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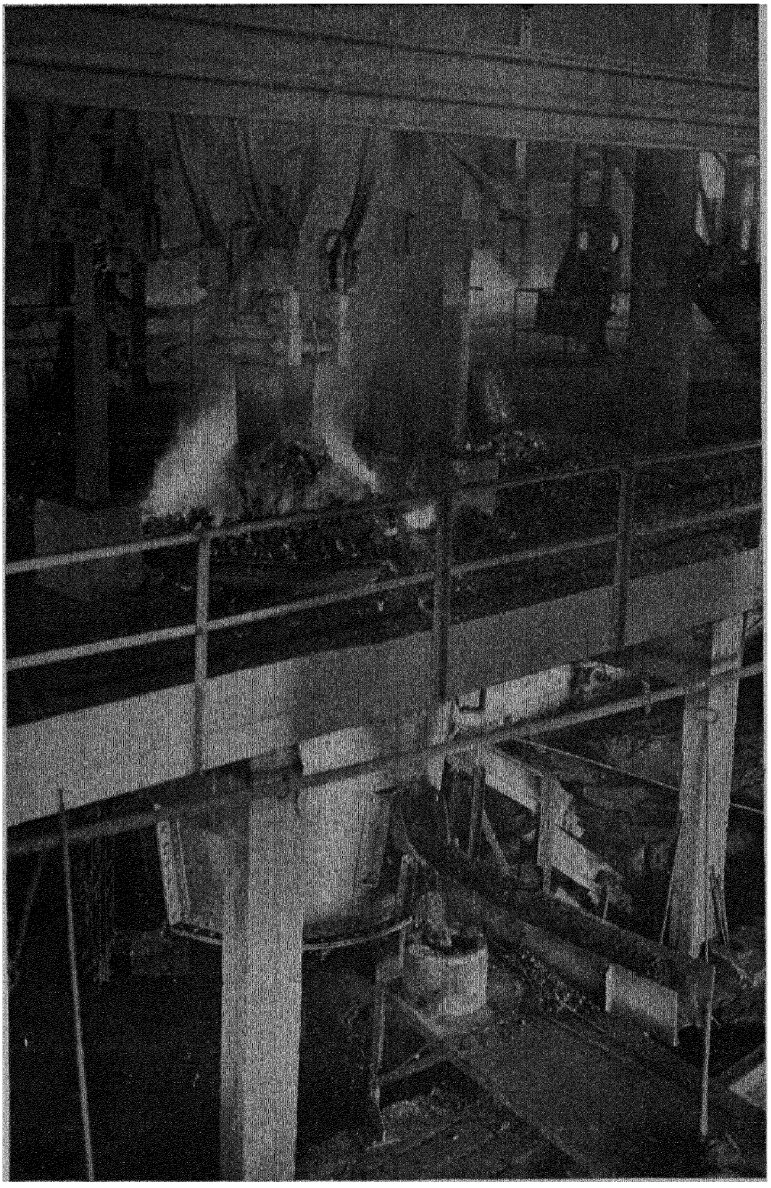
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Courtesy Union Minière du Haut Katanga, Elisabethville, Belgian Congo

One of the electric furnaces at Jadotville, Belgian Congo, producing cobalt alloy.

COBALT

by

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A. C. S. Monograph No. 108

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GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe rather

broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical sub-areas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

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Preface

Information on the chemistry and metallurgy of cobalt is widely scattered in technical literature. It appeared desirable to assemble and review critically existing data on this subject, and to present certain unpublished features and developments which have come within the author's experience with this metal and its compounds.

This monograph is written for two classes of readers: (1) The chemist, or other scientific worker, who has occasion to work with cobalt and wants accurate, up-to-date, and complete information; (2) the chemist or metallurgist who wishes to browse through this field in the hope of adding to his general knowledge or picking up ideas which may be applicable to his own sphere of work.

Cobalt is a metal which presents in its properties and metallurgy many similarities to other metals, but at the same time possesses a number of unique characteristics which may have favorable application to other elements or processes.

A very important function of a monograph, which is too often neglected, is that of directing attention to unexplored fields in a subject or at least to lanes which require illumination. In attempting to define clearly the present limits of our knowledge on cobalt we have tried also to point out promising lines of investigation.

The author is indebted to many individuals and corporations for information, and hopes that in all cases due credit has been given in the text. We would particularly like to record our gratitude to Mr. H. L. Talbot, Consulting Metallurgist, Anglo American Corporation of South Africa, Limited, for his interest and generous encouragement in this work.

In a volume such as this, which deals with cobalt from the standpoint of the mining engineer, geologist, metallurgist, chemical engineer, electrochemist, physicist, biochemist, soil technologist, and analytical chemist, there are bound to be numerous errors and omissions. A monograph only attains its highest value if it is kept up-to-date and improved by subsequent editions. With a view to future revision the author would be very grateful to receive suggestions and criticisms from readers.

Nkana, Northern Rhodesia R. S. YOUNG
June, 1948

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Chapter 1
Historical and General

In the sixteenth century the term *kobold*, a mischievous spirit, was applied to certain ores in the Hartz Mountains which on roasting not only failed to yield copper but emitted troublesome and dangerous fumes from the associated arsenic. It is probable that this expression was derived from the Greek κοβαλοσ[1]. Modifications of this local designation soon spread over Europe and the alchemical literature of that period has references to *kobalt*, *cobalt*, etc.

It was found that when cobalt ores were roasted to eliminate sulfur and arsenic, they gave on fusion with sand a beautiful blue glass called *smalt*. For a long time the alchemists believed the color was due to arsenic or bismuth, but in 1742 Brandt showed that the color arose from a new demimetal, *cobalt rex*. About 1780, Bergman and others studied the properties of cobalt and established its elemental character[7].

In the latter part of the seventeenth century invisible inks attracted considerable attention, and it was inevitable that the color changes of cobalt salts should be utilized for this purpose. In 1705 a colorless solution of bismuthiferous cobalt was used to give a green color on heating. The color phenomena in these impure products were often alleged to be caused by the presence of other metals, but finally the effects were correctly attributed to cobalt.

Although the beginning of the chemistry and metallurgy of cobalt may thus be said to date from the middle of the sixteenth century, some ancient blue glazes and glasses contain cobalt. A few samples of Egyptian and Babylonian pottery dating as far back as about 1450 B.C. are colored with cobalt. Some specimens of early Roman and Venetian blue glass owe their color to cobalt. On the whole, however, most of the ancient blue glasses and glazes were colored with copper compounds.

Towards the close of the nineteenth century the small world output of cobalt, derived chiefly from various European deposits in Germany, Norway, and Hungary, which had been worked for very long periods, was greatly augmented by the development of oxidized cobalt ores in New Caledonia. The New Caledonian deposits were discovered by Garnier in 1864, and the mines were opened about 10 years later. This remained the principal source of cobalt for some years until the rich silver-cobalt ores of Ontario, Canada, were exploited around 1903. It is probable that in

the period 1880 to 1905, New Caledonia furnished about 100,000 tons of ore averaging 3.0 to 3.5% cobalt[8].

A good description of the Ontario deposits and the metallurgical processes in use at that time is given by Drury[2]. Output rose from 16 tons of cobalt in 1904 to a maximum of 1553 in 1909, and thereafter declined to 337 in 1917.

About 1920 Union Minière du Haut Katanga began to extract the cobalt from their copper-cobalt ores of Katanga province in the Belgian Congo, and in a few years became the leading producer. The Belgian Congo still retains this position.

With the opening up of the great copper deposits of Northern Rhodesia around 1930 it was found that cobalt occurred in a small but fairly constant concentration in the copper ores of one producer, Rhokana Corporation Limited, at Nkana. Since then Northern Rhodesia has held second place in the world production of cobalt.

In 1933 the cobalt deposits of French Morocco, which had been discovered some years previously, produced 40 tons of cobalt. Production increased rapidly to 767 tons in 1938, placing this country in third position as a cobalt producer.

The principal smaller producers include:

(*1*) *Burma.* For many years between the World Wars, Burma yielded cobalt in two forms:

(a) Approximately 0.5% Co in a copper-lead matte.

(b) Up to 3 to 4% Co in a copper-nickel speiss.

(*2*) *Finland.* At Outokumpu, north-west of Lake Ladoga, cobalt occurs in cupriferous pyrite, and in 1939 a production of about 250 tons was reported in Quin's "Metal Handbook and Statistics"[9].

The Bethlehem Steel Co., which recovers by-product cobalt at its Cornwall iron-ore mine in Pennsylvania, and the St. Louis Smelting and Refining Co., which produces cobalt-nickel concentrate near Fredericktown, Mo., were the only producers of commercial cobalt ore in the United States in 1945 and 1946. Output and shipments were much greater than in 1944. The Bethlehem ore is processed at Wilmington, Del., the output being delivered to the Metals Reserve stockpile.

Prior to 1914 scarcely any cobalt metal was produced, the oxide being the marketable form of the element. About this period two factors were chiefly responsible for the development of methods designed to produce the metal. One was the war with its demand for research into the ferrous alloying metals, and the second was the support of the Canadian government for a comprehensive investigation by Kalmus and associates[3, 4, 5, 6] into the properties and uses of cobalt, in aid of the then rapidly-growing Canadian industry. In 1916 there was a world output of approximately 400 tons of cobalt oxide and 165 tons of cobalt metal.

