in 1937 Russia accounted for 38.4 per cent of the European production and about 4 per

[3] U. S. Bur Mines Econ. Paper No. 1, 1928.

TABLE 5[a]

COPPER PRODUCTION OF SPAIN AND PORTUGAL

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of European Total	Per Cent of World Total
1871–1880	219,408	21,941	49.9	15.41
1881–1885	241,142	48,228	60 6	21.81
1886–1890	299,870	59,974	66 0	21.69
1901–1910	563,267	56,327	55.2	7.39
1911–1920	448,849	44,885	38 2	3.68
1921–1925	205,916	41,183	50 7	3.49
1927	60,351	60,351	43 3	3 60
1929[b]	53,500	53,500	31 4	2 53
1933[b]	40,500	40,500	20.6	3.54
1937[b]	34,500	34,500	13 0	1.38

[a] U S Bur Mines Econ Paper No 1.
[b] Mineral Industry in 1938, Vol 47

TABLE 6[a]

COPPER PRODUCTION OF GERMANY

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of European Total	Per Cent of World Total
1871–1880	73,360	7,336	16.4	5 15
1881–1885	82,951	16,590	20 8	7.50
1886–1890	89,098	17,820	19.6	6.44
1901–1910	241,791	24,179	22 4	3 18
1911–1920	375,641	37,564	32 0	3 08
1921–1925	107,648	21,530	26.5	1 82
1927	31,306	31,306	23.3	1.87
1929[b]	32,100	32,100	18.8	1 51
1933[b]	34,200	34,200	17.4	2 90
1937[b]	36,200	36,200	13.6	1 44

[a] U S Bur Mines Econ Paper No 1
[b] Mineral Industry in 1938, Vol 47

cent of the world total. In these tabulations the entire Russian production is considered as European production.

The following quotation on the ore deposits and reserves of the U.S.S.R. are taken from The Mineral Industry.[4] These in turn were

[4] The Mineral Industry During 1938: Vol. 47, p. 151, McGraw-Hill Book Co, New York.

TABLE 7[a]

COPPER PRODUCTION OF RUSSIA

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of European Total	Per Cent of World Total
1871–1880	36,960	3,696	8.3	2 60
1881–1885	22,677	4,535	5.7	2 05
1886–1890	26,258	5,252	5.8	1 90
1901–1910	142,081	14,208	13.1	1 86
1911–1920	215,406	21,541	18.4	1.77
1921–1925	19,146	3,829	4.6	0.32
1927	13,227	13,227	9.5	0.79
1929[b]	28,400	28,400	16.6	1 34
1933[b]	36,000	36,000	18 4	3 15
1937[b]	102,000	102,000	38 4	4 07

[a] U S Bur Mines Econ Paper No 1
[b] Mineral Industry in 1938, Vol 47.

taken from the London *Mining Journal, Tsvetnie Metalli*, No 11, 1937, and *Der Ost-Express* (Berlin), December 1937.

The most extensive ore deposits occur in Kazakstan, the two main groups being the Kounrad ores near Karsakpai and the Balkash ores near the northern shore of Lake Balkash. The Urals also certain considerable deposits of copper ore, and other deposits occur in Uzbekistan, Bashkiria, Middle Volga, West Siberia, Transcaucasia, Leningrad Province, and the Kola Peninsula.

Construction of new works seems to be proceeding very slowly and some of the "Giants" projected some years ago still exist only on paper Of six important new works, under construction or projected, the Balkash plant, designed to produce 100,000 tons a year, and on which 300 million roubles have been spent since 1930, has not yet produced copper The Jezkazgan plant at Karsakpai in Kazakstan, which is intended to work on low-grade ores and to produce eventually 200,000 tons of black copper per annum, will be three or four years before it will begin to produce

Various decrees, regulations and conferences have attempted to deal with the problem of inefficiency in the last few years and a conference at Sverdlovsk found that the Ural works, which produce about four-fifths of the present copper output, had only fulfilled about 50 to 60 per cent of their programme in the first nine months.

U.S.S.R reserves of metallic copper in ore were estimated on January 1, 1935, to be 10,635,000 tons, distributed as follows: * * *

	Tons
Kazakstan	6,404,400
Urals	2,116,500
Uzbekistan	1,285,400
Bashkiria	330,500
Middle Volga	324,500
West Siberia	108,600
Caucasus	52,400
Leningrad Province	8,300
Karelia	4,900

Another quotation[5] from Bulletin 36 of the Imperial Institute (London), Vol 1, January–March 1938, is as follows:

> It will thus be seen that, adding present production of copper to the scheduled output of works under construction or proposed to be constructed in the next few years, the Soviet Union is planning for an eventual output, say within the next ten years, of about 500,000 tons of copper per annum.

Yugoslavia. The principal production of copper in Yugoslavia comes from the Mines de Bor, which, operated under French control, reported the production of 41,992 metric tons of copper in 1938 compared with 39,410 in 1937. An electrolytic refinery was completed and opened on July 2, 1938, and by the end of the year the production of this electrolytic plant was reported to be 1000 tons per month.[6]

Yugoslavia did not produce much copper previous to 1920, but since then it has become one of the important European producers (Table 8)

Norway, Sweden, Finland. The combined production of Norway, Sweden, and Finland is shown in Table 8. Most of this production is from Norway, although the Finnish production has increased in recent years

Other European Countries. Small amounts of copper are produced in *Austria*, *France*, and the *Island of Cyprus*. *Great Britain*, which formerly (Table 4) was the world's leading producer (from mines in Cornwall and Devon), no longer produces an appreciable amount of copper — by 1926 England produced only 0.01 per cent of the world's total.

ASIA

Japan is the principal copper producer in Asia, as may be seen from Table 9. Practically all the recorded Asiatic production previous

[5] Minerals Yearbook, 1939, p 123, U. S. Bur. Mines.
[6] Minerals Yearbook, 1939, p. 123, U S Bur. Mines.

TABLE 8[a]

COPPER PRODUCTION OF YUGOSLAVIA

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of European Total	Per Cent of World Total
1911–1920	4,476	448	0.31	0.03
1921–1925	34,930	6,986	8.6	0.59
1927	14,220	14,220	10.2	0 85
1929[b]	22,800	22,800	13.3	1.07
1933[b]	44,100	44,100	24 8	4.25
1937[b]	43,400	43,400	18 0	1 91

COMBINED COPPER PRODUCTION OF NORWAY, SWEDEN, AND FINLAND

1871–1880	32,032	3,203	7.2	2 25
1881–1885	19,139	3,828	4 8	1.73
1886–1890	13,560	2,712	3 0	0 98
1901–1910	63,680	6,368	5 9	0 83
1911–1920	62,432	6,243	5.4	0.52
1921–1925	6,715	1,343	1.6	0.11
1927	13,227	13,227	9.5	0.79
1929[b]	24,700	24,700	14 5	1 07
1933[b]	32,400	32,400	16 5	2 83
1937[b]	42,200	42,200	17 5	1 85

[a] U S Bur Mines Econ Paper No 1
[b] Mineral Industry in 1938, Vol 47

to 1900 was credited to Japan, and in the period 1900–1925, Japan produced more than 98 per cent of all Asiatic copper. In recent years the proportion produced by Japan has decreased (Table 9) owing to increased production by India, Turkey, and China.

Japan. The main producing districts of Japan are Besshi, Furukawa, and Ashio, all of which produce about the same grade of copper.[7] Statistics for Japanese production are given in Table 9.

AUSTRALASIA

Australasia has been a steady producer of copper for many years (Table 10); it has never been a large producer, however, and in recent years its production has been less than 1 per cent of the world's total.

Australasian production includes that from the islands of New Zealand, Tasmania, and Papua as well as from the Australian main-

[7] U S Bur. Mines, Econ. Paper No 1.

land; the important districts are Mount Lyell in Tasmania and Mount Morgan, Mugana, Chillogee, and Wallaroo in Australia. In recent

TABLE 9[a]

COPPER PRODUCTION OF JAPAN

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of Asiatic Total	Per Cent of World Total
1871–1880	38,080	3,808	100 0	2 68
1881–1885	41,068	8,214	100 0	3.71
1886–1890	75,964	15,193	100.0	5.49
1901–1910	430,883	43,088	97.5	5 65
1911–1920	854,326	85,433	99.5	7.01
1921–1925	329,664	65,933	96.5	5.58
1927	69,872	69,872	91.6	4.17
1929[b]	83,300	83,300	90.5	3 92
1933[b]	76,100	76,100	86 5	6.65
1937[b]	83,500	83,500	63.9	3.34

[a] U S. Bur Mines Econ Paper No 1.
[b] Mineral Industry in 1938, Vol 47

TABLE 10[a]

COPPER PRODUCTION OF AUSTRALASIA

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of World Total
1871–1880	123,648	12,365	8 68
1881–1885	63,037	12,607	5.70
1886–1890	51,506	10,301	3.73
1901–1910	377,219	37,722	4.94
1911–1920	427,932	42,793	3.51
1921–1925	75,685	15,137	1 28
1927	12,800	12,800	0 77
1929[b]	16,000	16,000	0.76
1933[b]	17,600	17,600	1.54
1937[b]	22,000	22,000	0.88

[a] U. S. Bur. Mines Econ Paper No 1.
[b] Mineral Industry in 1938, Vol. 47.

years the principal producer has been the Mount Lyell Mining and Railway Company, Ltd., Mount Lyell, Tasmania.

AFRICA

Africa today is one of the world's large producers of copper, but (Table 11) it is only in recent years that it has assumed an outstanding position. African production comes from three principal sources — (1) Katanga in the Belgian Congo, (2) Northern Rhodesia, and (3) South Africa. The bulk of the production previous to 1910 came from South Africa, with a little from Algeria, but today it is Katanga and Rhodesia that account for most of the African copper. These two areas are adjacent, and together they constitute the most important copper producing province in the world.

TABLE 11[a]

COPPER PRODUCTION OF AFRICA

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of World Total
1871–1880	42,112	4,211	2 96
1881–1885	31,268	6,254	2.83
1886–1890	71,033	14,207	2.85
1901–1910	65,659	6,566	0 86
1911–1920	288,606	28,861	2.37
1921–1925	425,355	85,071	7 20
1927	120,763	120,763	7 22
1929[b]	173,000	173,000	8 15
1933[b]	200,500	200,500	17 5
1937[b]	416,000	416,000	16 6

[a] U S Bur Mines Econ Paper No 1.
[b] Mineral Industry in 1938, Vol 47.

In South Africa the most important copper producer is the Messina Development Company in the Transvaal. There is also some production from Southern Rhodesia, and in the early days there was some copper produced from Algeria. In recent years (Tables 12 and 13) better than 90 per cent of Africa's copper has come from Katanga and Northern Rhodesia.

Katanga. The copper mines of the province of Katanga in the Belgian Congo are operated by the Union Minière du Haut Katanga which was organized in 1910. The principal production has been from oxidized copper ores. We have already discussed the various metallurgical treatments that have been employed in exploiting these deposits. In recent years considerable sulfide ore has been mined and treated; the importance of the sulfide ores in this district will likely

increase in the future. The brief history of the development of the Belgian Congo copper belt (up to 1936) which follows is taken from the *Mineral Industry* during 1936;[8] part of this material is quoted from the *South African Mining and Engineering Journal.*

> The Belgian Congo copper belt is some 10,000 square miles in area, being about 200 miles long and averaging 50 miles in width. Within this area no fewer than 200 separate potential copper mines exist, and of these less than 10 per cent have been worked Up to the end of 1935 about 1,500,000 tons of metal had been produced from 25,000,000 tons of ore, and shareholders had received about £7,000,000 in dividends The principal concentrator plant is at Panda in approximately the middle of the belt, and the smelter at Lubumbashi, near Elisabethville. An electrolytic leaching plant has recently come into operation at Panda to treat the lower-grade ore. It is estimated that the developed ore reserves amount to 78,000,000 tons, containing over 5,000,000 tons of copper.
>
> It was not until 1910, when the Union Minière had been formed and the Rhodesia Katanga Railway had reached Elisabethville, that vigorous development became possible The first two mines to be opened up were the Etoile, near Elisabethville, which stands in the southeastern portion of the Katanga copper belt, and the Kambove, about 80 miles from the capital These were the only producers until the Ruashi was opened in 1922, followed by the Luishia and Likasi mines, which produced rich oxide ores from shallow deposits In 1926 the Kipushi mine, now known as the Prince Leopold, began production on a large scale from its very rich copper-silver sulphide ore. This mine is at present [1936] the largest producer.
>
> The Union Minière du Haut Katanga produced in 1936, under the international curtailment agreement, about 130,000 metric tons This compares with the highest output of 139,000 tons in 1930. A new and elaborate development program has been elaborated which includes the opening up of the Sesa mine near Kamboroe and restarting of the reverberatory furnaces at Panda. The erection of a new roasting plant for its sulphurous ore is planned to be ready for operation towards the middle of 1938.

The copper production of the Belgian Congo is given in Table 12

Northern Rhodesia. Table 13 gives the production of copper in Rhodesia for a number of years. Previous to about 1930 this copper came from Southern Rhodesia, and it was not until about 1931 that the mines in Northern Rhodesia came into production. Since that time the copper fields of Northern Rhodesia have shown a rapid increase in production and are now producing considerably more than the rich deposits of Katanga (Tables 12 and 13); the Northern Rhodesia copper field is the greatest in the world. The following brief account

[8] The Mineral Industry during 1936, Vol. 45, pp 148–149, McGraw-Hill Book Co., New York.

TABLE 12[a]

COPPER PRODUCTION OF BELGIAN CONGO

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of African Total	Per Cent of World Total
1911–1915	39,947	7,999	36 7	0.74
1916–1920	124,141	24,828	69 0	1.82
1921–1925	338,835	67,767	79 7	5 73
1926	88,889	88,889	81 0	5 46
1928[b]	124,000	124,000	88 0	6 55
1930[b]	153,000	153,000	84.3	8 82
1932[b]	59,500	59,500	38 4	5.97
1934[b]	121,000	121,000	42 1	8 70
1936[b]	105,500	105,500	38 7	5.71
1937[b]	166,000	166,000	39 9	6.62

[a] U S Bur Mines Econ Paper No 1
[b] The Mineral Industry in 1938, Vol 47 (Production of Union Minière du Haut Katanga)

of the ore deposits of Northern Rhodesia is abstracted from an article by Bateman.[9]

The Northern Rhodesia copper belt lies adjacent to the boundary of the province of Katanga, Belgian Congo; the belt is about 140 miles long by 40 miles wide and trends in a northwesterly direction. N'Dola, on the main line of the Congo-Rhodesian Railway, is the distributing center from which branch lines extend to Roan Antelope (22 miles), Nkana (45 miles), and Mufulira (59 miles).

The presence of oxidized ores in Northern Rhodesia had long been known, but these low-grade oxidized ores compared unfavorably with the rich ore of Katanga. Work on oxidized ore commenced at the old Bwana M'Kubwa mine in 1903; copper shipments started in 1913, but after intermittent operations this mine was closed. Sulfides were disclosed by boring at N'Changa but their significance was not appreciated because they were mixed with oxides; the true importance of the sulfides was not realized until the sulfide zone had been penetrated at Roan Antelope in November, 1925. Later the Nkana, Mufulira, Chambishi, Baluba, and Extension deposits were discovered. The Roan, Nkana, Mufulira, and Chambishi deposits consist almost entirely of sulfide ore. The N'Changa contains mixed sulfides and oxides, and the Extension is largely oxidized ore.

[9] Bateman, A. M., The Northern Rhodesia Copper Belt: in Copper Resources of the World, Vol. 2, p. 713; published by XVI Internat. Geol. Cong., Washington, 1935.

TABLE 13[a]

COPPER PRODUCTION OF RHODESIA

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of African Total	Per Cent of World Total
1911–1915	4,528	905	4.0	0 08
1916–1920	17,155	3,431	9.5	0.25
1921–1925	14,916	2,983	3 5	0 25
1926	850	850	0 7	0 05
1931[b]	3,460	3,460	2 04	0 23
1932[b]	62,500	62,500	40 3	6 26
1933[c]	117,000	117,000	58 3	10 2
1935[d]	161,000	161,000	54 4	9 95
1936[d]	152,300	152,300	58 5	8 63
1937[e]	233,000	233,000	55.2	9 34

[a] U S. Bur Mines Econ Paper No 1
[b] The Mineral Industry during 1934, Vol 43 (Northern Rhodesia).
[c] The Mineral Industry during 1933, Vol 42 (Northern Rhodesia)
[d] The Mineral Industry during 1937, Vol 46 (Northern Rhodesia)
[e] The Mineral Industry during 1938, Vol 47 (Northern Rhodesia).

Intensive mine development began in 1927, and copper production at the Roan Antelope began in 1931. Rhokana (Nkana) made its first production in December 1931, and Mufulira in 1933. Up to the end of 1934 the district produced 356,300 tons of copper from 12,276,385 tons of ore.

The eventual tonnages of the Rhodesian mines are unknown, but they have been developed sufficiently to show that they are gigantic long-life deposits. The ore reserves and grades that have been officially announced (1935) are given in Table 14.

TABLE 14[a]

ORE RESERVES AND GRADE OF RHODESIAN DEPOSITS

Deposit	Group	Approximate Reserves (tons)	Percentage of Copper
Roan Antelope	Roan	104,000,000	3.43
Nkana	Rhokana	127,000,000	4.0
N'Changa	do .	95,280,000	3.53
N'Changa Extension	. do	46,500,000	6 9
Chingola	do .	2,000,000	7 0
Mufulira	Mufulira	116,000,000	4.41
Chambishi	. do .	25,000,000	3 46
Baluba	do	21,000,000	3 47

[a] Bateman, A M , op cit

At present[10] there are four large companies operating in Northern Rhodesia.

1. *Roan Antelope Copper Mines, Ltd.* The ore body in the Roan Antelope area is over 3½ miles long and has a maximum depth of about ½ mile. Up to the end of 1938 all ore mined was from above the 820-foot level, and this ore was hoisted through the Beatty shaft. The Storke shaft, 2644 feet deep, will handle ore from below the 820-foot level; this shaft is about 1⅓ miles west of the Beatty shaft and is located near the center of the ore body.

2. *Mufulira Copper Mines,* formed in 1930, controls the mining rights on the Mufulira, Chambishi, and Baluba areas.

3. *Rhokana Corporation, Ltd ,* controls the Mindola section and the Nkana section; the company operates a concentrator and smelter and also an electrolytic copper refinery and a cobalt segregation plant.

4. *N'Changa Consolidated Copper Mines, Ltd.,* was formed in March, 1937, to acquire the mining rights in four areas — Chingola, N'Changa, Mimbula, and Kakosa.

SOUTH AMERICA

The two principal copper producing countries in South America are Chile and Peru, although smaller amounts have been produced in Bolivia, Argentina, and Venezuela. The copper production of Chile and Peru is given in Tables 15 and 17.

Chile. Chile has been an important producer of copper since 1800, and this country has always contributed a substantial part of the world's total (Fig 2; Table 15).

1 *Chuquicamata,* the mine of the Chile Copper Company, is located at Chuquicamata in the province of Antofagasta. This is the largest copper mine in the world, and its ore reserves are the greatest Utah Copper approaches Chuquicamata most nearly in tonnage of ore reserves, but the Chuquicamata ore is more than twice as rich as Utah's. The ore mined at Chuquicamata has been principally oxide ore up to the present and the copper has been won by leaching and electrodeposition. The Chile Copper Company is a subsidiary of the Anaconda Copper Mining Company.

2. *Andes.* The Andes Copper Mining Company, also a subsidiary of Anaconda, operates the mine at Potrerillos in the province of Atacama. This is the "youngest" of the porphyries from a production

[10] The Mineral Industry during 1938, Vol. 47, p. 152, McGraw-Hill Book Co, New York.

TABLE 15[a]

COPPER PRODUCTION OF CHILE

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of South American Total	Per Cent of World Total
1871–1880	513,744	51,374	93.1	36 08
1881–1885	226,402	45,280	85 7	20 47
1886–1890	163,279	32,656	82.5	11 81
1901–1910	363,264	36,326	67.7	4.76
1911–1920	754,734	75,473	62.0	6.20
1921–1925	827,799	165,560	76 0	14 00
1927	264,242	264,242	81 2	15.78
1929[b]	350,000	350,000	83.8	16.5
1933[b]	180,000	180,000	86 0	15.7
1937[b]	455,000	455,000	91 5	18.2

[a] U S. Bur. Mines Econ Paper No 1.
[b] The Mineral Industry during 1938, Vol 47.

standpoint. Andes maintains a concentrator and smelter for sulfide ores and a leaching plant for oxidized ores.

3. *Braden.* The Teniente mine of the Braden Copper Company is located at Sewell in the province of O'Higgins; Braden is a subsidiary of the Kennecott Copper Corporation. The ore mined has been principally sulfides which are concentrated and smelted at the smelter at Caletones.

Table 16 gives the production of these three mines for 1936, 1937, and 1938 During this time these mines accounted for 91 to 92 per cent of the total Chilean production.

Peru. The Cerro de Pasco Copper Corporation is the principal copper producer in Peru; the copper ore comes from two districts — Cerro de Pasco and Morococha — which lie about 70 miles apart. These mines are located in the high Sierra of central Peru in the Department of Junin. These deposits differ from those of most other important copper districts in that they include large amounts of lead and zinc. The lead-zinc ores, however, are mined separately.

The copper production of Peru is given in Table 17. During 1936, 1937, and 1938 the Cerro de Pasco Corporation produced respectively 35,741, 37,547, and 39,230 short tons of copper;[11] these figures represented, in turn, 97.4, 95.0, and 97.9 per cent of the total Peruvian production.

[11] Mineral Industry during 1938, Vol 47

TABLE 16[a]

PRODUCTION OF COPPER FROM THE THREE LARGE CHILEAN COPPER MINES

	1936		
	Production (short tons)	Per Cent of Chilean Total	Per Cent of World Total
Chuquicamata	123,433	44.7	7.60
Braden	102,044	36.2	5.51
Andes	30,027	10.6	1.62
	1937		
Chuquicamata	200,402	44.0	8.00
Braden	159,085	34.9	6.35
Andes	60,478	13.3	2.42
	1938		
Chuquicamata	163,213	42.2	7.48
Braden	132,034	34.2	6.05
Andes	60,880	15 6	2.76

[a] The Mineral Industry during 1938, Vol 47, McGraw-Hill Book Co , New York.

TABLE 17[a]

COPPER PRODUCTION OF PERU

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of South American Total	Per Cent of World Total
1871–1880	12,544	1,254	2.27	0.88
1881–1885	2,285	457	0.88	0.21
1886–1890	896	179	0.42	0.06
1901–1910	145,945	14,595	27.3	1.92
1911–1920	384,903	38,490	31.7	3.17
1921–1925	203,655	40,731	18.7	3.45
1927	52,438	52,438	16.1	3.13
1929[b]	60,000	60,000	14.4	2.8
1933[b]	27,400	27,400	13.1	2.3
1937[b]	39,400	39,400	7.9	1.6

[a] U S Bur Mines Econ Paper No 1.
[b] The Mineral Industry during 1938, Vol 47.

NORTH AMERICA

The Continent of North America has long been the leading producer of copper in the world, as may be seen from the data in Table 18.

We shall consider this continent in more detail than has been devoted to the other continents.

The principal producer on the North American Continent is the United States, with Canada second in importance; both of these rank with the world's leading copper producing countries (Fig. 2). Mexico also produces a considerable amount of copper, and smaller amounts come from Cuba and Newfoundland.

Copper production in North America began with Cuba about 1820. The United States production began about 1850; and Mexico, Canada, and Newfoundland began to produce copper about 1880. As Table 18 shows, the importance of North America as a copper producer grew rapidly after 1870. In the period 1900–1920 the North American Continent produced more than two-thirds of the world's copper, but since then its rank has declined, largely for two reasons — the increase in African production and the decrease in production from the United States.

TABLE 18[a]

COPPER PRODUCTION OF NORTH AMERICA

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of World Total
1871–1880	221,245	22,124	15.54
1881–1885	308,220	61,644	27.88
1886–1890	562,684	112,537	40.69
1901–1910	5,127,971	512,797	67.23
1911–1920	8,219,061	821,906	67 44
1921–1925	3,573,679	714,736	60.46
1927	997,415	997,415	59.71
1929[b]	1,250,000	1,250,000	58 9
1933[b]	433,000	433,000	37.9
1937[b]	1,161,000	1,161,000	46 5

[a] U. S. Bur. Mines Econ Paper No 1
[b] Mineral Industry during 1938, Vol 47

MEXICO

Mexico has been a copper producer since about 1880, and for the past 50 years has accounted for about 3 to 4 per cent of the world's supply (Table 19).

There are three principal copper-producing districts in Mexico — Boleo in Baja California, Nacozari in the State of Sonora, and Cananea also in Sonora.

TABLE 19[a]

COPPER PRODUCTION OF MEXICO

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of North American Total	Per Cent of World Total
1881–1885	2,116	423	0 71	0.19
1886–1890	14,752	2,950	2.8	1.07
1901–1910	554,118	55,412	12.9	7.26
1911–1920	528,238	52,824	7.4	4.33
1921–1925	216,082	43,216	7.0	3.66
1927	63,760	63,760	7.5	3.81
1929[b]	86,700	86,700	6.9	4.1
1933[b]	43,700	43,700	10.1	3.8
1937[b]	51,500	51,500	4.4	2.1

[a] U S Bur Mines Econ Paper No 1
[b] Mineral Industry during 1937, Vol 47

Cananea. The Cananea district is the largest single producer in Mexico. The first copper mining at Cananea of which there is an authentic record was in 1881, although the district is reputed to have been the scene of mining operations for hundreds of years previous to this. The Cananea ore body produces gold, silver, and molybdenum as well as copper. The mines are operated at present by the Cananea Consolidated Mining Company, which is a subsidiary of Anaconda.

Nacozari. The district of Nacozari has also been known as a mining district for hundreds of years, but the first important production came soon after the Pilares mine was acquired by the Phelps Dodge Corporation in 1897. The present operating company is the Moctezuma Copper Company, a subsidiary of Phelps Dodge.

Boleo. The copper deposit at Boleo was discovered about 1868, and about 1885 the French house of Rothschild acquired the property and formed the Compagnie du Boléo to work it on a large scale. This company has operated the mines ever since.

CANADA

Although Canada has produced copper since 1880, it was not until about 1900 that it became a real factor in world production. Its importance has increased greatly in recent years (Table 20, and Figs. 2 and 5). In 1933 Canada accounted for over one-third of the North American production and almost 13 per cent of the world production (Table 20).

Quebec. There are two very active copper districts in Quebec — Rouyn and Eastern Quebec.

Rouyn.[12] The Rouyn district was the scene of a rush in the fall of 1922 as a result of a gold strike, although the Horne deposit had been staked 2 years before. The possibilities of this deposit as a copper mine was amply demonstrated when the Noranda Mines, Ltd., which was drilling in the Horne mine, cut 130 feet of solid sulfide ore containing $4.36 in gold to the ton and 8.23 per cent copper. The Horne mine is really a copper-gold mine since the value of precious metal produced is about equal to the value of the copper.

TABLE 20[a]

COPPER PRODUCTION OF CANADA

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of North American Total	Per Cent of World Total
1871–1880	112	11	0.06	0.01
1881–1885	5,365	1,073	1.82	0.49
1886–1890	12,111	2,422	2.16	0.88
1901–1910	253,663	25,366	4 95	3.33
1911–1920	444,394	44,439	5.42	3.65
1921–1925	196,645	39,329	5.50	3.33
1927	70,698	70,698	7.07	4.22
1929[b]	121,000	121,000	9.7	5.7
1933[b]	148,000	148,000	34.2	12.9
1937[b]	262,000	262,000	22.6	10.5

[a] U. S. Bur Mines Econ. Paper No. 1
[b] The Mineral Industry during 1938, Vol 47.

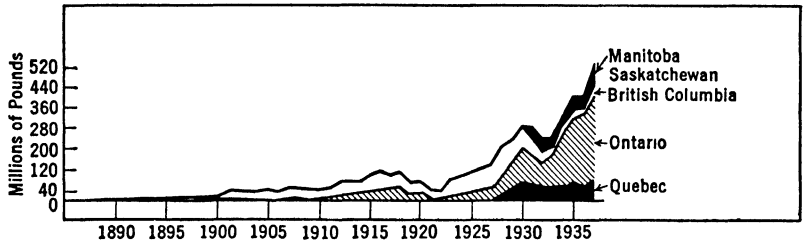
Eastern Quebec. Eastern Quebec was one of the earliest producing districts in Canada; the presence of copper ore was known as early as 1841, and production dates from about 1858. The production from this district is small, however, when compared with the other great Canadian copper districts.

Ontario. The copper-nickel mines of the Sudbury district make the Province of Ontario the largest copper producer in Canada. The first production was in 1886, and since then the district has developed steadily; today it produces about 90 per cent of the world's nickel, and is likewise one of the world's leading copper producers.

[12] The discussion of this, as well as the other copper districts in North America, is taken largely from Gardner, E. D., Johnson, C. H., and Butler, B. S, Copper Mining in North America: U. S. Bur Mines Bull. 405.

The principal company in the district is the International Nickel Company, and its two largest mines are the Frood and the Creighton. The Falconbridge Nickel Mines, Ltd., also operates in the district. The ores of the district yield important amounts of gold, silver, and platinum metals as well as nickel and copper.

Manitoba. The copper deposits of The Pas district have been developed only recently — there was very little production from them before 1930, but since then the production has been increasing rapidly.



(Data from Bull 405, U S Bur Mines, and The Mineral Industry During 1938, McGraw-Hill Book Co , New York)

FIG. 5. Canadian Copper Production.

There are two important mines in The Pas district — the Flin Flon mine, owned by the Hudson Bay Mining and Smelting Company, and the Sherritt-Gordon mine 30 miles east of Flin Flon, which is the property of Sherritt-Gordon Mines, Ltd. The Flin Flon operates on a copper-zinc deposit containing small amounts of gold and silver.

Since about 1933 Flin Flon has produced some copper from Saskatchewan; the Manitoba property is near the boundary between the two provinces. In Figure 5 the production figures for the two provinces are lumped together.

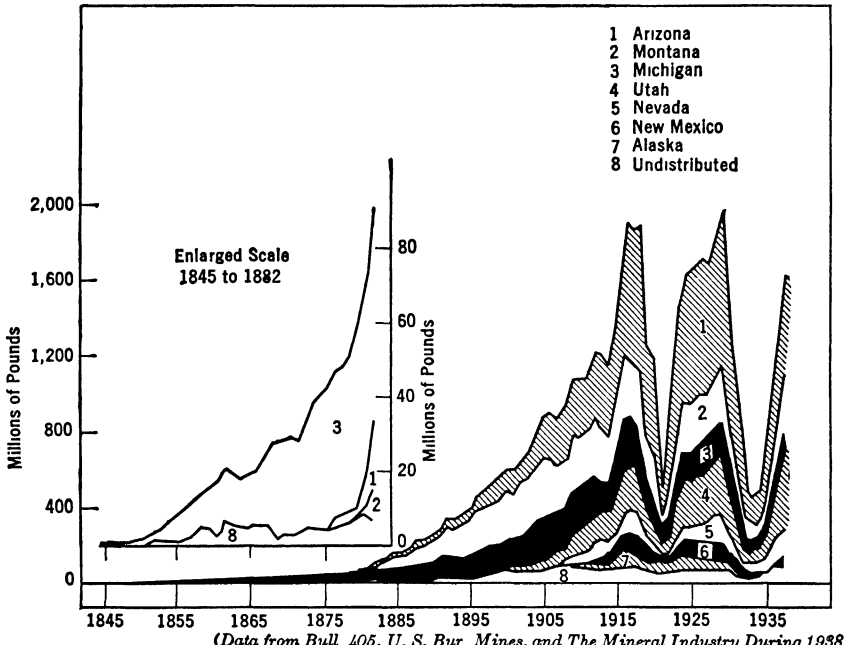
British Columbia. British Columbia from about 1900 to 1930 was the largest copper-producing province in Canada, but today it ranks below the eastern provinces. The mines near Rossland were large producers, but today they are idle. The other important districts in British Columbia are *Hidden Creek, Anyox,* and *Howe Sound* (*Britannia*).