Table 1. World Production of Cobalt, 1936–46, by Countries, in Metric Tons

(From U. S. Bureau of Mines "Minerals Yearbooks," 1936–46, and Quin's "Metal Handbook and Statistics")

Country	Cobalt-Bearing Material	1936	1937	1938	1939	1940	1941	1942	1943	1944	1945	1946
Australia	Cobalt oxide			20	13	12	13	14	15	9	10	11
Belgian Congo†	Cobalt alloy	710	1,540	1,550	1,120	2,410	2,280	1,650	2,060	1,870	3,100	
				1,320*					2,272*	3,750*		
Bolivia	Cobalt ore					2	2					
Burma	Cobaltiferous nickel speiss	214	298	238	229	218	73					
				205*								
Canada	Cobalt ores, oxide and metal	403	230	208	332	360	119	38	80	16	49	34
				208*								
Chile	Cobalt ore						2		3	5	1	
Finland	Cobaltiferous cupropyrite			250*								
Japan	Cobalt ore							1	3	15	11	
Morocco, French	Cobalt ore	371	581	720	680	330	65	3	216	243		
				767*					303*	525*		
Northern Rhodesia	Cobalt alloy	461	884	1,073	1,598	1,223	650	914	943	978	874	552
				1,463*								
United States	Cobalt ore					58	237	300	346	253		
Other countries				300								
Total		2,159	3,553	3,809	3,972	4,613	3,441	2,920	3,666	3,389	4,045	
				4,513*					3,965*	5,555*		

* Quin's "Metal Handbook and Statistics".

† Production figures for the Belgian Congo have been corrected to date through the courtesy of Union Minière du Haut Katanga.

Before the World War of 1914 to 1918 most of the world's cobalt went to the ceramic industry in the form of oxide to serve as glaze and coloring on china, pottery, porcelain, and glass. After this period, increasing proportions were used in tool steels, permanent magnets, and for other alloying purposes in the metal industries. Although it was first shown about 1910 that an addition of 5% cobalt to a high-speed steel containing 18% tungsten and 6% chromium improved the tool performance greatly, it was some years before such additions of cobalt became general in the tool steel

Table 2. Consumption of Cobalt in the United States
(From U. S. Bureau of Mines "Minerals Yearbooks," 1943-46)

	1943		1944		1945		1946	
	(lb)	(%)	(lb)	(%)	(lb)	(%)	(lb)	(%)
Metallic								
Stellite, stellite-type	2,041,409	52.1	1,757,673	41 0	1,617,353	43 3	496,090	15.4
and carbide type alloys							49,590	1 5
Magnets and magnet steels	1,032,374	26 4	1,322,097	33 2	1,105,880	29 8	1,456,522	45 2
High speed steels	399,736	10 2	361,437	9.0	335,059	9 0	224,049	6.9
Welding rod and stock for tipping tools	70,068	1 8	89,061	2 2	31,293	0 8	53,418	1 7
Dies and valve steel	29,604	0 8	36,865	0.9	25,566	0.7	16,104	0 5
Other	186,664	4.8	233,782	5 8	318,967	8.5	301,230	9.4
Total metallic	3,759,855	96 1	3,800,915	95 3	3,434,118	92.1	2,597,003	80 6
Nonmetallic								
Ground-coat frit	80,504	2.0	116,884	2.9	173,428	4.7	412,766	12 8
Pigments	39,384	1 0	53,654	1 3	100,789	2.7	170,662	5.3
Other	35,415	0.9	17,459	0 4	25,920	0.7	39,596	1.2
Total nonmetallic	155,303	3.9	187,997	4 6	300,137	8.1	623,024	19.3
Total	3,915,158		3,988,912		3,734,255		3,220,027	

industry. Cobalt is employed in many other fields which will be discussed in detail later, such as electroplating; catalysis in hydrogenation, dehydrogenation, and in drying oils; powder metallurgy; animal nutrition. On the whole the demand for, and production of, cobalt parallels the world's industrial progress, particularly in the metallurgical sphere.

It is reported in the U. S. Bureau of Mines, "Minerals Yearbook" for 1943, that cobalt is produced in 16 countries: but three, Belgian Congo, French Morocco, and Northern Rhodesia, contribute about 75 to 80% of the total. It is of interest to note that over three-quarters of the world's

cobalt comes from the continent of Africa, and that more than three-quarters of the cobalt mined is eventually used in the metallic state.

There appear to be rather wide differences in the production of cobalt reported from some countries by the U. S. Bureau of Mines, "Minerals Yearbooks"[10] and by Quin's "Metal Handbook and Statistics"[9]. These are illustrated in Table 1. The chapters on cobalt in the U. S. Bureau of Mines, "Minerals Yearbooks," written by H. W. Davis[10], present accurate

Table 3. Refiners or Processors of Cobalt in the United States
(From U. S. Bureau of Mines "Minerals Yearbook", 1944)

Refiner or Processor	Location of Plant	Cobalt Product* Made	Cobalt Raw Material* Used
African Metals Corp.	Niagara Falls, N. Y.	*A, B, C, F*	*G*
Ceramic Color & Chemical Manufacturing Co	New Brighton, Pa.	*C, D, E*	*G*
Chase Driers & Chemicals, Inc , W. S	Pittsburgh, Pa	*F*	*D*
Ferro Drier & Chemical Co	Bedford, Ohio	*E, F*	*B, H*
Ferro Enamel Supply Co	Cleveland, Ohio	*C, D*	*G*
Harshaw Chemical Co.	Cleveland, Ohio	*E, F*	*B, G*
McGean Chemical Co	Cleveland, Ohio	*E, F*	*B, I*
Mallinckrodt Chemical Works	St Louis, Mo	*E*	*B*
Nuodex Products Co Inc	Elizabeth, N J	*F*	*B, D*
Pyrites Co Inc., The	Wilmington, Del	*A, C, D, E*	*G*
Shepherd Chemical Co.	Cincinnati, Ohio	*C, E, F*	*C, D, G*
Standard Oil Co. of California	Richmond, Calif	*F*	*A, B*
Hilton-Davis Chemical Division, Sterling Drug Inc	Cincinnati, Ohio	*F*	*I*
Stresen-Reuter, Inc., Frederick A	Chicago, Ill	*E, F*	*B, D, H*

* Abbreviations *A*, metal (rondels, granules, powder); *B*, fines; *C*, oxide; *D*, hydrate; *E*, salts; *F*, driers; *G*, ore, alloy, concentrate, or speiss; *H*, carbonate; *I*, cobalt solution in process or reworking residues

and up-to-date information on this metal. It is regrettable that reliable production figures are lacking in so many cases, and that the compilation of statistics in this industry is not facilitated by a more rapid release of information by corporations and governments. Owing to the incomplete data, the yearly totals of world production must be regarded as only approximate. If anything, of course, these totals are on the low side. It appears likely that the world production has risen from slightly over 2,000 tons in 1936, to about 3,000 to 4,000 tons in 1946.

The distribution of cobalt among the arts and industries is shown in Table 2, which gives the consumption for several recent years in the United States.

Table 3, giving refiners and processors of cobalt in the United States in 1944, shows the range of raw materials used and cobalt products formed.

The price of cobalt on the New York metal market has not varied appreciably for many years from $1.50 to $2.50 a pound for 97 to 99% cobalt (Table 4). Increasing demand has been accompanied by the development of new producers.

Table 4. Prices of Cobalt (1927-1947)*

Year	Price (per lb; under 100 lb)
1927	$2.50
1928	2 50
1929	2.50
1930	2 50
1931	2.50
1932	2 50
1933	2.50
1934	2.50
1935	2 50
1936	2 50
1937	2.50
1938	1.92
1939	1.92
1940	1.92
1941	2.11
1942	2.11
1943	2 11
1944	2 11
1945	1.57
1946	1.57
1947	1.72

* From *Engineering & Mining Journal;* also *Metal & Mining Markets,* McGraw-Hill Publishing Co., New York.

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Chapter 2
Occurrence of Cobalt

Cobalt is not one of the abundant elements, but is nevertheless fairly widely diffused in nature. Most geochemists estimate that cobalt makes up 0.001% of the earth's crust compared with 0.020% nickel.

Cobalt as metal or oxide appears to be present in nearly all meteorites, together with nickel and iron. In contrast to nickel, however, which may occur in meteorites to the extent of 30%, cobalt is always less than 1%. Cobalt is present in the sun and stellar atmospheres. It occurs in sea water, mineral waters, soils, and in living organisms, both plant and animal. Traces of cobalt have been observed in many ores of iron, nickel, copper, silver, bismuth, antimony, manganese, zinc, etc.