Figure 5 shows the production of the various Canadian provinces from 1885 to 1937.

THE UNITED STATES

The United States, the largest producer of copper in the world, has maintained its supremacy for many years (Table 21; Fig. 2). From 1901 to 1927 this country has consistently produced more than half

of the world's copper, but in recent years its production has declined to about 30 per cent (Table 21), although the United States is still the largest producing country.



(Data from Bull 405, U. S. Bur Mines, and The Mineral Industry During 1938, McGraw-Hill Book Co., New York)

FIG. 6. Production of Copper in the United States.

Practically all the copper produced in the United States has come from the following states and territories — Arizona, Michigan, Montana, Nevada, Utah, New Mexico, Tennessee, California, and Alaska. We shall now consider them individually. Figure 6 is a graphic representation of the amount of copper produced by the various states since 1885, and Figure 7 also shows other production statistics for both states and districts.

Michigan. Native copper was discovered in the Lake Superior region in the seventeenth century by explorers who passed through, but the first production of copper from a lode mine did not come until 1844. After this the Michigan copper district (the Upper Peninsula) soon became the leading producer in the United States and maintained this position for many years.

The *Lake copper* produced from the Michigan native copper ores is a very pure product, and the fact that there is a special commercial name for this copper speaks for its importance in the world market.

TABLE 21[a]

COPPER PRODUCTION OF THE UNITED STATES

Year or Period	Production (short tons)	Average Yearly Production (short tons)	Per Cent of North American Total	Per Cent of World Total
1871–1880	208,768	20,877	94 2	14 66
1881–1885	294,337	58,867	95 5	26 62
1886–1890	526,071	105,214	93 5	38 04
1901–1910	4,281,714	428,171	83 5	56 13
1911–1920	7,160,559	716,056	87 3	58 75
1921–1925	3,099,996	619,999	86 8	52 44
1927	847,419	847,419	84 8	50 60
1929[b]	1,027,000	1,027,000	82 1	48 5
1933[b]	234,000	234,000	53.9	20.4
1937[b]	835,000	835,000	71 7	33 3

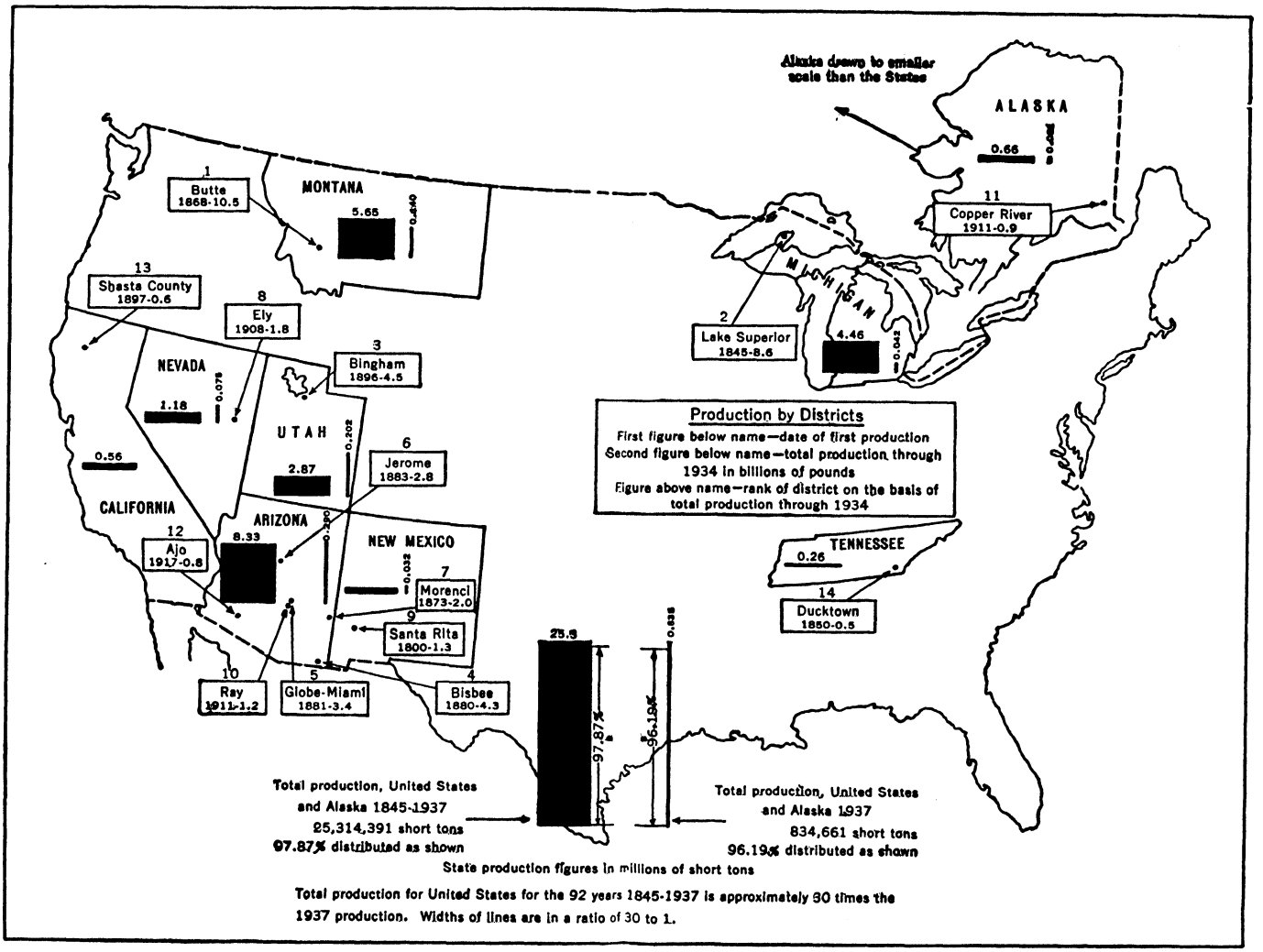
[a] U. S Bur Mines Econ Paper No 1.
[b] Mineral Industry during 1938, Vol 47

Before the advent of the electrolytic refining process, Lake copper was the purest metal available

The two principal operators in the district are the Calumet and Hecla Consolidated Copper Company and the Copper Range Company.

Montana. Practically all the copper mined in Montana has come from the mines of Butte in Silver Bow County. Butte was discovered as a gold camp in 1864 but copper began to be mined shortly after, and the importance of the copper increased until in 1887 the Butte production exceeded that of the Michigan mines. For a number of years Montana was the leading copper-producing state, but it has now been surpassed by both Arizona and Utah. The Butte district, however, has produced more copper than any other district in the United States.

Utah. The high rank of Utah as a copper producer is due to a single mine — the mine of the Utah Copper Company in Bingham Canyon near Salt Lake City. This is the greatest of the North American porphyry copper mines and is the second largest copper mine in the world — Chuquicamata alone exceeds it in copper reserves. As far as total production is concerned, the Bingham district is third among North American copper districts; Bingham, however, is a single large mine, whereas the two districts which have produced a greater quantity of copper (Butte and Michigan) both include several mines. The Utah ore contains only small amounts of gold and molybdenum, but the ore tonnage is so great that this mine ranks second in the United States in the production of gold and molybdenum.



(Data on States from Minerals Yearbook, 1938, U. S. Bur. Mines. Data on Districts from Bull. 405, U. S. Bur. Mines)

FIG. 7. Production of Copper by Eight Principal States and Alaska for 1845–1937 and for 1937. Production of Fourteen Principal Districts through 1934.

Arizona. Arizona is the largest copper-producing state in the Union, a position it has held for many years. Arizona, however, contains several large copper-mining districts, and thus differs from Montana, Utah, and Michigan, each of which contains only one important district. The Arizona copper districts are listed below.

Morenci. The Humboldt and Clay ore bodies are the two most important deposits in the Morenci district; Phelps Dodge is the only operating company in the district.

Warren (Bisbee). The most famous mine in the Warren (Bisbee) district is the Copper Queen; another is the Calumet and Arizona. Phelps Dodge Corporation and Shattuck-Denn are the operators in the Warren district.

Globe-Miami. The principal production in the Globe-Miami district has come from two large mines — the Miami and the Inspiration — operated by the Miami Copper Company and the Inspiration Copper Company, respectively.

Ray The Ray mines of the Nevada Consolidated Copper Company are at Ray, Arizona. This property is now a subsidiary of the Phelps Dodge Corporation.

Superior. The Silver King ore body in the Superior district is owned by the Magma Copper Company.

New Mexico. New Mexico contains only one large copper mine — the Chino mine at Santa Rita, which is one of the porphyry copper mines This property is a subsidiary of the Kennecott Copper Company.

Nevada. Nevada also has one large porphyry ore body — the mine of the Nevada Consolidated Copper Company at Ely. This is also a Kennecott subsidiary.

Alaska. There were two important copper-producing districts in Alaska — the Beatson mine on Latouche Island in Prince William Sound and the Kennecott mines in the Copper River district. Both of these have been worked out, and there is no longer any considerable copper production from Alaska. For a time (Figs. 6 and 7) these deposits, particularly Kennecott, produced a great deal of metal.

Other States. *Tennessee* has been a producer of copper since about 1847, the copper coming from the heavy sulfide (pyrrhotite) deposits in the Ducktown district. At present these ores are treated to recover sulfur (for sulfuric acid), iron, copper, and zinc — the copper might almost be considered a byproduct.

Most of the production of *California* has come from the Shasta County district (Fig. 7). One of the leading producers in the State at present is the Walker mine in Plumas County.

PRODUCTION TRENDS

The following discussion is taken verbatim from a paper by Croston[13] published in July, 1937, and this, together with Tables 22, 23, and 24, taken from the same article, gives an interesting account of the trend of copper production throughout the world.

In the years preceding the Civil War, and up to 1869, the principal individual copper producer of the world was the Mansfeld mine which has produced more or less regularly since the twelfth century. In that year Calumet and Hecla forged ahead, although its production was less than 6200 tons of copper. By 1877 the reorganized mines of Rio Tinto took premier position, with an output of slightly more than 27,000 tons, and maintained leadership until displaced by Anaconda in 1892 with an output of 37,500 tons. The first mine to produce more than 50,000 tons a year was Anaconda, in 1896, and with the exception of the years 1905–1907, when Calumet and Hecla again led, and 1908–1909, when the Copper Queen led, it maintained its position as the world's greatest copper mine until just before the depression [1929].

A study of the producers of a quarter of a century ago reveals that there were about 150 mines producing copper in substantial quantities, but only 26 had outputs in excess of 10,000 tons of metal annually Of these only 10 produced more than 20,000 tons and but two more than 50,000 tons, while there was but one mine capable of turning out 100,000 tons a year. The beginning of work on the porphyries brought in an era of large-scale low-cost mining, and the introduction of the flotation process and leaching made possible reasonably high recoveries at low cost. Today, through mergers, consolidations, and integration of the industry, a half dozen large units control the destinies of the copper trade of the world, with another half dozen smaller units sharing most of the remainder.

These companies, several of which can each produce about 500,000 tons of metal annually, have garnered the choicest ore reserves of the world and will continue to dominate world production without serious competition for many years to come. The smaller companies treating richer ores but with higher costs and slender reserves will have to operate under the umbrella of the giants. Improved mining methods, flotation, leaching and other processes have been a much greater boon to the large low-grade producers than to the smaller and richer mines. Usually the ore bodies of these smaller producers are not susceptible to the economies of such mining methods, and the improvements in recoveries and lowering of costs of newer treatment processes are either not advantageously employable or exert but a minor effect on production costs.

Having the technical skill and the necessary finances, it appears probable that any new deposits of size will gravitate to the control of the present

[13] Croston, J J, Recent Trends in Copper Production; Ore Reserves and Costs· Am Inst Min & Met. Eng Tech. Paper 826 (Mining Technology), July 1937.

great producers, as the funds required for the large-scale development and equipment of a great copper deposit are prodigious. The copper industry has completed the same cycle observed in other great industries — the concentration of the business into fewer hands. There will always be a considerable number of small copper producers, but they will no longer have any considerable weight in the industry.

The period since the World War has seen the rise of the British as important factors in world copper production, and today the streams of copper flow from mine to market quite differently from the way they did ten years ago At that time American producers dominated world markets, American-owned companies controlled most of the Latin-American production and in addition refined most of the rest of the world's copper. Now Katanga refines its own production in Belgium, the Rhodesian output goes to England for treatment, Canadian production is refined within the Dominion, while other Continental refineries are handling business formerly done here. Even the Japanese are treating some of the Chilean output as as well as their own, and recently have contracted to handle the output of the Granby [British Columbia] concentrator.

Within the past few years a tariff wall has been erected for the protection of domestic producers America no longer consumes more copper than all of Europe, although she may do so again later, for Europe has been using more and more copper per capita for some years Should the trend continue, European-controlled mines will share in a large part of this business. Domestic producers apparently will operate primarily to supply domestic demands, and American-controlled foreign producers will sell in foreign markets in competition with European-controlled companies, or, when prices are high enough and demand sufficient, will supplement the needs of the domestic fabricators.

The next decade will witness the inauguration of several new large producers. One company, N'Changa Consolidated Copper Mines, Ltd , has just been organized with a capital of about $25,000,000 to exploit some of the ore bodies owned by Rhokana. Others are to be anticipated in Northern Rhodesia, Belgian Congo, and Uganda, all controlled by existing copper interests There is also the possibility of copper from African colonies of France and Portugal if developments are favorable. In Latin America, Anaconda has the Santiago property in reserve, and there are the Rio Blanco and Ferrobamba deposits A number of properties are under development in Sweden, Finland, Serbia, Turkey, and elsewhere in Europe, which might in the aggregate turn out substantial tonnages of copper. In Canada a number of properties are nearly ready for production, on some plants have been built but not yet operated on account of the condition of the market, but soon Sherritt-Gordon, Waite-Amulet, Aldermac, Normetal and perhaps Coast Copper will be adding their quota. Here in the United States, the Mountain City property of Anaconda is already in production. Howe Sound is building a concentrator for its Chelan property, while Phelps Dodge has a large tonnage available at Morenci when times are propitious. Bagdad

may get into moderate sized production in time. These potential producers of the future will in the aggregate, together with the expected increases in output of large existing producers, more than offset any decline in output through the exhaustion of older properties, and serve to assure the world of adequate supplies of copper for a long time to come. While a considerable increase in the total consumption of copper is to be expected with the passing years, the rate of increase of production of virgin metal should gradually taper, and more of the demand be filled by secondary copper. It is probable that secondary copper, important as it is now, will play a vastly greater role in the future.

Table 22 gives the output of the world's principal copper mines The figures were assembled from the annual reports of the individual companies, official statements or private communications, except where noted as unofficial estimates, calculations from copper content of ores, concentrates or matte, etc. The latest available data cover the year 1935, and the comparison is made with 1932, the low point of recent copper production. The years 1929 and 1930 cover the culmination of the recent boom, while 1912 enables us to look back a quarter of a century. The present dominance in the industry of the newer producers will be noted. Not included in the table are a large number of copper mines that were in production in 1912, but have shut down permanently.

The above quotation, including Tables 22, 23, and 24, gives a picture of the important copper mines of the world and their copper reserves as the situation existed in 1935. Of course these figures are changing as time goes on, and they will continue to change in the future. A few items which indicate some of these changes are:

1. The Chino porphyry deposit at Santa Rita, New Mexico (which was idle in 1935 and is not listed in Table 22), is now in production, and the new copper smelter at Hurley, New Mexico, which was blown in in 1939 is smelting the concentrates from the Chino ore.

2. With respect to the Canadian producers mentioned in Mr. Croston's discussion, following are the production figures for 1938.[14]

Producer	1938 output (short tons)
Aldermac	6,195
Normetal	2,350
Sherritt-Gordon	14,511
Waite-Amulet	8,886

3. The property of the Howe Sound Company on Lake Chelan in the State of Washington is now milling about 1200 tons of ore per day in its mill at Holden, Washington.

[14] The Mineral Industry during 1938, Vol. 47, McGraw-Hill Book Co., New York.

TABLE 22

ANNUAL OUTPUT, IN SHORT TONS, OF WORLD'S LEADING COPPER MINES[a]

Company	1935	1932	1930	1929	1912[b]
Custom Smelters					
Amer Smelt & Ref Co	204,452	138,648	440,784	616,398	66,000
Amer Metal Co	129,061	107,704	235,666	245,856	
U. S Smelt., Ref & Min. Co.	1,671	531	2,986	2,558	10,576
Groups.					
Anaconda[c]	258,972	139,339	323,706	495,285	173,117
Kennecott[d]	209,135	82,536	173,058	250,567	130,000
Phelps-Dodge[e]	88,438	41,544	56,479	88,590	141,723
Mines·					
Chile[f] (Chuquicamata)	131,994	40,685	89,596	149,788	(j)
Katanga	118,698	59,595	153,165	151,008	2,664
International Nickel[g] (Ontario)	116,505	28,832	54,872	40,917	11,000
Braden[h] (Chile)	112,010	49,871	80,993	88,163	4,750
Anaconda (Butte)[f] (Montana)	77,371	48,787	98,617	148,507	148,487
Utah[h]	59,233	30,006	80,569	148,313	45,683
Roan Antelope[i] (Rhodesia)	56,753	42,233	1,133	(j)	(j)
Rhokana[i] (Rhodesia)	56,447	54,408	(j)	(j)	(j)
Bor (Yugoslavia)	42,990	33,245	26,966	22,790	8,250
Noranda (Quebec)	37,239	31,507	38,071	25,813	(j)
Nevada Consolidated[h] (Nevada)	33,830[k]	29,992	70,990	133,137	62,757
Calument & Hecla & subsidiaries (Mich.)	33,336	16,899	58,199	67,347	65,006
Cerro de Pasco (Peru)	31,989	22,910	43,200	49,993	28,219
Mufulira[i] (Rhodesia)	31,498	(j)	(j)	(j)	(j)
Andes[f] (Chile)	28,641	11,619	47,023	81,332	(j)
Rio Tinto (Spain)	(l)	(l)	(l)	(l)	44,716
Mansfeld (Germany)	25,890	27,703	23,268	25,235	22,600
Hudson Bay (Manitoba)	24,509	21,079	1,186	(j)	(j)
Greene-Cananea[f] (Mexico)	21,061	18,410	21,212	29,413	24,630
Nippon[m] (Japan)	(n)	19,518	24,865	19,225	(n)
Furukawa (Japan)	19,010	20,035	18,536	17,886	14,763
Mount Lyell[o] (Tasmania)	15,642	12,271	10,995	8,739	5,159
Magma (Arizona)	15,193	10,853	15,942	19,128	(j)
Miami (Arizona)	14,870	7,907	34,600	29,421	16,416
Mitsubishi (Japan)	14,672	15,207	14,040	12,092	11,287
Sumitomo (Japan)	14,475	14,005	18,895	20,792	10,024
Outokumpu (Finland)	12,180[p]	7,329	5,680	4,960	(j)
Granby (British Columbia)	11,752	19,324	23,416	30,427	14,553
Fujita[q] (Japan)	(j)	10,370	10,954	10,139	8,795
Cyprus[p]	13,000	2,305	4,500	5,000	(j)
Northern Peru Min & Smelt Co[r]	(n)	(n)	10,701	11,158	(j)
Messina[i] (Transvaal)	10,656	10,598	9,751	7,616	700
United Verde Extension (Arizona)	9,985	17,876	22,783	32,056	(j)
Tennessee[s]	8,964	3,815	7,190	7,624	6,626
Boleo (Mexico)	8,670	11,487	13,889	12,903	14,168
Copper Range (Michigan)	8,380	6,094	11,897	12,099	38,909
Indian Copper (India)	7,728	4,962	3,331	1,831	2,683[t]
Matahambre (Cuba)	7,672	6,533	17,299	16,515	2,500[u]
Howe Sound[g] (British Columbia)	7,214	1,103	22,633	21,516	7,150
M'Zaita (Chagres) (Chile)	6,704	(n)	4,100	3,000	3,480
Naltagua (Chile)	5,926	5,460	4,339	6,770	1,225
Sulitjelma (Norway)	5,811	(l)	(l)	(l)	5,500
Bolidens (Sweden)	5,785	3,805	(j)	(j)	(j)
Tocopilla (Chile)	5,264[v]	(n)	5,207[v]	(n)	250
Disputada de Las Condes (Chile)	5,016[v]	(n)	3,990[v]	(n)	(n)
Orkla (Norway)	(l)	(l)	(l)	(l)	(l)
Mountain City (Nevada)	4,100	(j)	(j)	(j)	(j)
Tharsis (Spain)	(l)	(v)	(l)	(l)	3,782
Burma[i, w] (Burma)	3,946	5,871	8,416	(n)	(n)
Inspiration (Arizona)	3,758	8,512	32,803	53,654	(j)
Mother Lode (Alaska)	3,333	1,716	4,823	6,121	(j)
Buchans[r] (Newfoundland)	3,259	2,373	1,054	1,032	(j)
Cons Copper & Sulphur (Quebec)	2,339	2,746	2,489	2,177	925
Falconbridge (Ontario)	2,515	1,197	656	(j)	(j)

TABLE 22 (*Continued*)

Company	1935	1932	1930	1929	1912[b]
Mines (*continued*)·					
Mt. Morgan[t] (Australia)	1,668	259	(*j*)	(*j*)	10,394[z]
Shattuck-Denn (Arizona)	1,381	(*y*)	4,167	6,368	1,255
Minor producers during 1935.					
Walker (California)	822	535	7,888	7,516	(*j*)
Huelva Copper[t] (Spain)	(*n*)	1,534	(*n*)	2,281	(*n*)
Pena Copper (Spain)	343	645	1,008	923	888
Sunshine (Idaho)	673	357	198	133	(*j*)
Carlota	635	(*n*)	(*n*)	(*n*)	(*n*)
Shenandoah-Dives (Colorado)	367	879	629	315	(*j*)
Ohio (Utah)	380	(*y*)	1,024	1,108	3,277
Cons Min & Smelt of Canada[g] (B C)	319	384	7,064	4,173	1,457[o]
Roros (Norway)	211	(*l*)	(*l*)	(*l*)	650
Mason & Barry (Portugal)	(*n*)	257	226	218	3,963
Ouancos (Chile)	(*l*)	(*l*)	(*l*)	(*l*)	(*l*)
Majden Pek	(*l*)	(*l*)	(*l*)	(*l*)	(*l*)
Plakalnitza		(*l*)		(*l*)	(*l*)
Bagdad (Arizona)	86[z]	(*j*)	(*j*)	(*j*)	(*j*)
Important producers idle during 1935					
Consolidated Coppermines[y] (Nevada)		870	16,306	11,366	1,919
Otavi Mines,[y, aa] (S W Africa)		2,646	16,645	13,889	6,435
Quincy[y] (Michigan)		(*y*)	5,470	2,230	10,317
Sherritt-Gordon[y] (Manitoba)		4,965	(*j*)	(*j*)	(*j*)
Mazapil[y] (Mexico)		(*y*)	4,378	6,239	6,778
Corocoro United[y] (Bolivia)		(*y*)	1,654	4,528	2,058
California-Engels[y] (Arizona)		(*y*)	2,036	5,550	(*j*)
Poderosa[y] (Chile)		577	2,711	2,905	2,539
Iron Cap (Christmas)[y] (Arizona)		107	3,462	2,209	(*j*)
Tezuitlan[t, v] (Mexico)		(*y*)	1,781	1,719	(*bb*)
Gatico (Chile)		(*y*)	(*n*)	(*n*)	1,936
Mindouli (French Congo)		(*y*)	198	639	(*j*)
Equipped for production·					
Waite-Amulet (Quebec)	(*y*)	(*y*)	(*j*)	(*j*)	(*j*)
Aldermac (Quebec)	(*y*)	(*z*)	(*y*)	(*j*)	(*j*)

[a] Includes principal groups and custom smelters Does not include U S S.R.
[b] Figures for 1912 include production of individual companies since consolidated
[c] Own mines and subsidiaries (Chile, Andes, Greene-Cananea) Custom ores (including Walker and Mountain City) and toll treatments
[d] Own mines in Alaska, Utah, Nevada (Arizona and New Mexico shut down since April 1933 and October 1934, respectively) and Chile
[e] Properties in United States only since September 1931 (when Moctezuma in Mexico was shut down) including Calumet & Arizona and New Cornelia, but not United Verde, recently acquired
[f] Included in Anaconda total
[g] Sales, not production
[h] Included in Kennecott total
[t] Year ended June 30 following
[j] Not yet in operation.
[k] Ely alone, previous years include Ray and Chino.
[l] No recent figures available — approximate relative rank shown by position
[m] Saganoseki, Hidachi and smaller properties, in 1912 Hidachi alone produced 8651 tons.
[n] Not available
[o] Year ended September 30.
[p] Unofficial estimate
[q] Kosaka only.
[r] Included in American Smelting & Refining Company total
[s] Not including Ducktown, since acquired.
[t] Old Cordoba output
[u] Estimate under old ownership
[v] Estimated copper content of concentrate.
[w] Estimated copper content of matte.
[z] Year ended May 31 following for predecessor.
[y] Shut down
[z] Small experimental production.
[aa] Year ended March 31 following.
[bb] Shut down during 1912.

TABLE 23

World Copper Reserves Including Copper Contained in Important Tonnages in Other Metal Deposits

Company	Date of Estimate	Reported Ore Reserves (short tons)	Average Copper Content (per cent)	Total Metallic Content of Deposit (short tons of copper)
United States:				
Anaconda (Butte)	Oct 1, 1935	75,000,000[a]	4 00	3,000,000
Bagdad Copper	Dec 31, 1932	48,000,000	1 08	518,400
Cons Coppermines	Apr 20, 1934	35,000,000	1 10	385,000
Gray Eagle		1,045,000	3 23	33,754
Inspiration Cons	Oct 1, 1935	69,010,770	1 373	947,518
Miami Copper	Jan 1, 1936	84,624 869	0 938	794,163
Mother Lode	May 26, 1934	104,000	11 59	12,054
Mountain City	Oct 1, 1935[b]			100,000[a]
Kennecott Copper[c]				
Ely property	July 5, 1935	77,000,000	1 22	939,400
Ray property	July 5, 1935	81,448,000	1 51	1,229,865
Chino property	July 5, 1935	170,839,000	1.23	2,101,320
Bingham property	Dec 3, 1930	640,000,000	1 07	6,848,000
National Copper	1929	900,000	2.3	20,700
Old Dominion	1931	2,000,000	2.00	40,000
Phelps Dodge[d]	1932	388,146,550	1.13	4,386,056
Seneca Copper	Dec 31, 1930	3,486,895		
Tennessee[e]	Dec 31, 1935	6,148,132	1 60	98,370
United Verde Extension	Dec 31, 1935	61,000	7 00	4,270
Van Dyke	Apr 31, 1931	1,000,000	5 00	50,000
Not reported Unofficial estimates				
Michigan	1934	100,000,000	1.00	1,000,000
California, Montana, New Mexico, Arizona, Tennessee, etc		70,000,000	2 143	1,500,000
Canada and Newfoundland[f]				
Aldermac	Apr 1, 1936	1,743,760	2 00	34,875[g]
British Columbia Nickel	Feb 28, 1936	1,042,200	0 46[h]	4,794
Denison Nickel	1936	741,240	1 05[i]	7,783
Falconbridge Nickel	Dec 31, 1935	4,059,475	0 91[j]	36,941
Granby Cons	Dec 31, 1933	13,449,900	1 81	243,443
Great Falls	Dec 31, 1935	300,000	1 00[k]	3,000
Howe Sound (Britannia)	Dec 31, 1935	10,000,000	1 30	130,000
Hudson Bay	Dec 31, 1935	24,770,000	2 10[l]	520,170
International Nickel	Dec 31, 1935	205,590,592	2 00[m]	4,111,812
Mandy	1929	98,000	6 5[n]	6,370
Noranda	Dec 31, 1935	31,029,000	2 51	779,082[o]
Normetal	Jan 1, 1934	700,000	3 00[p]	21,000
Ontario Nickel	Apr 1, 1936	116,000	1 04[q]	1,206
Sherritt-Gordon	Dec 31, 1932	4,783,175	2 41[r]	115,419
Sudbury Basin	Dec 31, 1929[s]	833,000	2 80[t]	23,533
Sunloch	1918[s]	4,500	3 00	4,500
Waite-Amulet	Dec 31, 1933	955,445[u]	4 50	43,023
Buchans	Dec 31, 1934	6,375,000	1 50[v]	94,625
Newfoundland:				
Gull Lake	1929	1,300,000	2.70	35,100
Mexico[w]				
Greene-Cananea	Oct. 1, 1935			240,000[x]
Moctezuma[y]	1930	3,500,000	2.70	94,500

TABLE 23—(*Continued*)

Company	Date of Estimate	Reported Ore Reserves (short tons)	Average Copper Content (per cent)	Total Metallic Content of Deposit (short tons of copper)
Cuba:				
S A Minas de Matahambre	1933	939,000	4 75	44,603
Nicaragua				
Tonopah Nicaragua	1918[s]	1,492,088	5 059[z]	75,485
Venezuela				
South American	1932	400,000	3 50	140,000
Peru [aa]				
Fundicion de Magistral		3,000,000	7 00	210,000
Ferrobamba		6,778,000[bb]	3 56	241,450
Chile [cc]				
Andes Copper	Dec 31, 1935	112,549,287	1 47	1,654,475
Kennecott (Braden)	Dec 31, 1935	205,019,050	2 18	4,469,415
Chile	Dec 31, 1935	938,931,000	2 15	20,187,023
Rio Blanco[dd]		42,000,000	2 3	966,000
Santiago[ee]	Dec 31, 1921	52,819,282	2 11	1,116,078
Australasia				
Lake George	1931	2,880,000	0 75[ff]	21,600
Mount Elliott	1929	1,916,550		100,936
Mount Lyell	Sept 30, 1936	8,825,000	1 90[gg]	167,675
Mount Morgan	June 30, 1936	7,506,652	1 77[hh]	132,868
Wallaroo and Moonta	1935	618,000	3 77	23,302
Asia [ii]				
Burma	June 30, 1936	3,914,182	0 87[jj]	34,053
Indian	Dec 31, 1935	950,801	3 19	30,331
Europe [kk]				
Huelva Copper	[mm] 1933	3,358,739	1 10	36,936
Huelva (Pyrites de)	[mm] 1933	6,613,460	0 58	38,360
Imperial Chemical.	[mm] 1933	3,913,201	1 04	40,593
Pena	[mm] 1933	3,314,634		
Rio Tinto	[mm] 1933	5,000,000	1 40	70,000
St Gobain.	[mm] 1933	1,653,465	1 39	22,983
San Platon.	[mm] 1933	440,924	3 50	19,290
Seville	[mm] 1933	5,511,550		
Tharsis	[mm] 1933	100,861,365	0 75	756,460
Bolidens Gruvaktiebolag	1934	5,900,000	2 00	118,000
Outokumpu	[nn] 1933	9,369,635	4 00	374,785
International Nickel-Petsamo	[nn] 1934	5,511,550	1 30	71,650
Foldal	[oo] 1933	330,693	1 63	5,401
Grong	[oo] 1933	8,487,787	2 21	187,392
Orkla	1935	20,000,000	2 5	500,000
Roros	[oo] 1933	771,617	1 00	7,716
Sulitjelma	[oo] 1933	5,070,911	1 77	89,622
Mansfeld A G	[pp] 1933	[qq]		650,163
Rammelsberg	[pp] 1933	1,615,986	4 27	69,005
Stadtberger Kupferhutte	[pp] 1933	688,937	1 6	11,023
Sontrau-Richelsdorf	1936	[rr]		440,924
Plakalnitza	[ss] 1933	165,347	2 50	4,134
Cyprus		20,000,000[tt]	2.10	420,000
U.S.S R [uu]				
Developed or drilled				6,302,347
Probable				4,146,449
Possible				7,421,412
Total		1,532,398,293		17,789,468

TABLE 23—(*Continued*)

Company	Date of Estimate	Reported Ore Reserves (short tons)	Average Copper Content (per cent)	Total Metallic Content of Deposit (short tons of copper)
Africa [vv]				
Katanga	Dec 31, 1934	78,000,000	6.50	5,070,000
Sud Katanga	1934			
Tchinsenda Mine		16,534,650	4.00	661,386[ww]
Mokambo Mine				338,614
Mufulira	June 30, 1936			
All properties		160,390,000	4.12	6,608,068
Rhodesia-Katanga	Aug 1, 1936			
Kansanshi Mine		11,000,000	4 25	467,379[xx]
Rhokana				
All properties	June 30, 1936	269,454,435	4 12	11,101,523
Roan Antelope	June 30, 1936	95,637,987	3 43	3,280,383
Falcon Mines	1933	56,000	7 3	4,088
Messina (Transvaal)	June 30, 1936	1,268,030	2 231	28,290
Zambesia				
Kolembe Mine	1932	330,000	4 50	14,850

[a] Boston News Bureau, Dec 16, 1935 "The engineering expert who examined the Montana properties for the bankers gave it as his opinion that the Butte mines can produce 300,000,000 lb of copper annually for the next 20 years" The estimate of 75,000,000 tons is based on the assumption of a 4 per cent content, which is not official In the prospectus of the $55,000,000 issue of debentures, dated Oct 1, 1935, Mountain City was credited with 100,000 tons of copper metal

[b] Anaconda Copper Mining Co prospectus dated Oct 1, 1935 Materially increased since the date of estimate

[c] Not including Alaskan or Chilean properties

[d] Including Moctezuma in Mexico, but not United Verde, since acquired, which has substantial reserves

[e] Not including Ducktown, acquired in 1936

[f] No data available on the reserves of Coast Copper, George Gold and Copper or Island Copper, all in British Columbia, or the long established Consolidated Copper and Sulphur Co , Ltd , in Quebec No recent data are available regarding Newfoundland properties although substantial amounts of copper are contained at the Tilt Cove and other deposits.