The important cobalt minerals are sulfides, arsenides, and oxidized compounds. Cobalt occurs in veins with other minerals such as bismuth, silver, and also in the decomposition products of the weathering of basic igneous rocks. The vein deposits may occur in conglomerates, limestones, quartzite, etc., and are generally found near intrusive igneous rocks. Cobalt has less pronounced siderophilic tendencies than nickel and little of it is contained in the magmatic and pyrometamorphic deposits. It is rather abundant in some mesothermal ores, usually associated with arsenic, nickel, and silver. In combination with sulfur it occurs as linnaeite in many places, in Mississippi Valley lead-zinc deposits, and the copper deposits of Northern Rhodesia and Katanga. In arsenical minerals cobalt is usually associated with nickel, silver, and gold, whereas in sulfide minerals cobalt generally occurs with copper.

The following cobalt minerals have been described [2, 8, 9, 11, 15]:

Alloclasite, (Fe, Co) (As, Bi)S, with part of the cobalt replaced by iron.
Annabergite, $(Co, Ni)_3(AsO_4)_2 \cdot 8H_2O$.
Asbolite, an impure mixture of manganese and other oxides, containing 4 to 35% CoO. An example is $CoO \cdot 2MnO_2 \cdot 4H_2O$.
Badenite, $(Co, Ni, Fe)(As, Bi)_3$.
Bieberite, $CoSO_4 \cdot 7H_2O$.
Bismuth-skutterudite, $(Fe, Co)(As, Bi, Sb)_3$.
Bismuto-smaltite, $Co(As, Bi)_2$, a skutterudite containing bismuth.
Cabrerite, $(Ni, Mg, Co)_3(AsO_4)_2 \cdot H_2O$.
Carrollite, $CuCo_2S_4$.
Cattierite, $(Co, Ni, Fe)S_2$, (88.1:3.8:8.6) or (87.5:6.7:5.8).

Cobaltite, CoAsS.
Cobaltomenite, $CoSeO_3 \cdot 2H_2O$.
Cornetite, $Cu_3P_2O_8 \cdot 3Cu(OH)_2$, frequently containing cobalt.
Cuproasbolite, hydroxide of cobalt, copper, and manganese.
Danaite, (Co, Fe) AsS.
Erythrite, $Co_3As_2O_8 \cdot 8H_2O$.
Ferrocobaltite, $FeAsS \cdot {}_nCoAsS$.
Forbesite, $H_2(Ni, Co)_2(AsO_4)_2 \cdot 8H_2O$.
Gersdorffite, (Ni, Fe, Co)AsS.
Glaucodite, (Co, Fe)AsS.
Hauchecornite, $(Ni, Co)_7(S, Sb, Bi)_8$.
Hengleinite, $(Co, Ni, Fe)S_2$.
Heterogenite, $CoO \cdot 2Co_2O_3 \cdot 6H_2O$ or $CoO \cdot 3Co_2O_3 \cdot CuO \cdot 7H_2O$.
Heubachite, $3(Co, Ni, Fe)_2O_3 \cdot 4H_2O$.
Jaipurite, CoS.
Julienite, hydrated cobalt chloronitrate.
Kerzinite, a peat containing nickel silicate and cobalt.
Keweenawite, $(Cu, Co, Ni)_2As$.
Koeltigite, $(Cu, Co, Ni)_3(AsO_4)_2 \cdot 8H_2O$.
Lavendulane, an arsenate of cobalt and copper
Ledouxite, $(Cu, Co, Ni)_4As$.
Linnaeite, Co_3S_4, where cobalt may be replaced to some extent by nickel, copper, or iron.
Lebeckite, $4CuO \cdot \frac{1}{2}Co_2O_3$ $Mn_2O_3 \cdot 4H_2O$
Lusakite, a cobalt-bearing silicate $8(RO \cdot Al_2SiO_5)$.
Maucherite, $(Ni, Co)_3As_2$.
Mohawkite, $(Cu, Co, Ni)_3As$.
Nickel skutterudite, $(Ni, Co)As_3$.
Penroseite, $2PbSe_2 \cdot 3CuSe \cdot 5(Ni, Co)Se_2$
Petzite, $(Ag_2, Al_2, Fe, Co)(Te, As)$.
Polydymite, $(Co, Ni, Fe)_4S_5$.
Rammelsbergite, $(Ni, Co)As_2$.
Remingtonite, a hydrated cobalt carbonate.
Roselite, $(Ca, Co, Mg)_3As_2O_8 \cdot 2H_2O$.
Safflorite, (Fe, Co)As_2 or $CoAs_2$.
Schulzenite, $2CoO \cdot Co_2O_3 \cdot CuO \cdot 4H_2O$.
Siegenite, $(Fe, Co, Ni)_3S_4$
Skutterudite, $CoAs_3$.
Smaltite, $CoAs_2$.
Sphaerocobaltite, $CoCO_3$.
Stainierite, $(Co, Al, Fe)_2O_3 \cdot H_2O$.
Sychnodymite, $(Co, Cu)_4S_5$.
Tilkerodite, a lead selenide containing cobalt
Transvaalite, $Co_2O_3 \cdot nH_2O$.
Tricuite, hydroxide of cobalt and colloidal copper.
Vaesite, $(Co, Ni, Fe)S_2$ (7.2:88.0:4.8) or (—:98.0:2.0).
Villamaninite, $(Cu, Ni, Co, Fe)(S, Se)_2$.
Violarite, $(Ni, Fe, Co)_3S_4$.
Willyamite, $CoS_2 \cdot NiS_2 \cdot CoSb_2 \cdot NiSb_2$.
Winklerite, $2Co_2O_3$, $Ni_2O_3 \cdot 2H_2O$.

Principal Cobalt Minerals

Cobalt Sulfides

Carrollite. Carrollite is a steel-grey mineral with a hardness of 5.5, a specific gravity of 4.85, and a theoretical formula of $CuCo_2S_4$ or $CuS \cdot Co_2S_3$, containing 20.53% Cu, 38.06% Co, and 41.41% S. Analyses of selected specimens of Nkana carrollite have yielded results very close to the theoretical formula. For instance one gave Cu 19.58%, Co 36.97%, S 40.60%, with 1.5% insoluble material, 1.2% iron, and a trace of antimony. Another specimen of carrollite gave Cu 20.62%, Co 37.90%, and S 41.14%, with 0.20% iron, and a trace of silica.

Linnaeite. There are several linnaeites found in the Belgian Congo, Mississippi Valley lead-zinc deposits, and in other parts of the world, having the general form Co_3S_4, where cobalt may to some extent be replaced by nickel, copper, or iron. In fact carrollite may be considered a linnaeite, but owing to its characteristic composition at Nkana, and its importance, it has been considered separately. Linnaeites may contain from 31 to 40% cobalt, depending upon the quantity of iron, nickel, or copper present.

Cobalt Arsenides

Smaltite ($CoAs_2$). Smaltite is the principal cobalt arsenide, and is the chief mineral of the German, Canadian, and French Moroccan ores. It is often associated with silver, as in the Cobalt district of Ontario, or with gold, as in French Morocco. This grey mineral, with a metallic luster and a specific gravity of 6.5, and cubic structure, has a theoretical cobalt content of 28.2%.

Safflorite ($CoAs_2$). Safflorite is found associated with smaltite in Canada, Morocco, etc., and crystallizes in the orthorhombic system in contrast to smaltite.

Skutterudite ($CoAs_3$). This mineral, like smaltite, crystallizes in the cubic system, but has a cobalt content of only 20.8%. In Morocco the deposits at depth are smaltite-skutterudite, with native gold in quantities ranging from 3 to 300 grams per metric ton.

Cobalt Sulfo-Arsenides

Cobaltite (CoAsS). Cobaltite is found in the Cobalt district of Ontario, in Burma, Australia, and other localities, associated with cobalt arsenides. It is a greyish mineral with a metallic luster, specific gravity of 6.3, and when pure contains 35.5% Co.

Oxidized Cobalt Minerals

Asbolite. This term designates an impure mixture of manganese and cobalt oxides, *e.g.*, $CoO_2 \cdot MnO_2 \cdot 4H_2O$, and the cobalt content may vary

from 4 to 35%. The specific gravity of the mineral is about 1.1 and its hardness 1 to 2. Cobalt contained as silicate in basic igneous rocks is concentrated during oxidation as asbolite. Asbolite is the principal cobalt

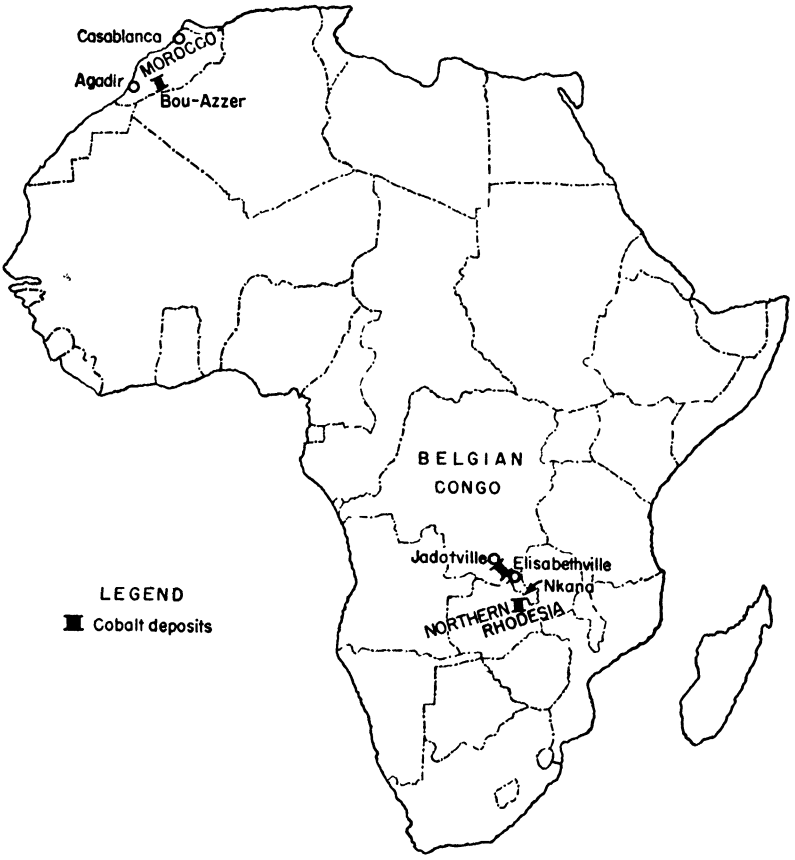


FIGURE 1. Cobalt deposits in Africa.

mineral of New Caledonia, and is also found in small quantites in Northern Rhodesia.