[g] Plus 0 75 oz silver and 70c gold (@ $35/oz) per ton

[h] Plus 1 41 per cent nickel

[i] Plus 0 81 per cent nickel and $3 in gold and platinum

[j] Plus 1 93 per cent nickel

[k] Arbitrary assumption of 1 per cent Company reports 2 per cent combined copper and nickel

[l] Plus 3 86 per cent zinc, 1 28 oz silver and $2 80 gold (@ $35/oz) per ton

[m] Estimated, currently treating ore higher in copper, and with nearly 3 per cent nickel.

[n] Plus 16 per cent zinc and $5 gold and silver (at prices then prevailing) per ton.

[o] Plus 5,605,515 oz of gold

[p] Plus 13 5 per cent zinc and 4 3 oz silver per ton

[q] Plus 0 87 per cent nickel, some platinum, gold and silver.

[r] Plus 61c gold and silver (at prices then prevailing)

[s] No change as of Dec 31, 1935

[t] Plus 5 8 per cent zinc, and minor amounts of lead, silver and gold.

[u] Not including 300,000 tons of 11 52 per cent zinc ore

[v] Plus 15 8 per cent zinc, 7 7 per cent lead, 3 60 oz silver and 0 05 oz gold per ton.

[w] No data available on Boleo, Inguaran, Mazapil, Tecolote, Tezuitlan or Triunfo.

[x] Anaconda prospectus for $55,000,000 debentures, dated Oct 1, 1936, gives minimum reserves sufficient to produce a rate of 60,000,000 lb for 8 years Probable reserves are believed by others to bring the total close to three-quarters of a million tons of metal

[y] Included in Phelps Dodge total

[z] Plus $1 54 gold (@ $35/oz) per ton.

[aa] No data available for Cerro de Pasco or Northern Peru

[bb] Not exploited since date of estimate A recent estimate is 2,013,000 tons of 3 98 per cent copper within 100 ft of surface, and an indeterminate tonnage of about 3.15 per cent copper below.

No data available on Bolivian reserves (Corocoro).

[cc] No data available on M'Zaita (Chagres), Chanaral, Disputada, Copiapo, Gatico Naltagua, Ouancos, Poderosa or Tocopilla.

[dd] According to A H Rogers (January 1937)

[ee] No exploitation since date of estimate.

[ff] Plus 12 94 per cent zinc, 7.5 per cent lead, some gold and silver. No exploitation since date of estimate

[gg] Plus some gold and silver.

[hh] Plus 0 218 oz gold per ton

[ii] No data available on reserves of Japanese producers — Fujita, Furukawa, Mitsubishi, Nippon or Sumitomo.

[jj] Plus 23 6 per cent lead, 14 5 per cent zinc, 18 2 oz silver per ton, some nickel

[kk] No data available on reserves of Bor or Majden-Pek

[mm] Spanish reserves from "Cobre en Espana," Int Geol Congress, 1933 Huelva copper is credited with an additional 795,868 tons of probable ore same grade Pyrites de Huelva is credited with an equal amount of probable ore of the same copper content Imperial Chemical Industries, Ltd , has 4,034,455 tons of probable ore containing 40,708 tons copper metal Rio Tinto has 166,786,000 tons positive pyrite and 77,162,000 tons of probable pyrite ore, in addition to the porphyry St. Gobain has probable reserves of 7,700,000 tons of pyrite. San Platon has an equal amount of probable ore of same copper content. Tharsis has 106,097,338 tons of probable ore of the same copper content.

[nn] Finnish reserves from Saksela Int Geol Congress, 1933

[oo] Norwegian reserves, except Orkla, from Foslie. Int Geol Congress, 1933.

[pp] Mansfeld, Rammelsberg and Stadtberger reserves from Fulda Int Geol Congress, 1933.

[qq] Mansfeld reserves are given as 23 sq km , or somewhat over 20,000,000 tons of copper ore. Of this 8 km are developed, and 15 still are undeveloped In the 700 years of its existence 117 sq km have been worked out Rammelsberg has an additional 38,581 short tons of copper metal in probable reserves

[rr] According to C W Wright· Spec Sup No 3, Mineral Trade Notes, U. S Bur Mines (Sept 19, 1936) This company under management of Mansfeld and under heavy German subsidy, has some 480 workers, has sunk a number of shafts and drill holes and developed this estimated tonnage

[ss] According to Boncev Int Geol Congress, 1933

[tt] Skouriotissa mine only Mavrovouni deposit now largest producer, but no data available on tonnage

[uu] Based on figures of Riddell and Jermain Russian Copper *Eng and Min Jour.* (Feb 1935)

[vv] No data available on reserves of Mindouli (French Congo); Bembe (Portuguese West Africa); Kafue (Northern Rhodesia), Umkondo (Southern Rhodesia), Tsumeb (Southwest Africa); South African Copper (Cape Province) or Northern Transvaal (Messina) Copper in Transvaal

[ww] Including Mokambo reserves the total is more than 1,000,000 tons of metal, although Mokambo tonnage is not stated

[xx] Plus 220,000 oz. of gold, or 70c per ton (gold @ $35/oz.).

TABLE 24

SUMMARY OF WORLD'S REPORTED RESERVES OF COPPER IN SHORT TONS

Region	Tonnage of Ore				Metal Content Officially Reported but Ore Tonnage and Grade not Stated	Tonnage of Metallic Copper in Deposits
	Officially Reported and with Grade	Unofficially Estimated and with Grade	Officially Reported, Unofficial Estimate of Grade	Officially Reported, No Grade Stated		
United States	1,605,327,321					18,408,870
		170,000,000				2,500,000
				3,486,895		
					3,100,000	3,100,000
Total						24,008,870
Canada .	102,000,695					2,101,864
			205,890,592			4,114,812
Total						6,216,676
Mexico, Cuba, Central and South America	1,364,427,707					28,989,029
		3,000,000				210,000
					240,000	240,000
Total						29,439,029
Australasia	21,746,202					446,381
Asia	4,864,983					64,384
Europe (not including U S S R)	199,754,017					2,843,360
				8,826,184		
					1,091,087	1,091,087
Total .						3,934,447
Africa .	632,671,102					27,235,967
					338,614	338,614
Total						27,574,581
U S S R						
Developed or drilled					6,302,347	6,302,347
Probable					4,146,449	
Possible					7,421,412	
Total					17,879,468	
World Total by classes (not including U.S S R)	3,930,792,027					80,089,855
		173,000,000				2,710,000
			205,890,592			4,114,812
				12,313,079		
					4,769,701	4,769,701
Grand Total not including U S S R.						91,684,368
Grand Total including U S S R						97,986,715
Grand Total including U S S R probable and possible						109,554,576

SMELTERS AND REFINERIES IN THE WESTERN HEMISPHERE

In our discussions of metallurgical processes in previous chapters we have mentioned many smelters and refineries. At this point we shall briefly summarize the essential facts about the copper treatment plants in the Americas. Figure 8 is a schematic drawing which indicates the location of these plants, and Table 25 gives the essential data concerning them.

Smelters and refineries represent large capital outlays, and they are not erected unless there is a reasonable assurance that there will be an adequate supply of raw material for their operation. Copper smelting and refining is not practicable on a small scale, and smaller mines generally concentrate their ore and then ship the concentrate to one of the large established smelters.

A few words of explanation are necessary in connection with Figure 8 and Table 25. The map in Figure 8 does not show all the smelters and refineries in the Western Hemisphere, but it does include all the important ones; most of these have been referred to in previous chapters. There have been copper smelters which were important in the past but are no longer operating — these have been omitted. All in all, however, the plants shown on the map smelt and refine the great bulk of American primary copper, as well as a large proportion of secondary copper. Strictly secondary copper plants are not shown. Another smelter is now (1941) under construction at the Morenci property of the Phelps Dodge Corporation.

Only one native copper smelter is shown in Michigan; there are others (Table 25), but all are in the same district. Two are operating at the present time.

The copper refineries on the eastern seaboard of the United States and Canada have been indicated as electrolytic refineries to emphasize the difference between them and the smelters located near the producing mines. Although it is probably true that the most important function of these plants is the electrolytic refining of crude copper, some of them include complete smelting equipment (Table 25) and can handle copper ores, concentrates, and scrap of various kinds, as well as blister copper.

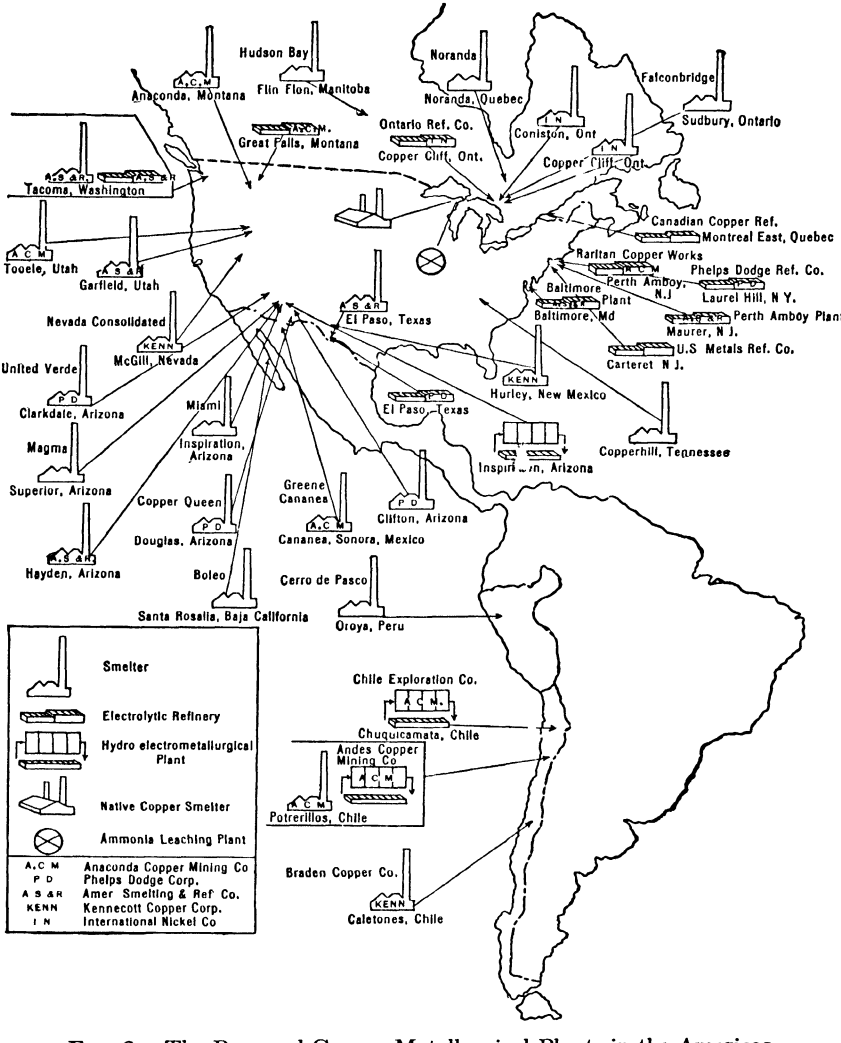


FIG. 8. The Principal Copper Metallurgical Plants in the Americas.

TABLE 25[a]

COPPER REDUCTION PLANTS AND REFINERIES IN THE WESTERN HEMISPHERE

SMELTERS

Plant	Location	Operating Company	Equipment	Capacity	Source of Raw Material	Remarks
Anaconda	Anaconda, Montana	Anaconda Copper Mining Company (A C M)	8 reverberatories 7 converters	600 tons of charge per furnace day.	Principally the concentrates from Butte ores.	Plant includes copper and zinc concentrators, electrolytic zinc plant, acid plant, and phosphate plant.
Miami	Miami, Arizona	International Smelting Company (A.C M subsidiary)	4 reverberatories 5 converters	875,000 tons of charge per year.	Handles output of Globe-Miami district. Concentrates from Miami and Inspiration mills and cement copper from Inspiration leaching plant.	
Tooele	Tooele, Utah	International Smelting Company (A C M subsidiary)	2 reverberatories 5 converters	400,000 tons of charge per year	Largely custom ores and concentrates.	Includes a lead smelting department.
Andes	Potrerillos, Chile	Andes Copper Mining Company (A C M. subsidiary)	3 reverberatories 4 converters	90 tons of blister copper per converter day on 40% matte.	Concentrate from sulfide ores, Potrerillos mine.	Includes a leaching plant for oxide copper ore from the Potrerillos mine.
Cananea	Cananea, Sonora, Mexico	Cananea Consolidated Copper Company (A C M subsidiary)	2 reverberatories 6 converters	50,000 tons of copper per year.	Concentrate from Cananea sulfide ore.	
Garfield	Garfield, Utah	American Smelting and Refining Company (A S. and R.)	5 reverberatories 8 converters	1,500,000 tons of charge per year.	Concentrates from Magna and Arthur mills, which treat the ore from Kennecott's Bingham Canyon mine.	

[a] Compiled from various sources, principally from the *Mines Register, 1940*, Atlas Publishing Co , New York Other data are largely from articles previously cited in the text.

Hayden	Hayden, Arizona	do .	2 reverberatories Converters	360,000 tons of charge per year.		
El Paso	El Paso, Texas	do . .	2 reverberatories Converters	240,000 tons of charge per furnace year.	Custom material. Formerly treated the concentrates from Chino, New Mexico, before the construction of the Kennecott smelter at Hurley.	Includes a lead smelting department.
Tacoma	Tacoma, Washington	.. do	Reverberatory and converter plant	500,000 tons of charge yearly.	Custom ores and concentrates from the coasts of North and South America as well as from the interior	Includes an electrolytic copper refinery.
Nevada Consolidated	McGill, Nevada	Nevada Consolidated Copper Corporation (subsidiary of Kennecott)	3 reverberatories Converters	1200 tons of charge per furnace day	Concentrate from ore from mine at Ely.	
Chino	Hurley, New Mexico	do. . .	1 reverberatory 2 converters		Concentrate from Chino mine.	Blown in May 2, 1939.
Braden	Caletones, Chile	Braden Copper Corporation (subsidiary of Kennecott)	Reverberatories 4 converters		Concentrate from El Teniente and other Braden mines.	
Copper Queen	Douglas, Arizona	Phelps Dodge	4 reverberatories 4 converters	12,000 tons of copper per month	Concentrates from Ajo (New Cornelia) and Bisbee, Arizona, also from Moctezuma in Mexico	
United Verde	Clarkdale, Arizona	United Verde Copper Company (subsidiary of Phelps Dodge)	6 reverberatories 4 blast furnaces 8 converters	5000 tons of charge per day	Concentrates from United Verde (Jerome) and others	
Clifton	Clifton, Arizona	Phelps Dodge	Reverberatories 4 converters		Concentrates from mills at Clifton and Morenci	
Magma	Superior, Arizona	Magma Copper Company	Reverberatory and converter plant	2000 tons or more of copper monthly	Concentrates from mill at Superior.	

TABLE 25 (*Continued*)

SMELTERS

Plant	Location	Operating Company	Equipment	Capacity	Source of Raw Material	Remarks
Cerro de Pasco	La Oroya, Peru	Cerro de Pasco Copper Corporation	2 reverberatories 6 converters	144,000,000 pounds of copper per year	Concentrate from Morococha mines	Also lead smelter, refinery, and bismuth plant.
Tennessee	Copperhill, Tennessee	Tennessee Copper Company	1 blast furnace 1 converter	1,500,000 pounds of copper monthly	Copper concentrates and massive sulfide ore from Ducktown deposits	Blast furnace makes matte from low-grade massive sulfide ore. Copper concentrates are smelted in the converter Plant produces iron oxide sinter, zinc concentrates, and sulfuric acid.
Noranda	Noranda, Quebec	Noranda Mines, Ltd.	2 reverberatories 4 converters	1260 tons of charge per furnace day	Concentrates and ores from Horne mine and others in the Rouyn district	
Copper Cliff	Copper Cliff, Ontario	International Nickel Company.	7 reverberatories 19 converters	1000 tons of charge per furnace day	Concentrates from Frood, Creighton, and other mines of the International Nickel Company.	Nickel-copper smelter — part of the furnace equipment used for nickel smelting.
Coniston	Coniston, Ontario	... .do..... .	4 blast furnaces 5 converters	850,000 tons of charge yearly.		Nickel-copper smelter. Produces nickel-copper "bessemer matte."
Flin Flon	Flin Flon, Manitoba	Hudson Bay Mining and Smelting Company	1 reverberatory 2 converters	1000 tons or more of charge per day.	Concentrates from Flin Flon, Sherritt-Gordon, and others of The Pas district Also treats residues from the zinc plant	Includes zinc plant.

Falconbridge	13 mi. N E. of Sudbury, Ontario	Falconbridge Nickel Mines, Ltd.	1 blast furnace 2 converters		Sulfide ore and sintered concentrates.	Smelter produces copper-nickel "bessemer matte," which is sent to Norway for refining
Boleo	Santa Rosalia, Baja California	Compagnie du Boleo	6 reverberatories 2 converters	About 250 tons of charge per furnace day	Sulfide ores from the Boleo deposits.	The low sulfur content of the Boleo ores makes it necessary to add gypsum or other sulfur-bearing material to the charge to obtain the proper grade of matte.

Native Copper Smelters

Calumet and Hecla	Hubbell, Michigan	Calmuet and Hecla Consolidated Copper Company	2 reverberatory melting furnaces 3 reverberatory refining furnaces	280 tons of concentrate per melting furnace day.	Native copper concentrates and copper oxide precipitate from ammonia leaching	
Copper Range	Near Painesdale, Michigan	Copper Range Company		90,000,000 pounds of copper per year	Native copper concentrate.	
Quincy	Near Hancock, Michigan	Quincy Mining Company	5 reverberatories (2 in use, 3 spares)	10,000 to 12,000 tons of copper per year	. do	

Electrolytic Refineries

Great Falls	Great Falls, Montana	Anaconda Copper Mining Co. (A C M.)	1530 refining tanks — multiple system	162,000 tons of copper per year	Anodes from Anaconda smelter.	Includes an electrolytic zinc plant and a copper wire mill.
Raritan Copper Works	Perth Amboy, New Jersey	.....do . .	2988 refining tanks — multiple system 3 anode furnaces 5 cathode furnaces	276,000 tons of copper per year	Blister from Tooele, Miami, and A C M plants in Chile and Mexico. Occasionally some from Anaconda	Silver refinery at Raritan treats anode mud from Raritan and Great Falls.

TABLE 25 (*Continued*)

ELECTROLYTIC REFINERIES

Plant	Location	Operating Company	Equipment	Capacity	Source of Raw Material	Remarks
Phelps Dodge Refinery (Laurel Hill)	Laurel Hill, New York	Phelps Dodge	550 refining tanks — series system	270,000 tons of copper per year	Blister from Phelps Dodge smelters, also custom refining	Includes a copper smelter with 1 blast furnace, converters, and blister casting equipment Smelter can produce 40,000 tons of blister per year.
Phelps Dodge Refinery (El Paso)	El Paso, Texas	.....do.....	1152 refining tanks — multiple system 1 anode furnace 2 cathode furnaces	120,000 tons of copper per year	Anodes and blister from Phelps Dodge smelters in Arizona.	
A S and R (Perth Amboy plant)	Maurer, New Jersey	American Smelting and Refining Company (A S and R)	Multiple system	132,000 tons of copper per year.	Blister from A S and R. smelters, also custom material	Includes a lead refinery.
A.S. and R. (Tacoma)	Tacoma, Washington	. do . . .	946 tanks — multiple system 3 cathode furnaces	120,000 tons of copper per year	Anodes from Tacoma smelter, also custom material.	
A.S. and R (Baltimore)	Baltimore, Maryland	. do.... .	Employs both multiple and series system	360,000 tons of copper per year.	Blister from A S and R. smelters, also custom material	
U. S. Metals Refining Company	Carteret, New Jersey	U. S Metals Refining Company	1880 refining tanks — multiple system 4 anode furnaces 3 cathode furnaces	240,000 tons of copper per year	Largely custom material, also blister from company smelters.	Includes a copper smelter, lead smelter, and lead refinery. The copper smelter is equipped with 1 reverberatory furnace and 2 converters and has a capacity of 250,000 tons of charge per year.

Ontario Refining Company	Copper Cliff, Ontario	Ontario Refining Company (International Nickel, Consolidated Mining and Smelting Company, and Ventures, Ltd)	1230 refining tanks — multiple system 3 anode furnaces 230-ton arc-type electric melting furnaces	150,000 tons of copper per year	Principally blister copper from Copper Cliff smelter	
Canadian Copper Refiners, Ltd.	Montreal East, Quebec	Canadian Copper Refiners, Ltd. (Noranda and Hudson Bay)	468 refining tanks — multiple system 1 anode furnace 1 cathode furnace	75,000 tons per year	Anodes and blister from Noranda and Flin Flon smelters.	

Hydro-Electrometallurgical Plants

Chuquicamata	Chuquicamata, Chile	Chile Exploration Company (A.C M. subsidiary)	13 leaching vats each of 11,500 tons capacity Electrolytic plant contains 1098 tanks with a total of 60,000 anodes, 4 reverberatory melting furnaces	16,800,000 tons of ore per year.	Oxide ore from the Chuquicamata mine	Batch percolation system of leaching is used.
Andes	Potrerillos, Chile	Andes Copper Mining Company (A.C M. subsidary)	9 leaching vats each of 7500 tons capacity Part of the ore is leached in a slimes plant. Electrolytic plant contains 576 commercial tanks and 54 starting-sheet tanks	7500 tons of ore per day in leaching plant.	Oxide ore from Andes Company mine.	Six-day counter-current sulfuric acid leach followed by counter-current washing Smelting plant for sulfide concentrate on same location. Sulfur from sulfide roasting used to make acid for leaching.

TABLE 25 (*Continued*)

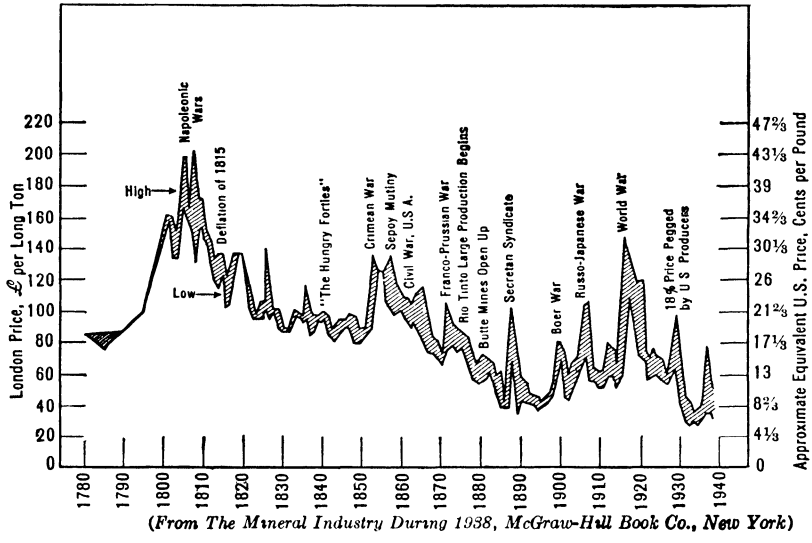
HYDRO-ELECTROMETALLURGICAL PLANTS

Plant	Location	Operating Company	Equipment	Capacity	Source of Raw Material	Remarks
Inspiration	Inspiration, Arizona	Inspiration Consolidated Copper Company	Both sand and slime leaching plants Sand leaching division contains 13 vats each of 9000 tons capacity Electrolytic plant contains 120 commercial tanks with a total of 11,520 anodes	9000 tons of ore per day	Mixed oxide and sulfide ore	Leached with acid and ferric sulfate to attack sulfide copper. Counter-current percolation, 13-day cycle of washing and leaching

Ammonia Leaching Plants. The only operating ammonia leaching plants in the Western Hemisphere are located in Michigan and are operated by Calumet and Hecla. They are used to leach finely divided native copper from conglomerate ores and reclaimed tailing from older operations. Ammonia leaching is operated in connection with gravity and flotation concentrations.

THE PRICE OF COPPER

Copper prices are quoted in cents per pound on the New York market, and in pounds sterling per long ton on the London Metal Exchange. The price fluctuates in a series of peaks and depressions, not only in annual average from year to year, but from month to month and



(From The Mineral Industry During 1938, McGraw-Hill Book Co., New York)

FIG. 9. London Copper Prices.

even from day to day. Prices are quoted on "spot copper" for immediate delivery, and on "copper futures" for delivery at some stated time in the near future (1 month, 3 months, etc.).

Figure 9 is a graph of the price of copper on the London Exchange from 1780 to 1938 — this curve shows the high and low quotations for each year. This figure shows that the all-time high came during the Napoleonic wars when the price reached £200 per long ton; the lowest price was during the depression in 1932 and 1933 when copper was quoted at less than £30 per long ton — almost a hundred-fold decrease from the highest price. In spite of the violent fluctuations in price,

this graph shows that the price of copper has gradually decreased from 1800 to the present time.

Just before 1890 there was an effort (" The Secretan Syndicate ") to " corner " the world's copper market, and in 1930 the United States producers attempted to peg the price of copper at 18 cents per pound.

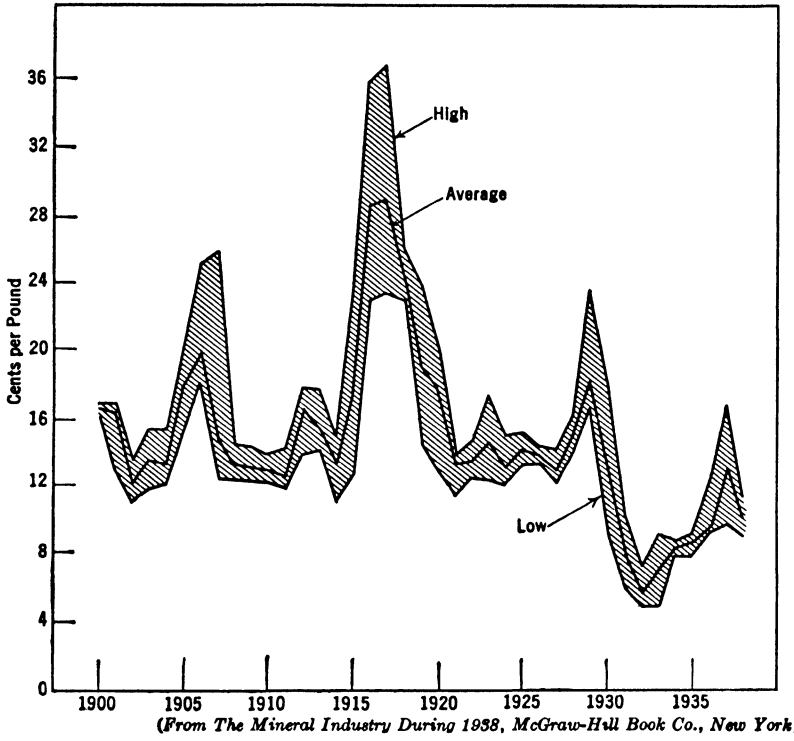


FIG. 10. United States Copper Prices.

Neither of these efforts had any long-time effect on the price of copper — in fact both were followed by sharp drops in price (Fig 9).

The all-time high copper price in the United States came in July, 1864, when the average price was 55 cents per pound; the lowest price, 4.775 cents per pound was quoted in January and February, 1933. Figure 10 shows the high, low, and average New York prices during the period 1900–1938; note that these prices show practically the same fluctuations as the London prices during the corresponding period (Fig. 9).

The graphs in Figure 11 show the fluctuation of the average yearly New York prices — the lower curve gives the actual market prices in

cents per pound, and the upper curve gives the " intrinsic " price of copper as corrected for the purchasing power of United States money. This curve shows smaller fluctuations than the lower curve and emphasizes the general downward trend of copper prices.

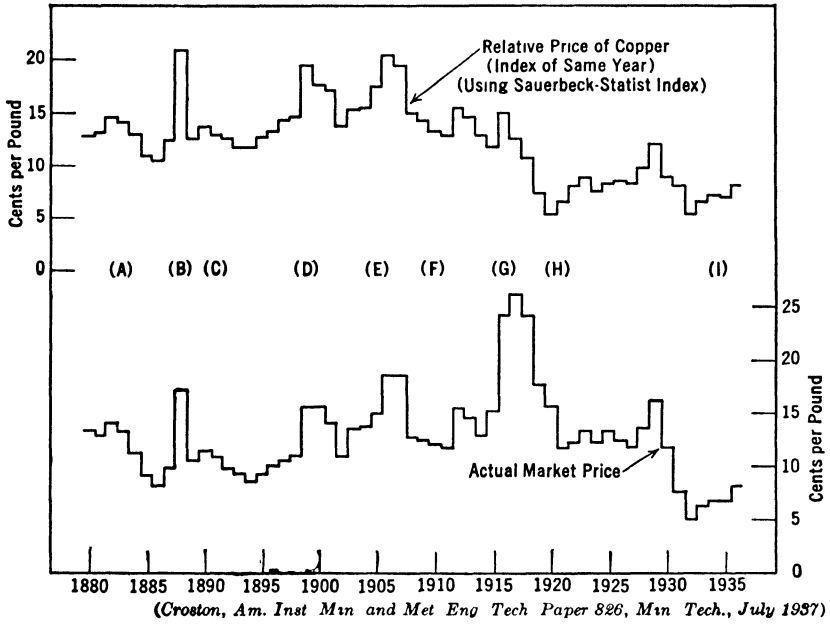


FIG. 11. United States Copper Prices.

COST OF PRODUCING COPPER

When copper is quoted at 12 cents per pound in New York that means that the buyer will pay 12 cents per pound for electrolytically refined copper cast into standard wirebars, cakes, billets, etc , and laid down in New York or vicinity. Certainly then a pound of copper disseminated throughout a 2 per cent ore buried 1000 feet below the surface of an Arizona mountain does not represent 12 cents worth of value to its owner. The total cost of mining, smelting, refining, and transporting metal must be less than the market price before there is any profit in the operation. High-cost operations must necessarily cease when the price of copper drops.