Heterogenite. This cobalt mineral is essentially a hydrated cobalt oxide, usually containing copper, and occasionally nickel and iron. It may contain up to 57.3% cobalt, and is one of the principal minerals of the Katanga deposits.

Sphaerocobaltite ($CoCO_3$). This mineral is found in the Belgian Congo and to a small extent in Northern Rhodesia.

Erythrite ($3CoO \cdot As_2O_5 \cdot 8H_2O$). Erythrite varies in color from pale crimson to orange-red, and is found as an oxidation product of cobalt arsenide minerals in Canada, Germany, Morocco, etc. Its specific gravity is 3.0 and its cobalt content 29.5% when pure.

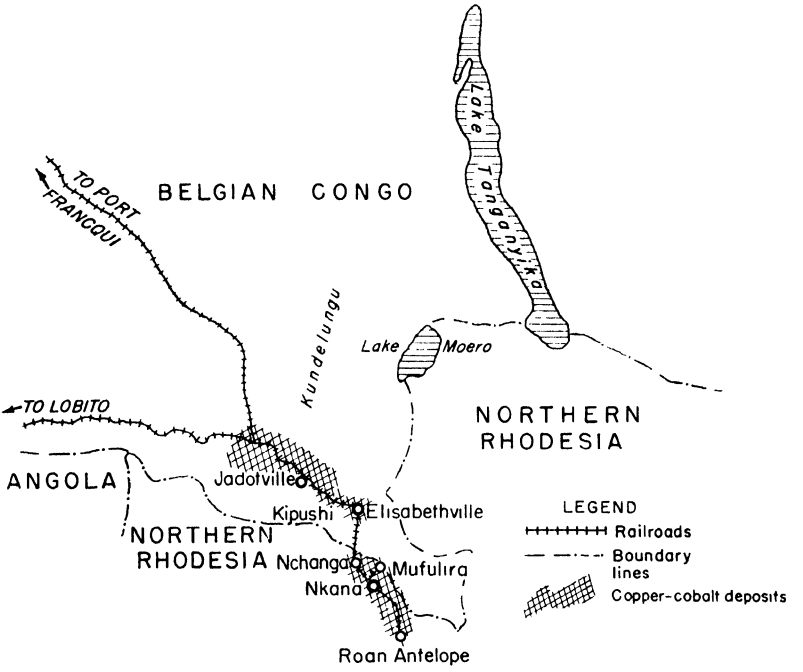


FIGURE 2. Cobalt deposits of Northern Rhodesia and Belgian Congo

Major Cobalt Deposits

Belgian Congo. In the Belgian Congo the cobalt ores are chiefly oxidized, and no sulfide cobalt has yet been worked. The cobalt ores of the Union Minière are local enrichments in cobalt of cobalt-bearing copper ores, or in some cases copper and cobalt-bearing formations from which some of the copper has been leached out by weathering. Up to recent times, the cobalt ores have been derived largely from a number of small enrichments in mines near Elisabethville and Jadotville in the southern part of the Belgian Congo. Now most of the cobalt comes from copper ores, mainly from around Kolwezi, in which the cobalt content is lower.

The principal minerals are heterogenite, sphærocobaltite, cornetite, tricuite, asbolite, and cuproasbolite.

Northern Rhodesia. In Northern Rhodesia the cobalt occurs chiefly as

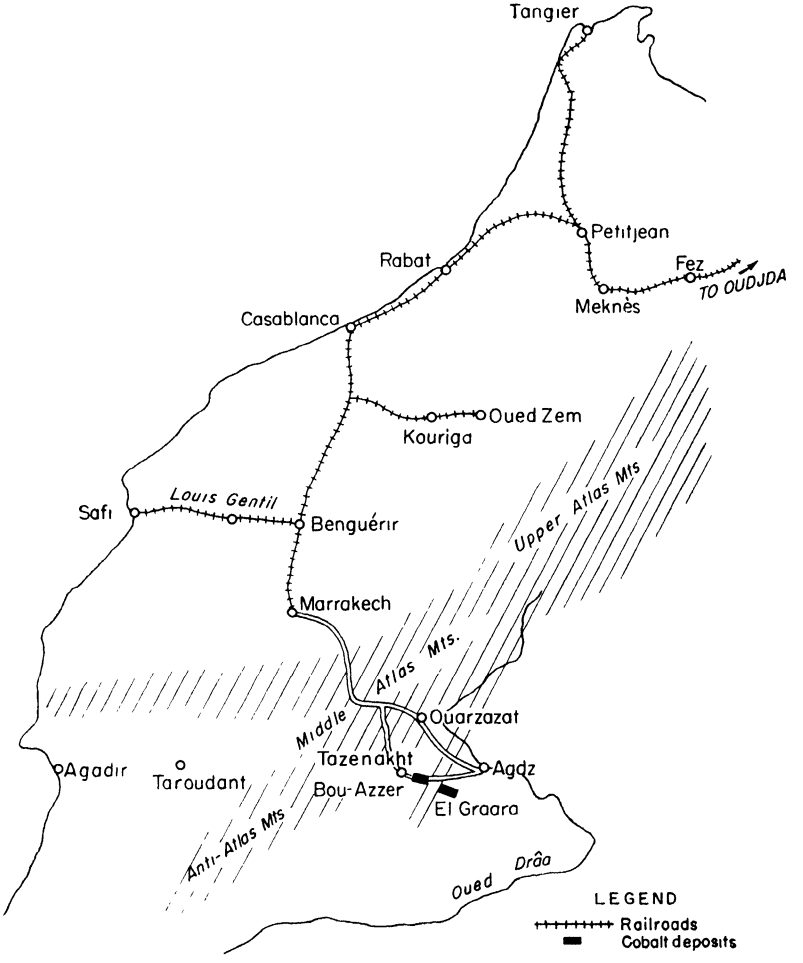


FIGURE 3. Cobalt deposits of French Morocco.

carrollite, but an oxidized form of cobalt is also found and forms a small and varying proportion of the cobalt content in the mill feed of Rhokana Corporation.

The carrollite is closely associated with the copper minerals throughout the sediments of the ore horizon, but it is not evenly distributed and the cobalt content of the ore varies from a trace to over 3%, with an average of 0.25% in the Nkana North and South orebodies and 0.07% in the Mindola orebody. This gives an average mill feed to Rhokana concentrator of about 0.13% Co.

Where the cobalt content is low, around 0.07%, it appears to be fairly evenly distributed throughout the ore. Where the cobalt content is high, around 0.50%, the carrollite tends to be concentrated in the porous sandstone and cherty ore which are the two upper members of the ore horizon, and to some extent in the lowest part of the argillite forming the hanging wall.

Microscopic examination has shown that the carrollite generally occurs as finely disseminated grains with cubic outlines. It appears to be one of the early ore minerals, and is older than chalcopyrite and bornite which cut and replace it.

Practically all of the cobalt present in the copper and cobalt concentrates at Nkana is free and unattached. It is possible by gravity concentration to produce a high grade cobalt concentrate with a good recovery from the flotation middlings if the product is classified and the sands treated on tables.

French Morocco. The cobalt deposits of French Morocco lie in a rocky desert region in the south of the Atlas Mountains near Bou-Azzer about 250 kilometres east of the port of Agadir. They are the property of La Société Minière de Bou-Azzer et du Graara, whose head office is at Casablanca. The deposits of cobalt and nickel are found in veins at or near the contact of serpentine and diorite rocks. The gangue is principally carbonate. Smaltite, skutterudite, and safflorite are the cobalt minerals, while niccolite and other nickel-arsenic minerals are also present. Gold, varying from 3 to 300 grams per ton, is found in smaltite-skutterudite minerals. Silver is also found in varying quantities but always less than 50 grams per ton. An analysis of a smaltite-skutterudite mineral reported by Perrault[11] gives:

	%
Co	12.8
Ni	4.0
Fe	5 5
As	74 0
S	1.9
Inso'uble	0.6
	98.8

In general the commercial ore of Morocco does not have nickel or iron exceeding 20% of the cobalt, although some deposits have more nickel than cobalt.