Let us briefly mention a few of the factors which govern the cost of copper production:

1. *Size of ore deposit.* Large-scale operations always show lower costs per ton of ore mined than smaller mining operations, and unless

the small deposit is unusually rich, the large deposit will generally show a lower mining cost per pound of copper.

2. *Nature of the ore deposit.* The structure of the ore body determines the mining method to be employed Disseminated ore deposits which can be mined by bulk methods such as open-cut or block-caving, show lower mining costs than vein deposits which require selective mining.

3. *Grade of ore.*

4. *Accessibility to refinery and market.*

5. *Daily output.*

6. *Presence of other metals in the ore.* When ore contains other valuable metals, part of the mining and treatment cost may be charged off against them.

7. *Amenability of the ore to concentration.*

8. *General market conditions* — price of supplies, wages, taxes, etc.

These factors and many others affect the cost of producing copper, and it is not surprising that this cost should vary widely from mine to mine and even that there should be considerable variation at the same mine from year to year. As an example, the reported costs of producing copper in 1929 ranged from 5 62 to 22 0 cents per pound.[15] An analysis of cost presented by the Federal Trade Commission and based upon the returns of 85 companies[16] showed the distribution of total costs to be approximately as follows:

	Per Cent
Mining	43.00
Depletion of ore	4 50
Purchases of ore	3.00
Transportation of ore	5 25
Smelting	36 50
Transportation to refinery	5.25
Refining	6.50
Administration	5.50
Selling	1 00
	110 50
Less credit for precious metals	10.50
	100.00

This cost distribution will vary considerably from one mine to another, depending upon many factors as we have noted; in particular, they will be markedly changed when the ore contains other revenue-

[15] The Mineral Industry during 1929, Vol 38

[16] *The Mines Handbook, Vol. 16,* Atlas Publishing Co., New York, 1925.

producing materials in addition to copper (gold, nickel, molybdenum, etc.).

Table 26 gives the estimated intrinsic costs of producing copper for a number of companies for five different years. These are not actual costs (except for 1935) but are adjusted to the purchasing power of the 1935 dollar so that comparison may be made between the yearly costs for each company.

In closing this section we shall quote two more paragraphs and Table 26 from Mr. Croston's paper.[17]

> Production costs as a whole have steadily lessened over a long period of years, and intrinsic costs, adjusted to a constant purchasing currency, while not exhibiting the marked fluctuations of actual costs, nevertheless show the same trends.
>
> While the actual price in terms of currency may exhibit a marked advance if war or severe inflation takes place, the long-term trend of intrinsic copper prices shows a steady decline in the relative value of the metal in terms of its ability to purchase other commodities This suggests that the markets of the world are aware of the fact that regardless of temporary expedients to control production and prices, there will be many sources that will produce copper cheaply in ample volume for the world's needs.

[17] Croston, J J , op cit. p 17.

TABLE 26

Estimated Intrinsic Costs of Producing Copper, in Cents per Pound

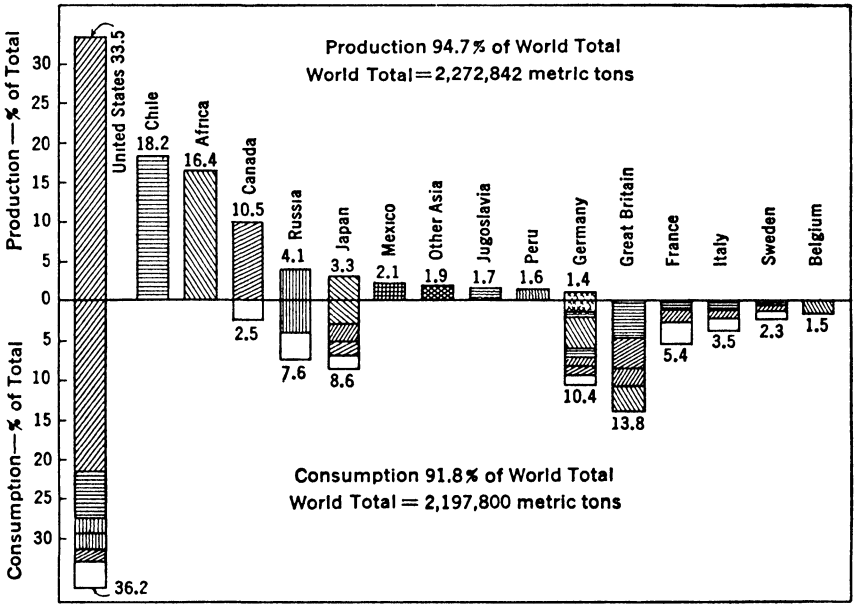
[Costs for years prior to 1935 adjusted to purchasing power of 1935 dollar after depreciation and all credits, except where noted It is realized that the fluctuations in the purchasing power of the dollar are not exactly reflected by similar changes abroad. Many of the foreign producers contract expenses in other foreign countries for supplies, equipment, some salaries, transport both ocean and rail, refining, sales and head office expenses However, for all practical purposes it is believed that the variations in the real value of money in the United States had similar counterparts abroad]

Company	1935	1929	1924	1920	1917
Anaconda[a]	6 8	(b)	8 32	8 16	9.19
Calumet & Hecla	7 96	9 65	10.19[c]	11 05[c]	8 85[c]
Copper Range	8 26[c]	12 16[c]	14 59[c]	9 23[c]	8 58[c]
Inspiration	32 66[d]	9 65	8 96	7 37	7.08
Kennecott	6 4[e]	6 54[e]	8.61	6 42	5 34
Magma	5 62	8 64	6 44	9 49	11.30
Miami	9 02	10 07	9 21	6 17	8 51
Mother Lode	4 57[f]	5 65[c]	5 83	4 49	(b)
Phelps-Dodge	7 15[e]	10 40[c]	9 99	7 94	9 02
Shattuck-Denn	11 22	10 57	8 20	12 20[c]	9 01[c]
U.V.X.	7 13	7 13[c]	6 75[c]	5 11	4 17
Utah	7 50	5 58	7 24	6 82	7 49
Walker[g]	10 98	9 06	(b)	(b)	(b)
Granby	8 82	8 44	8 64[c]	8 27[c]	9 49[c]
Boleo	6 31	12 04	10 84	8 24	15 06
Greene-Cananea	4 48	5 54	10 68	8 45	11 91
Andes	7 00	7 92	(l)	(l)	(l)
Chile	6.02	6 63	8 72	6 84	12 73
Naltagua	9 19	(b)	(b)	(b)	(b)
Cerro de Pasco	(b)	5 04	6 11[c]	5 71	8 17
Bor	5 52	9 95	(b)	(b)	(b)
Indian	11 41	12 75	(l)	(l)	(l)
Mt. Lyell	7 55	8 01	7.97	9.08	12 51
Katanga	7 22	12 25	8.88	8.87	4 33[h]
Mufulira[i]	6 67	(l)	(l)	(l)	(l)
Rhokana[j]	7 13	(l)	(l)	(l)	(l)
Roan Antelope[j]	5 78	(l)	(l)	(l)	(l)
Messina	6.80[k]	9 33	10.36	13 33	(b)

[a] Estimate Butte.
[b] Not estimated.
[c] No depreciation.
[d] Charging shutdown and other expenses against 2 months operation.
[e] Cost per pound crediting fabricating operations.
[f] Including depletion, no depreciation.
[g] Cost of pound of copper in concentrate.
[h] Working cost only, no charges.
[i] Blister cost
[j] Calculated on basis of electrolytic for all output.
[k] Cost credits export subsidy, Actual cost perhaps 7.7c.
[l] Not yet in operation.

CONSUMPTION OF COPPER

The countries which are the largest consumers of copper are the highly industrialized countries. The United States has for years been the largest consumer of copper, followed by Great Britain, Germany, Japan, and Russia. Of the important consuming countries, the United States is the only one that can, if necessary, produce the copper it needs from within its own boundaries; all the other consumers must import. Russia, however, may some day be self-sufficient in this



(Largely from Data in The Mineral Industry for 1938, McGraw-Hill Book Co., New York)

FIG 12 World Production and Consumption of Copper in 1937.

respect. Many large producers — Africa, Chile, Mexico, Peru — export practically all their copper, and although Canada is one of the important consumers it exports most of its production.

Figure 12 shows the comparative consumption and production of copper for a number of countries during the peak year 1937. An attempt has been made to indicate imports and exports from one country to another, but this is only approximate, as it is impossible to do justice to the complex picture of the industry in a simplified diagram. Thus the United States consumes about as much copper as it produces, but a large part of the consumed copper is imported and a good deal of domestic copper is exported. In the recent past, Great Britain

and Belgium, for example, have been exporters of copper which they had refined; the original source of this metal, however, was Africa, Chile, Canada, and other producing countries.

SECONDARY COPPER

The importance of secondary or scrap copper as a source of copper is continually increasing as the world's total supply of metallic copper increases. Copper and its alloys are relatively resistant to corrosion, and there are few uses for copper (comparable to the use of lead in paint pigments) which "use up" the metal and put it in such a form that it is difficult or impossible to reclaim.

Before we consider the methods of treating secondary copper and the statistics which show the importance of scrap copper in the world markets, let us consider the meaning of the term *secondary* or *scrap* copper.

Secondary Copper — Definition. As a general thing, *primary copper* refers to copper produced directly from ore, whereas *secondary copper* applies to copper secured from other sources. The term *virgin copper* means metal which has never been alloyed or fabricated, and the term is practically synonymous with *primary copper.*

Secondary copper is commonly called *scrap copper;* certain classes are called *junk.* These terms may connote a certain inferiority in the product, but it should be emphasized that there is no intrinsic difference between refined copper made from scrap and virgin copper — no metallurgical or chemical test will distinguish one from the other. Many refineries and smelters handle scrap copper along with the copper from ores and concentrates, and in 1930 there were only three large copper companies in the United States that were producing strictly primary electrolytic copper.[18]

Scrap may be classified in a number of ways, and we shall refer to some of these shortly. In general, scrap comes either from the salvaging of old machinery and other metal products or is a byproduct of certain fabricating and casting operations. In the first category we find such items as copper wire obtained from replacing or repairing trolley, power, and telephone lines; automobile radiators; copper pipe, castings, and forgings obtained by wrecking houses, machines, ships; etc. Examples of the second category are billet crops, sheet punchings and clippings, faulty ingots, turnings, brass skimmings, etc.

Copper scrap may consist of pure copper, such as transmission wire, or it may be brass, bronze, or other alloy scrap. The terms *new scrap*

[18] Tzach, Samuel, Scrap and the Copper Market: Eng. and Min. Jour., Vol. 134, No. 7, p. 293, 1933.

and *old scrap* are also used. Old scrap generally refers to metal obtained from scrapping machinery, etc.; i.e., metal that has been in service for some time. New scrap means metal wastes from such operations as fabrication of sheet metal; for example, the remnants of copper sheets left after cutting circular blanks from the metal would be considered new scrap.

Although the bulk of secondary copper comes from metal and alloy scrap, a certain amount is recovered from roll scale or other oxidized copper; copper sulfate, carbonate, silicate, and other compounds; foundry ashes, drosses and skimmings; etc. Classifications of the common types of copper-bearing scrap metal are given in Table 27.

TABLE 27[a]

STANDARD CLASSIFICATION FOR OLD METALS

No. 1 Copper Wire. To consist of clean untinned copper wire not smaller than No 16 B & S Wire gauge to be free from burnt copper wire which is brittle and all foreign substances

No. 2 Copper Wire. To consist of miscellaneous clean copper wire which may contain a percentage of tinned wire and soldered ends but to be free of hair wire and burnt wire which is brittle; the tinned wire not to be over 15 per cent of the total weight.

No. 1 Heavy Copper. This shall consist of untinned copper not less than 1/16 inch thick and may include Trolley Wire, Heavy Field Wire, Heavy Armature Wire, that is not tangled, and also new untinned and clean copper clippings and punchings, and copper segments that are clean.

Mixed Heavy Copper. May consist of tinned and untinned copper, consisting of copper clippings, clean copper pipe and tubing, copper wire free of hair wire, and burnt and brittle wire free from nickel-plated material.

Light Copper. May consist of the bottoms of kettles and boilers, bath tub linings, hair wire, burnt copper wire which is brittle, roofing copper and similar copper, free from radiators, brass, lead, and solder connections, readily removable iron, old electrotype shells and free of excessive paint, tar, and scale

Composition or Red Brass. May consist of red scrap brass, valves, machinery bearings and other parts of machinery, including miscellaneous castings made of copper, tin, zinc and/or lead, no piece to measure more than 12 inches over any one part or to weigh over 60 lbs., to be free of railroad boxes, and other similarly excessively leaded material, cocks and faucets, gates, pot pieces, ingots and burned brass, aluminum composition, manganese and iron.

Railroad Bearing. Shall consist of railroad boxes or car journal bearings, must be old standard used scrap, free of yellow boxes, also iron-backed boxes, and must be free of babbitt, also free of excessive grease and dirt.

Cocks and Faucets. To be mixed clean red and yellow brass, free of gas cocks and beer faucets, and to contain a minimum of 35 per cent red.

Heavy Yellow Brass. May consist of heavy brass castings, rolled brass, rod brass ends, chandelier brass, tubings, not to contain over 15 per cent of tinned and/or nickel-plated material; no piece to measure more than 12 inches over any one part and must be in pieces not too large for crucibles Must be free of manganese mixture, condenser tubes, iron, dirt and excessive corroded tubing. Must be free of aluminum brass containing over 0.20 per cent aluminum.

TABLE 27 — *Continued*

STANDARD CLASSIFICATION FOR OLD METALS

Yellow Brass Castings. Shall consist of brass castings in crucible shape, that is, no piece to measure more than 12 inches over any one part; must be free of manganese mixtures, tinned and nickel-plated material, and must be free of visible aluminum brass.

Light Brass. May consist of miscellaneous brass, tinned or nickel plated that is too light for heavy brass, to be free of gun shells containing paper, ashes or iron, loaded lamp bases, clock works and automobile gaskets. Free of visible iron unless otherwise specified.

Old Rolled Brass. May consist exclusively of old pieces of sheet brass and pipe free from solder, tinned and nickel-plated material, iron, paint and corrosion, ship sheathing, rod brass, condenser tubes and Muntz metal material.

New Brass Clippings. Shall consist of the cuttings of new sheet brass to be absolutely clean and free from any foreign substances and not to contain more than 10 per cent of clean brass punchings to be not smaller than ¼ inch in diameter.

Brass Pipe. Shall consist of brass pipe, free of nickel plated, tinned, soldered or pipes with cast brass connections. To be sound, clean pipes free of sediment and condenser tubes.

No. 1 Red Composition Turnings. To be free of railroad car box turnings and similarly excessively leaded material, aluminum, manganese and yellow brass turnings; not to contain over 2 per cent free iron; to be free of grindings and foreign material especially babbitt Turnings not according to this specification, to be sold subject to sample.

No. 1 Yellow Rod Brass Turnings. Shall consist of strictly rod turnings, free of aluminum, manganese, composition, Tobin and Muntz metal turnings; not to contain over 3 per cent free iron, oil or other moisture; to be free of grindings and babbitts; to contain not more than 0 30 per cent tin and not more than 0 15 per cent combined iron

No. 1 Yellow Brass Turnings. Shall consist of yellow brass turnings, free of aluminum, manganese and composition turnings; not to contain over 3 per cent free iron, oil or other moisture; to be free of grindings and babbitts. To avoid dispute, to be sold subject to sample.

Auto Radiators (Unsweated). All radiators to be subject to deduction of actual iron. The tonnage specification should cover the gross weight of the radiators, unless otherwise specified.

[a] National Association of Waste Material Dealers, Inc., Standard Classification for Old Metals, *Circular O*, effective as of June 1, 1940

Treatment of Scrap and Other Secondary Copper. The treatment of copper-bearing scrap and other secondaries does not involve any processes which differ from the metallurgical methods used for the production of primary copper; often the scrap is treated in smelters and refineries where it is mingled with the main flow of primary copper. There are also plants which produce refined copper (fire refined or electrolytic) using only scrap as raw material.

With respect to treatment of scrap, the following items are important.