Bou-Azzer is about 186 miles from the railroad at Marrakech and this limits its development. Proved resources are 36,000 metric tons. At

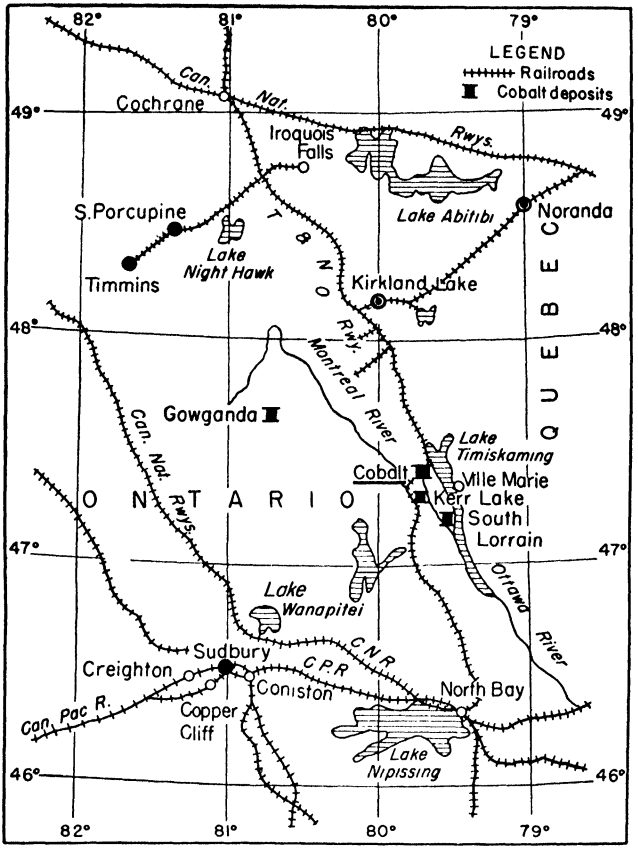


FIGURE 4. Cobalt deposits of Ontario, Canada.

present the mine has several levels, the deepest being 175 metres. The average cobalt content of commercial ore is 11 to 12%, although there are other commercial-grade ores with a cobalt content as low as 0.75 to 1.25%.

Canada. The cobalt deposits of Canada have been described many times in mining and geological literature[1, 2, 4, 7, 8, 13]. The principal ones

occur at Cobalt, Ontario, 260 miles north of Toronto. Mineralization includes native silver and bismuth, argentite, smaltite, cobaltite, erythrite, niccolite, safflorite, skutterudite, glaucodot, mispickel. An example of high-grade, hand-sorted ore would be:

	%
Ag	7
Co	7 9
Ni	4 3
Fe	5 0
Cu	0.1
As	30.2
S	1.7
SiO_2	4 2
CaO	15.0
MgO	2.7

In the veins the arsenide of nickel and cobalt may fill the whole vein or may be distributed in calcite or dolomite gangue. Lindgren[8] holds that the calcite gangue was the earliest mineral and was replaced by all arsenides, sulfo-salts, and native metals.

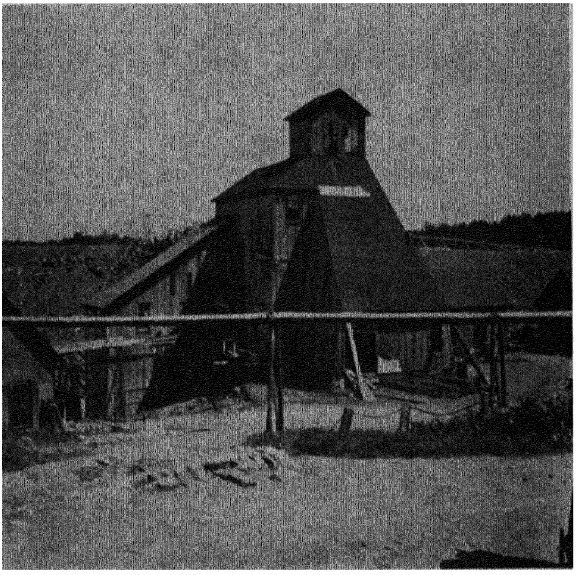
The copper-nickel ores of the International Nickel Company of Canada in the Sudbury district contain 3 to 5 parts of cobalt for every 100 parts of nickel. Cobalt tends to go into the converter slags where its content may increase from 0.05% in the mill feed to 0.30% in converter slag. Some of this is lost with reverberatory slag and most of the balance of the cobalt finds its way to electrolytic nickel which contains in the neighbourhood of 0.40% cobalt. Owing to the low content of cobalt in the incoming ores, no attempt is made to recover cobalt separately at Copper Cliff, but it may be remarked that the huge tonnages treated would, if complete recovery of cobalt were practicable, place this source among the front rank of world cobalt producers.

It was reported at the Annual Meeting of the International Nickel Company of Canada on April 28, 1948, that a plant to recover cobalt had been recently brought into operation at the Port Colborne nickel refinery, and that it was now producing approximately 15 tons of metal in oxide per month.

It is interesting to note that molybdenite and gold have been found associated with cobalt arsenide in British Columbia and French Morocco. At Great Bear Lake in Canada cobalt occurs with silver and pitchblende in a gangue of quartz and rhodochrosite[6]. It was the stain of cobalt bloom on the rocks of Echo Bay in Great Bear Lake, recorded by two government geologists in 1900, that led many years later to the discovery and development of Canada's great uranium deposit.

United States of America. During the war small quantities of cobalt were obtained in the United States from two principal sources. The Bethlehem Steel Company recovered cobalt from magnetite mined at Cornwall, Pa., where the ore contains less than 0.05% Co.

The St. Louis Smelting and Refining Company began producing cobalt commercially at its property near Fredericktown, Mo., in 1944. The deposit here is a complex lead-copper-nickel-cobalt ore.

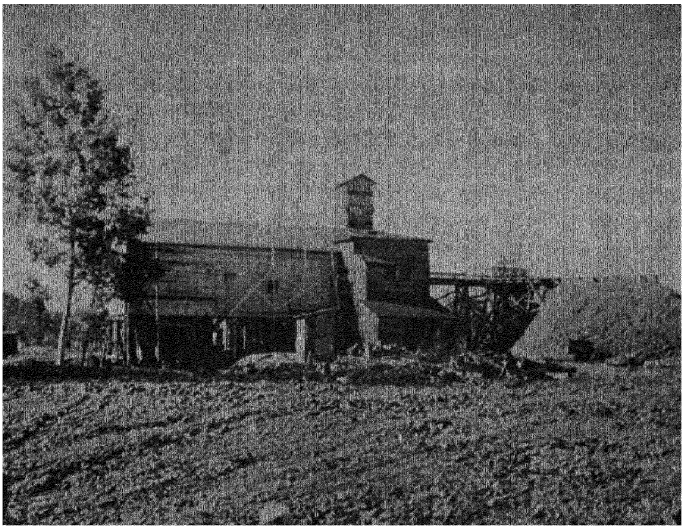


Courtesy Canadian Bureau of Mines, Ottawa

FIGURE 5. Miller Lake O'Brien Mine near Gowganda, Ontario, producer of silver and cobalt. Property of Siscoe Gold Mines Ltd.

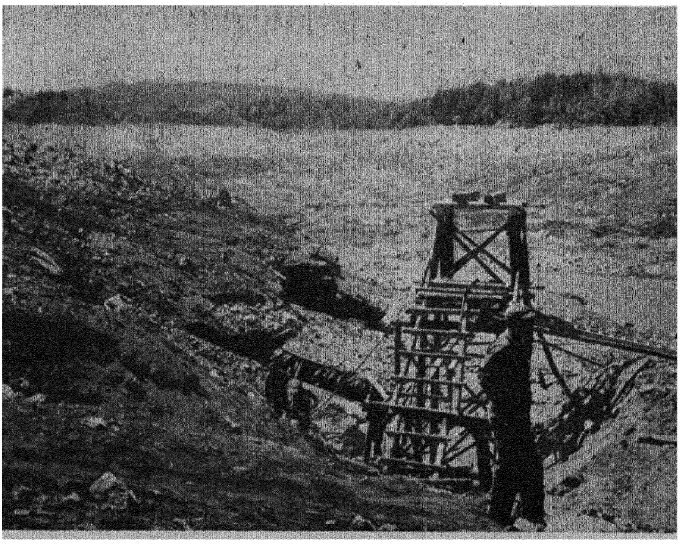
In the Goodsprings mining district of Nevada, cobalt occurs as stainierite, $Co_2O_3 \cdot H_2O$, and during World War II the U. S. Bureau of Mines made extensive investigations on the metallurgical treatment of these deposits[14]. The average analysis of mineable ore from the Goodsprings district probably will not exceed 0.5 to 0.75% Co.