1. The principal step in the treatment of all scrap is to sort it

according to quality and grade. The importance of this step is indicated by the rigid specifications applied to the commercial classifications of scrap copper and alloys (Table 27). In most plants which treat scrap the incoming material goes to a large storage room where the necessary sorting is done before the scrap goes to the melting furnaces.

2. Light scrap is usually compressed into compact bales which facilitate handling and charging; this treatment applies to light bulky material such as turnings and borings, light sheet, and tangled wire.

3. Some secondary copper-bearing material may be treated by mechanical or other processes which have essentially the same function as ore dressing operations. Sorting of scrap is practically the same as hand picking of ore; gravity concentrators may be used to concentrate the prills of metal in foundry ashes and sweepings; magnetic separators are employed to remove particles of iron or steel; etc. Soldered parts such as automobile radiators may be *sweated* or heated to melt out the solder. These and other methods are employed to separate undesirable substances from the higher-grade scrap.

4. The metallurgical treatment given to scrap depends on its chemical analysis. No. 1 copper is practically the equivalent of cathode copper and may be charged directly into wirebar furnaces. No. 2 copper is generally considered the equivalent of anode copper and may be charged into an anode furnace or it may be fire refined and cast directly into wirebars. Impure scrap and some alloy scrap is charged into converters; and copper oxides, sulfates, silicates, carbonates, etc., go into the blast furnaces or reverberatory furnaces.

5. The methods indicated above summarize the treatment ordinarily given secondary copper-bearing products at plants which have the standard equipment for smelting primary copper. In such a case, for example, brass scrap would go into the converter where the zinc and other alloying metals would be oxidized.

A considerable amount of alloy scrap is purchased and used in making alloys of similar composition. Thus a brass foundry might remelt brass scrap for new ingots and add only the amount of virgin metals necessary to regulate the composition. Much of the new alloy scrap is used in this way. A fabricating plant may buy sheet stock from a brass rolling mill and then return the waste clippings, turnings, etc., to the sheet mill to be remelted and cast. In this way there is created a closed circuit for the consumption of brass scrap.

6. Scrap metal is not only a competitor of copper ore, but the higher grades of copper scrap are in direct competition with virgin copper. When compared with copper ores containing 1 or 2 per cent copper, even

foundry ashes containing 5 per cent copper represent a superior raw material; and with brass scrap containing 70 per cent copper and copper scrap containing 90 to 99 per cent copper there is virtually no comparison. This does not mean, however, that a purchaser can redeem his original investment by selling fabricated copper articles for junk, as a considerable portion of the price of any fabricated metal is the cost of fabrication.

The Importance of Secondary Copper. The statistical summary given in Tables 28 and 29 show the relations of virgin and secondary copper in the United States. It is difficult to present a simple picture of the relation of scrap to virgin copper because of the complex nature of the scrap market, but these figures show the undoubted importance of secondary copper.

The following quotation from Tzach[19] applies to the data in his table here reproduced as Table 28.

> Illuminative general facts to be noted from the table are: (1) The average total secondary copper for the years 1920–1931 — 419,352 tons — was 59 per cent of the average United States smelter output, 42 per cent of the average primary refined production, and 66 per cent of the United States virgin consumption. (2) Output of electrolytic copper from scrap by primary refiners during 1920–1932 averaged 10 per cent of the virgin refined output, 19 per cent of the smelter output, and 15 per cent of the consumption of virgin. (3) The combined output of secondary copper as copper by primary and secondary refiners for 1920–1931 averaged 17 per cent of the refined virgin output, 25 per cent of the smelter production, and 28 per cent of the virgin consumption (4) In depression years like 1921–1922, when copper output was drastically curtailed by a mine shutdown, and again in 1930, 1931, and 1932, the ratio of secondary copper recovered both as copper and in alloys was well above the average. (5) The trend in the percentages of total scrap recovery used by primary refiners has been distinctly upward, from 13 per cent in 1920 to 30 per cent in 1930.

Table 29 gives some further statistics on scrap copper in the United States during the 5-year period 1933–1937. The following facts may be noted from this tabulation.

1. The yearly tonnage of total secondary copper increased steadily throughout this period, although the 1928 and 1929 productions of scrap (Table 28) were greater than any shown in Table 29.

2. The percentages which compare secondary and primary production were generally higher in the 1933–1937 period than in 1920–1932.

3. Probably the most significant comparison is the ratio of secondary copper to smelter output (A/B, Table 29). This shows that during

[19] Tzach, Samuel, op. cit., p 293

TABLE 28

RELATIONS OF U. S. SECONDARY COPPER AND VIRGIN COPPER, 1920–1932

(Weights in Short Tons)

Year	A Total U. S. Virgin Consumption	B Total U. S. Virgin Refined Output	C U. S. Smelter Output	D Total U. S. Secondary Copper Recovery (Includes Copper Content of Brass and Other Alloys)	Percentages		
					D/A	D/B	D/C
1920	526,919	772,260	604,531	312,460	60	40	57
1921	305,494	503,212	252,793	217,300	71	43	86
1922	448,317	667,849	475,143	335,900	75	50	70
1923	650,237	995,615	717,500	410,900	63	41	57
1924	677,371	1,120,717	817,125	388,360	58	35	48
1925	700,506	1,107,091	837,435	420,210	60	38	50
1926	785,068	1,155,874	869,811	479,800	61	42	55
1927	711,480	1,169,868	842,020	490,200	69	42	58
1928	804,269	1,254,544	912,950	536,400	67	44	59
1929	889,293	1,376,112	1,001,432	626,550	71	46	63
1930	632,508	1,097,611	697,195	467,200	74	43	67
1931	451,033	771,903	521,356	347,000	76	45	67
1932	259,601	395,993	272,005	(a)	..	.	..
Total	7,842,096	12,388,649	8,821,296	[b] 15,032,220	..	..	..
Average	603,238	952,973	678,561	[b] 419,352	66	42	59

TABLE 28 (*Continued*)

RELATIONSHIP OF U. S. SECONDARY COPPER AND VIRGIN COPPER, 1920–1932

Year	E Secondary Copper Produced by Primary Refiners	Percentages				F Secondary Copper Produced as Copper by Secondary Refiners	Percentages		
		E/A	E/B	E/C	E/D		F/A	F/B	F/C
1920	40,994	8	5	7	13	57,006	11	8	9
1921	53,243	17	11	21	24	45,777	15	9	18
1922	73,005	16	11	15	22	40,395	9	6	8
1923	65,719	10	7	9	16	75,581	12	8	11
1924	77,409	11	7	9	20	64,091	9	6	8
1925	99,180	14	9	12	24	84,520	12	8	10
1926	112,559	14	10	13	23	87,541	11	8	11
1927	104,934	15	9	12	21	96,066	14	8	11
1928	116,300	14	9	13	22	113,700	14	9	12
1929	167,079	19	12	17	26	130,521	15	9	13
1930	140,270	22	13	20	30	104,530	17	9	15
1931	78,064	17	10	15	23	110,236	24	14	21
1932	60,194	23	16	22	..	(a)	..	..	..
Total	1,188,950	..	..	..	.	[b] 1,009,964	..	..	..
Average	91,458	15	10	19	21	[b] 84,164	13	8	12

[a] Not available.
[b] For 12 years, 1920–1931.
Columns A, C, D, E, F, from U. S. Bureau of Mines Publications.
Column B from American Bureau of Metal Statistics Year Book.

TABLE 29[a]

SCRAP COPPER STATISTICS IN THE UNITED STATES, 1933–1937

	Short Tons						Per Cent of Total Scrap — Average
	1933	1934	1935	1936	1937	5-Year Average	
Copper as metal	193,100	220,400	270,000	260,000	285,600	245,820	56.3
Copper in alloys other than brass	54,000	72,100	94,300	105,300	102,000	85,540	19 6
	247,100	292,500	364,300	365,300	387,600	331,360	75 9
From new scrap (not including brass)	40,000	35,000	45,000	40,000	61,600	44,320	10.2
From old scrap (not including brass)	207,100	257,500	319,300	325,300	326,000	287,040	65.7
	247,100	292,500	364,300	365,300	387,600	331,360	75.9
Brass scrap melted:							
New clean scrap	54,000	45,000	60,000	88,400	88,000	67,080	....
Old scrap	76,000	76,300	60,800	82,000	118,400	82,700	....
	130,000	121,300	120,800	170,400	206,400	149,780	...
Copper content of brass scrap (averaging 70 per cent copper):							
New scrap	37,800	31,500	42,200	61,900	61,600	47,000	10.8
Old scrap	53,200	53,400	42,400	57,400	82,900	57,860	13.3
	91,000	84,900	84,600	119,300	144,500	104,860	24.1
A. Total secondary copper from all sources	338,100	377,400	448,900	484,600	532,100	436,220	100.0
B. U. S. smelter production	225,000	244,200	381,300	611,400	834,700	459,320	
C. U. S. refinery production (from primary copper)	370,800	445,400	588,800	823,000	1,066,800	658,960	
D. U. S. consumption	382,000	417,000	577,000	808,000	878,000	612,400	

TABLE 29 (*Continued*)

SCRAP COPPER STATISTICS IN THE UNITED STATES, 1933–1937

		Short Tons					
		1933	1934	1935	1936	1937	5-Year Average
Percentages	$\frac{A}{B}$	150	161	118	79	64	95
	$\frac{A}{C}$	91	85	76	59	50	66
	$\frac{A}{D}$	88	90	78	60	61	71

[a] The Mineral Industry during 1938, Vol 47, McGraw-Hill Book Co , New York.

the depression years 1933 and 1934 the total secondary production was 1½ times the smelter production, which is a measure of the amount of domestic virgin copper produced. The average for the 5-year period shows that secondary production was almost equal (95 per cent) to the smelter output.

4. Line C refers to United States refinery output from virgin copper. The difference between this and the smelter output is largely due to the inclusion of foreign copper shipped here for refining. Line D gives the United States consumption of copper as determined from refinery shipments — it means essentially the consumption of *primary* copper, but a certain amount of secondary copper is included in these figures.

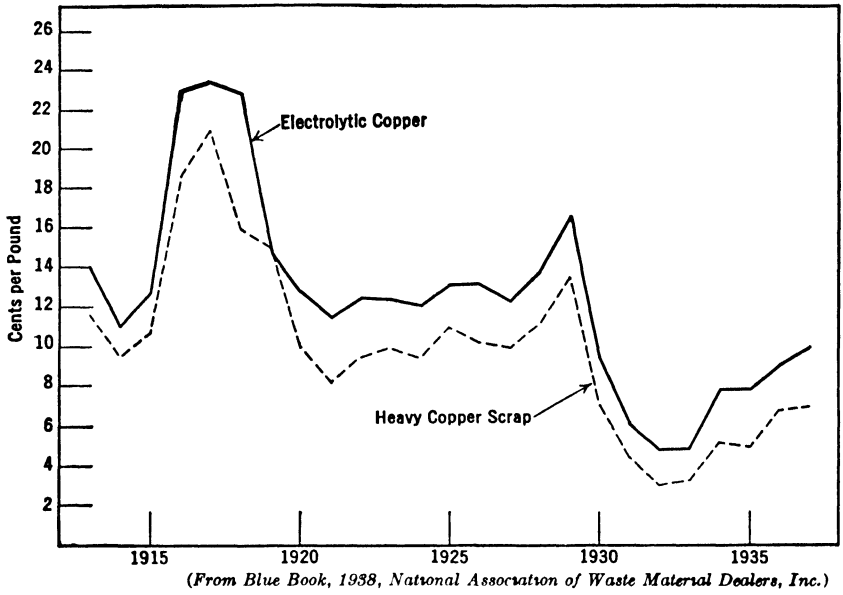
5. This table also gives a distribution of the various kinds of scrap. Brass scrap accounts for about one-fourth of the total, the remaining three-fourths being copper and other alloys. Pure copper scrap constitutes a little over one-half of the total (56.3 per cent for the 5-year average). Brass scrap is about half new scrap and half old scrap; the copper and other alloy scrap is about 85 per cent old scrap.

It will be evident from these figures that secondary copper is an extremely important factor in the metal market, and there can be little doubt that its importance will increase as the world's stock of the metal becomes larger. Eventually, as the amount of metal in circulation increases and the ore deposits become exhausted, it may happen that the production of virgin copper will dwindle to the point where it is just sufficient to supply the amount of copper "used up" or "destroyed," i.e., copper in such form that it cannot be salvaged economically.

The Price of Scrap. The price of scrap copper is variable. Not only does the price fluctuate much like the price of virgin copper because of market conditions but the price also depends upon the type of scrap. The following points are of importance in this connection.

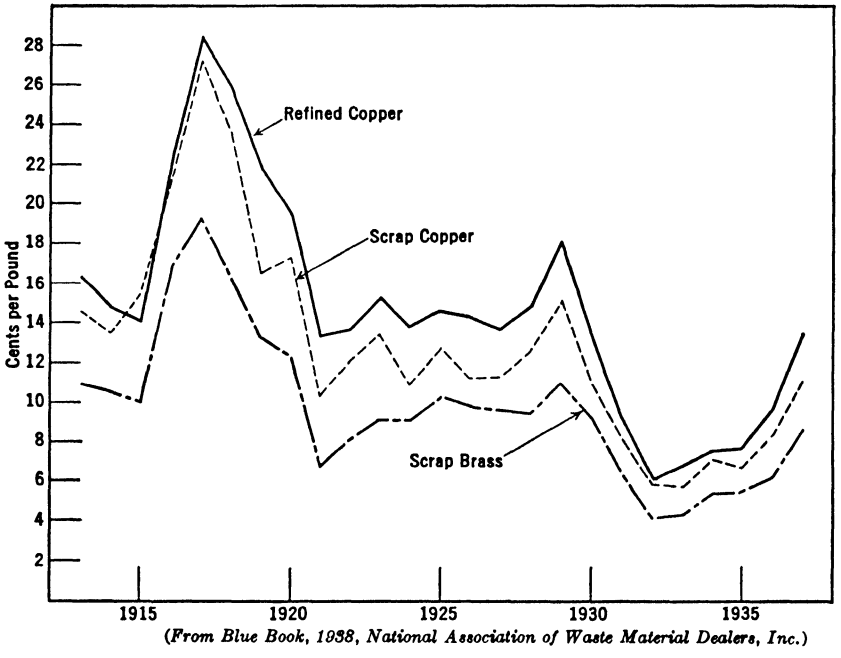
1. Although No. 1 scrap copper may be chemically equivalent to electrolytic copper, it must be melted and cast into wirebars, cakes, slabs, etc., as required by the fabricators before it becomes the commercial equivalent of electrolytic copper. The price of this scrap is usually about 2 cents per pound less than the price of electrolytic copper, and this price differential is due largely to the unfavorable physical condition of the scrap.

2. The price obtained for alloy scrap will depend upon the purchaser. A copper smelter or refinery will ordinarily pay for only the contained copper, but, for example, a brass foundry might pay a slightly higher price for certain types of brass scrap because it could utilize both the copper and zinc content of the scrap.



(From Blue Book, 1938, National Association of Waste Material Dealers, Inc.)

FIG. 13. Copper Prices.



(From Blue Book, 1938, National Association of Waste Material Dealers, Inc.)

FIG. 14. Average Prices of Copper Exports from the United States.

3. Prices of virgin copper and copper scrap usually show the same general trend (see Figs. 13 and 14).

Figure 13 shows the prices of electrolytic copper and heavy copper scrap for the 25-year period 1913–1937. The prices plotted are the "low" prices for each, for each of the years in question. As a general rule there is a fairly constant difference of about 2 cents per pound between the two prices. In the rapid decline in prices which took place after the War, the price of virgin copper dropped even faster than the scrap price for a short period; in 1919 the lowest price quoted for heavy scrap copper was 15 cents (January), but the low for electrolytic copper in 1919 was 14.75 cents (March). These figures give only an approximate comparison of prices as they represent the lowest price for the year and the prices of electrolytic and scrap copper did not always reach their low points in the same month.

Figure 14 is a plot showing the average price of exports from the United States during the same 25-year period 1913–1937. This illustrates the relative prices of refined copper, copper scrap, and brass scrap. This diagram shows that with the sharply rising metal prices in 1916, the average price of scrap copper for the year rose above that of refined copper.

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