In the Blackbird district of Idaho, cobalt occurs as cobaltites, associated with copper, and the Bureau of Mines undertook an extensive program of diamond drilling and sampling in this area in the period 1941–44[12]. The cobalt content of the drill holes appears to be between 0.02 and 2.66% Co, with two representative samples of ore quoted as 0.39 and 0.95% Co.



Courtesy Canadian Bureau of Mines, Ottawa

FIGURE 6. Silver Miller Mines Ltd., Cobalt, Ontario, one of the largest operators in Canada.



Courtesy Canadian Bureau of Mines, Ottawa

FIGURE 7. Kerr Lake Lease, Cobalt, Ontario. The lake has been drained and shows old open cuts and new shaft head frame.

Metallurgical investigations on these ores have been conducted by the Bureau and will be available in due course.

Finland. In Finland the cupriferous pyrite of Outokumpu contains the following:

Cu	4–4.45%
Fe	27%
S	26%
Zn	1%
SiO_2	39 0%
Co	0 1–0 2%
Ni	0.1%
As	trace
Au	1 gm/ton
Ag	12 gm/ton

Burma. The copper-lead mines of the Burma Corporation furnished the following cobaltiferous products:

(1) Matte containing 40 to 45% Cu, 20 to 30% Pb, about 1% Ni, 0.3 to 0.8% Co, and 2,000 to 3,000 gm Ag per ton. This was treated at the Nord-Deutsche Affinerie at Hamburg and amounted to about 15,000 tons annually.

(2) Speiss containing 29 to 30% Ni, 15 to 17% Cu, 3 to 4% Co, 800 to 1,000 gm Ag per ton. About 4,000 to 5,000 tons a year were treated in Germany.

New Caledonia. In New Caledonia the cobalt is found as asbolite, and the composition of the mineral is rather variable: Co 1.6 to 7.8%, Mn 7.1 to 21.4%, Fe 7 to 17.5%, SiO_2 20 to 50%, CaO + MgO 0 to 10%.

Minor Cobalt Deposits

Australia. Cobalt has been reported from many districts in Australia in a variety of forms, as sulfide, arsenide, and oxide, associated with nickel, copper, manganese, silver, bismuth, chromium, tungsten. Though some of the deposits are apparently quite rich, they are all small, and output from Australia has varied from nil to 40 tons annually.

It is interesting to record that Woodward[18] describes the purification of cobalt from the zinc solution of the Electrolytic Zinc Company of Australasia Ltd. with nitroso-β-naphthol from the cold copper- and cadmium-free solution. In practice the calculated amount of sodium β-naphtholate is added to the solution, then sufficient sodium nitrite, and finally sulfuric acid to form the nitroso salt. About 60 pounds of cobalt per day is precipitated as red cobalt nitroso-β-naphtholate. It is not known whether this quantity of 10 tons per annum appears in Australia's statistics.

Brazil. Cobalt is associated with nickel at Jacuba, São José do Tocantins, State of Goyaz, in Brazil[10].

Chile. At the beginning of this century several small mines in Chile produced, over a period of several years, about 50 to 60 tons of cobalt. Just before World War II, the production of cobalt was again commenced in Chile, but without much success, judging by the output recorded of only 10 tons in the period 1939 to 1944[16].

China. A small production of cobalt has been carried on in China for a very long period, serving the ceramic industry. Statistics are not available on the output, but it is insignificant in world trade.

France. Perrault[11] discusses the occurrence of cobalt minerals in France and in other European countries, but these deposits are too small for development.

Germany. Although the deposits of cobalt in Saxony and elsewhere in Germany are now almost exhausted, small quantities are still obtained as a by-product from the copper deposits of Mansfield. Refinery slags from this source yield a product containing about 28% Cu, 21% Ni, 9% Pb, 1.4% Co, 21% SiO_2. Other residues and slimes of customs refineries in Germany contain appreciable quantities of cobalt, all of which is recovered. Large quantities of pyrites from Sweden, Finland, Spain, Cyprus, etc., were used in Germany as a source of sulfur, and some of these contained enough cobalt to warrant extraction from the roasted residue.

Japan. A small cobalt-copper sulfide deposit in Japan has been exploited for a dozen years, producing about 24 tons of cobalt metal annually. It is interesting to observe that, although cobalt is a rare metal in Japan, Japanese metallurgists have been for many years the pioneers in the development of cobalt alloys for magnets.

U.S.S.R. The oxidized nickel minerals of Russia contain about 1 to 2% Ni and 0.05 to 0.2% Co. Some cobalt is recovered from the nickel smelting operations, but details are lacking on this matter. Since the nickel smelting is carried on by blast furnace, converter, and electric furnace operation, it is probable that cobalt accumulates in converter slags which are occasionally treated in an electric furnace under reducing conditions to give a high-cobalt product amenable to eventual chemical processes.

Identification of Cobalt Minerals

Chemical Identification

Dry Method. Cobalt compounds give a blue bead with borax or sodium metaphosphate in both the oxidizing and reducing flames of the blow pipe. Prolonged heating in the reducing flame minimizes the interference from iron or manganese, but reduces the cobalt to metal when it assumes a grey appearance similar to nickel.

On the charcoal stick cobalt compounds give grey metallic cobalt,

which can be removed by means of a magnetized knife blade, placed on filter paper, moistened with HCl, and dried. Cobalt gives a blue color to the paper.

Wet Method. Much more positive and satisfactory identification is secured by the following qualitative chemical determinations.

(I) To a small quantity of the sample dissolved in acids add 2 to 3 ml of 70% ammonium acetate solution, 1 to 2 ml of 50% tartaric acid solution, 10 ml of 60% ammonium thiocyanate, 5 ml of 20% sodium thiosulfate solution, 3 ml of 10% sodium phosphate solution, and 10 ml of a mixture of 3 parts of amyl alcohol to 1 part of ether. Transfer to a separatory funnel and shake thoroughly. If cobalt is present, the upper layer will be colored blue. No other element, to the author's knowledge, will interfere. The blue color can be detected when only 0.2γ of cobalt is present.

(II) Nitroso-R-salt is a very sensitive indicator for cobalt, but requires the removal of copper. Dissolve a small quantity of the unknown sample in HCl or H_2SO_4, dilute to appropriate volume and gas out copper and other Group 2 metals with H_2S. Boil off the latter, add 1 gram of sodium acetate and 2 ml of 0.5% solution of nitroso-R-salt in water. Boil, add 2 to 5 ml HNO_3 and boil for a minute or two to destroy any red color which is also produced by iron. If cobalt is present, a permanent red color, not affected by boiling with HNO_3, is produced. A detectable red develops if cobalt is present in only 5 parts per million. For qualitative work no other element is apt to interfere to an extent sufficient to mask the red.

Microchemical Identification

It is difficult to differentiate carrollite from pyrite under the microscope. Mr. J. Vaes of the Union Minière du Haut Katanga[17] has found a modification of the contact print method of Gutzeit[3] and Hiller[6] satisfactory. He covered a polished section of carrollite with filter paper moistened with dilute HCl and passed a current from a car battery through the mineral and paper. After drying, the paper showed a faint rose color due to cobalt chloride. When a drop of copper mercuric thiocyanate was added to the dry paper a blue diffuse spot surroundered by a red aureole was formed immediately. The blue color was due to cobalt, the red to iron.

Gutzeit[3] uses gelatin-impregnated paper from which the silver has been dissolved by sodium thiosulfate, and 5% KCN solution. After electrographic attack at 8 volts for 30 seconds, a direct orange print of cobalticyanide is obtained. Nitroso-R-salt in sodium acetate solution gives a red print with cobalt, iron, copper, and other metals, but brief washing in 2:1

HNO_3 destroys the red color of other metals while that of cobalt remains unchanged.

The Geological Survey and Museum of London recommend treatment of the polished section with a drop of 5% mercuric chloride. Most carrollites show a brown to iridescent stain while pyrite is unaffected. Some carrollites, however, give a negative reaction to this test. They state that the following microchemical test is of greater diagnostic value. Dig out a few grains of the mineral from the polished section with a needle under the microscope. Decompose the mineral with 1:1 HNO_3, leach the residue with a drop of 1:7 HNO_3, transfer the drop and merge it with a drop of 5% potassium mercuric thiocyanate solution in water. Copper precipitates as yellowish-green prisms and moss-like clumps, whereas cobalt precipitates separately as indigo-blue prisms. If only pyrite is present, the drop on treatment with potassium mercuric thiocyanate would merely turn red without formation of a precipitate.

It has been found at Rhokana Corporation that an experienced microscopist can make a fair differentiation between pyrite and carrollite by giving the briquetted sample the minimum of polishing. Carrollite polishes more readily than pyrite, and the scarred appearance of the latter serves to distinguish it from carrollite.

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Chapter 3
Metallurgy of Cobalt

Few base metals exhibit, in their processing from ore to refined metal, such a diversity of metallurgical operations as does cobalt. Depending upon the original form of the cobalt, whether arsenide, oxide, or sulfide, one may encounter gravity, magnetic, and flotation concentrating operations; blast furnace, reverberatory furnace, and electric furnace practice; operations of roasting, leaching, chemical precipitation, electrolysis, pyrometallurgical and hydrometallurgical oxidation and reduction, with accompanying purification and filtration steps.

We shall describe in turn the metallurgical practices in the Belgian Congo where almost all ores are oxide, in Northern Rhodesia with sulfides predominating, in French Morocco and Canada where cobalt arsenides are treated, and in German refineries with their variety of by-products containing cobalt. The refining treatment of the copper-cobalt-iron alloy of Northern Rhodesia and Belgian Congo will be described under the practice at Deloro Smelting and Refining Company, Limited, and at German refineries.

Belgian Congo

Union Minière du Haut Katanga is the sole producer of cobalt in this country. Its processes will be described in their present status.

Production of Crude Cobalt Alloy

The cobalt-bearing ores and concentrates containing their metallic components in an oxidized form are reduced in electric furnaces. They belong to the following classes:

(*1*) *Cobalt Ores.* These are local enrichments of cobalt occurring in several copper mines in the vicinity of Elisabethville and Jadotville. The metallic constituents are oxidized and the cobalt is always accompanied by copper and iron minerals. The cobalt content varies from 4 to 12 per cent. Lump ore is fed directly to the electric furnaces, while the fine ores are first sintered. The principal cobalt minerals are heterogenite, sphaerocobaltite, cornetite, asbolite, etc.

(*2*) *Concentrates from Ore Dressing of Copper Ores with Lower Cobalt Content.* These ores also have their metallic components in the oxidized state. Depending upon their nature, they are treated either by bulk

flotation, or by washing, picking, and jigging. The middlings, or in some cases the concentrates and middlings, from the washing and jigging treatments are subjected to flotation. The products from these operations are concentrates containing from 6 to 14% cobalt with about the same iron content, and a slightly higher percentage of copper.

The coarsest of these concentrates, above ⅜ inch, are charged directly into the electric furnace, whereas the fines are first sintered.

(3) *Cobalt-Bearing Refinery Slag.* One of the products of the reduction of the cobalt: copper ores and concentrates in the electric furnaces is crude copper containing 4.5% Co and 89.5% Cu. This product is subjected to the usual fire refining. The refinery slag from this operation which contains about 15% Co is charged into the electric furnaces with the lump ore and the sintered fine ores and concentrates.

Electric Furnace Operation. From the above three classes of material, a composite feed to the electric furnace is produced.

The electric reduction furnaces will not operate satisfactorily with any appreciable quantity of fines in the charge, especially if these undergo a substantial fire loss upon heating. The ores and concentrates below ⅜ inch are sintered on a Dwight Lloyd machine with about 10% of their weight of breeze coke or fine coal, and the return fines are screened out from this sinter.

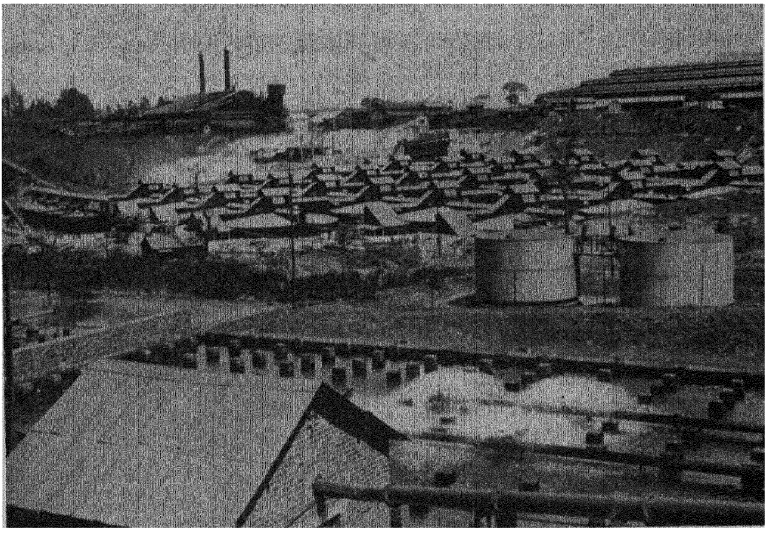
The lump ore, the coarse concentrate, and the sinter, together with lump lime as a flux and coke as conductor and reducer, are charged into six electric furnaces

The furnaces are of 600 kw on single phase current and have an upper diameter of over six feet. Voltage is kept at 120 volts and the current is 5,000 to 5,500 amperes.

The products of the reduction are slag and two alloys. The slag, which has 0.3% Cu and 0.4% Co, is run through a water-cooled slag hole. The copper, cobalt, and a large part of the iron in the charge are reduced with some silicon to their metallic state into two alloys.

The white alloy, which is the lighter, has 15% Cu, 12% Co, 39% Fe, and 1.6 to 2.0% Si. The heavier red alloy has 89% Cu and 4.5% Co. These alloys are tapped together in a ladle, and by adjusting the quantity and size of coke in the electric furnace charge, the silicon in the white alloy is kept above 1.5%. Above this silicon content the white alloy segregates in the ladle into a layer which comes out on top of the red alloy. The alloys are poured separately, the heavy red alloy by tapping the bottom of the ladle and the light white alloy by pouring from the lip. The white alloy is cast into ingots or granulated into shot in a stream of water. The red alloy is refined for copper and the resultant slag, containing 15% Co, is returned to the electric furnace charge.

The white alloy from the Belgian Congo is normally exported to the



Courtesy Union Minière du Haut Katanga, Elisabethville, Belgian Congo

FIGURE 8. Electrolytic copper plant at Jadotville, where cobalt-containing residues are obtained.

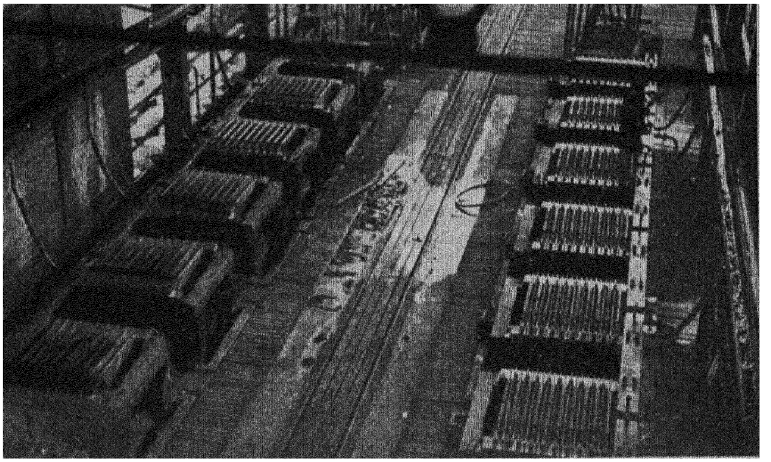


Courtesy Union Minière du Haut Katanga, Elisabethville, Belgian Congo

FIGURE 9. Electric furnace building at Jadotville for cobalt production.

cobalt refinery at Oolen in Belgium, although during the war this alloy was refined at a plant in Niagara Falls, N. Y., operated by the Union Carbide and Carbon Corporation.

The refining operations in Belgium follow, in general, the practice described later for the treatment of Rhokana alloy by the Deloro Smelting and Refining Company.



Courtesy Union Minière du Haut Katanga, Elisabethville, Belgian Congo

FIGURE 10. Cobalt electrolytic cells at Jadotville.

Production of Electrolytic Cobalt

A new electrolytic process has been developed and is turning out 140 tons of cobalt per month at Jadotville. The operations are briefly summarized below.

The slime residues from the copper leaching plant contain the largest part of the cobalt in the oxidized copper ores and a small part of the copper as entrained sulfates. This dilute pulp entrains solution which contains 15 gpl Cu and 5 to 6 gpl Co, together with Fe, Mg, Mn, etc. It is transferred by a packless pump to agitating cells where Ca $(OH)_2$ is added to bring the pH to 3.5 to 3.8. From there it is passed to a series of thickeners from whence the solution goes to electrolytic cells for decopperizing, while the pulp goes to a series of washing thickeners. The solution of the latter goes back to the primary thickener while the pulp goes to waste.

The solution containing about 7 gpl Cu and 3 gpl Co is electrolyzed at a high current density with air agitation at the bottom of the lead anodes. Satisfactory copper cathodes are obtained, though a small portion of the

copper falls to the bottom of the tank in a finely-divided form. This copper can be readily ground to minus 400 mesh for sink-and-float or powder metallurgy purposes. The decopperized solution contains about 1 gpl Cu, 3 gpl Co, and 7 gpl H_2SO_4. It passes to a series of Pachucas where $Ca(OH)_2$ is added to bring the pH to 5.0–5.5, the range where most of the remaining copper is precipitated.

From the Pachuca the product passes to a thickener where the pulp is returned to the agitating cells at the head of the circuit. The solution, containing 0.2 gpl Cu is passed through a series of cementation cells containing cobalt shot. Here the copper is removed to 0.0005 gpl and the cobalt content of the solution is 3 to 3.5 gpl.

The solution passes to agitating cells where $Ca(OH)_2$ is added to precipitate the cobalt, and thence to a thickener. The solution passes to waste and the pulp goes to a Shriver press. The filter cake goes to repulping cells where it is mixed with return solution from the tank house. This pulp passes to the cobalt electrolytic cells, where electrolysis is carried out using mild steel cathodes and lead anodes, provided with air agitation. Current density is 300 amperes per square meter. When once a film of cobalt is secured on the cathode, stripping is easy. A part of the metallic cobalt falls to the bottom of the tank where it is later separated from MnO_2, etc., by an electromagnet.

The cathode deposit which has been stripped from the cathode plates and collected from the bottom of the tanks contains 3 to 4% zinc and a little entrained basic sulfate. It is melted in a Héroult type electric furnace, thereby driving off most of the zinc. Sulfur is removed with a high lime slag. The small quantity of zinc remaining is then removed by agitating the bath. The bath is deoxidized and then granulated into shot by passing it into a stream of water

The pulp from the cobalt electrolytic cells goes to a Pachuca where H_2SO_4 is added to dissolve the remaining cobalt precipitate at pH 2 to 4. It passes to a thickener, from which the solution goes to evaporators. From the latter the solution passes to the repulping cells ahead of the electrolytic section. The pulp goes to an Oliver filter where the cake is discharged to a dump, and the solution goes back to the thickener ahead of the Oliver filter.

A flowsheet illustrating the present practice for electrolytic cobalt at Union Minière is shown in Figure 11.

Northern Rhodesia

The output from the sole producer of cobalt in Northern Rhodesia, Rhokana Corporation Limited, is derived from the small quantity of cobalt in its copper ores at Nkana.

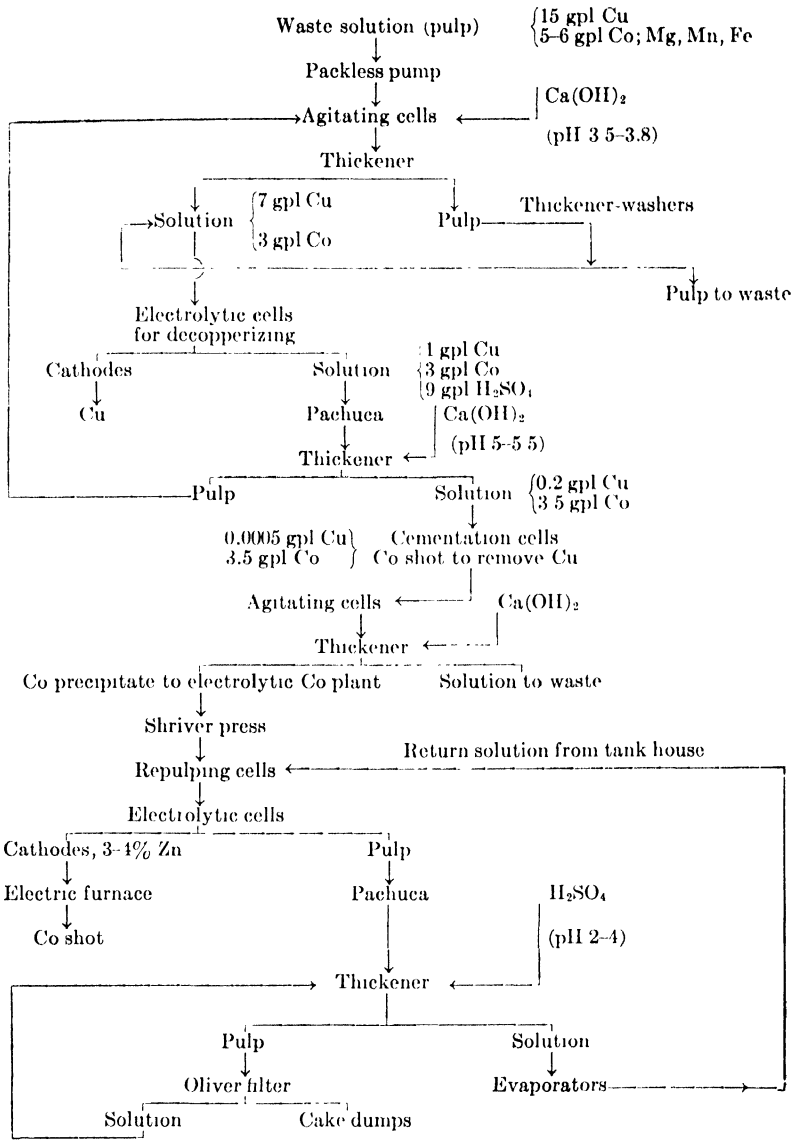


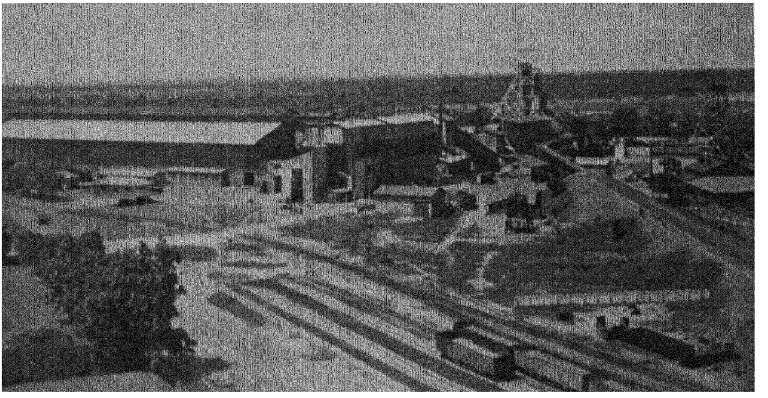
FIGURE 11. Electrolytic cobalt production at Union Minière du Haut Katanga, Belgian Congo.

Concentrating

The feed to Rhokana's large copper concentrator averages about 3% Cu and 0.13% Co. The other constituents of the mill feed in percentages are: Fe 2–3, S 1 to 2, SiO_2 40 to 50, Al_2O_3 11 to 13, CaO 7 to 8, MgO 6 to 7.

The principal cobalt mineral is carrollite, $CuCo_2S_4$, but about 5 to 10% of the cobalt occurs as an oxidized form, probably asbolite or sphaerocobaltite. The copper minerals are closely associated with the gangue, but at the degree of fineness of the flotation feed, approximately 70% minus 200 mesh, carrollite shows only slight attachment.

Two concentrates are made at Nkana for ease in subsequent metallurgical treatment. The frother employed is pine oil, added at the rate of ap-



Courtesy Rhokana Corp., Ltd., Nkana, No. Rhodesia

FIGURE 12. Concentrator of Rhokana Corporation, Ltd., Nkana.

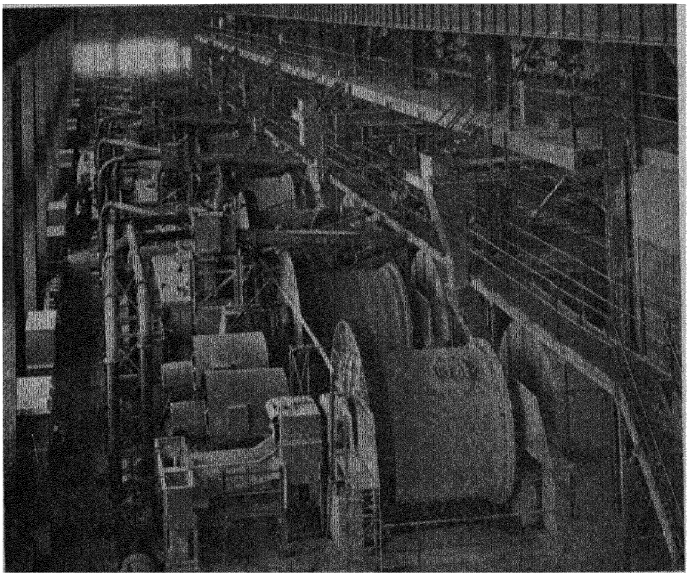
proximately 0.05 lb per ton of ore. The collector used is potassium ethyl xanthate, added at the rate of about 0.05 lb per ton. An alkalinity of approximately pH 10 is maintained for the flotation feed by the addition of about 2 lb of lime per ton of ore.

A copper concentrate, containing a high copper and low cobalt content is made by the addition of a minimum quantity of xanthate and pine oil to the initial section of the flotation circuit. Carrollite is depressed by lime, and the minimum addition of the collector and frother results in the flotation of the copper minerals away from the carrollite. Lime is used as a selective depressant between the copper and cobalt minerals, and with the alkalinity employed in the concentrator, the relative order of floatability is chalcocite, bornite, chalcopyrite, carrollite, and pyrite. This is possibly associated with the relative rate of oxidation under these conditions.

A "cobalt" concentrate is then made by greatly increasing the xanthate

and pine oil additions, and recirculating various flotation pulps. This results in flotation of the carrollite along with the balance of the copper minerals not removed in the initial treatment. The excess of frother and collector overcomes the depressant action of lime on carrollite, and the latter is again able to float with the copper minerals.

The production of two concentrates at Nkana thus depends solely on the depressant effect of lime on carrollite, on differences in concentrations of



Courtesy Rhokana Corp., Ltd., Nkana, No. Rhodesia

FIGURE 13. Ball-mill section of concentrator at Rhokana Corporation, Ltd., Nkana.

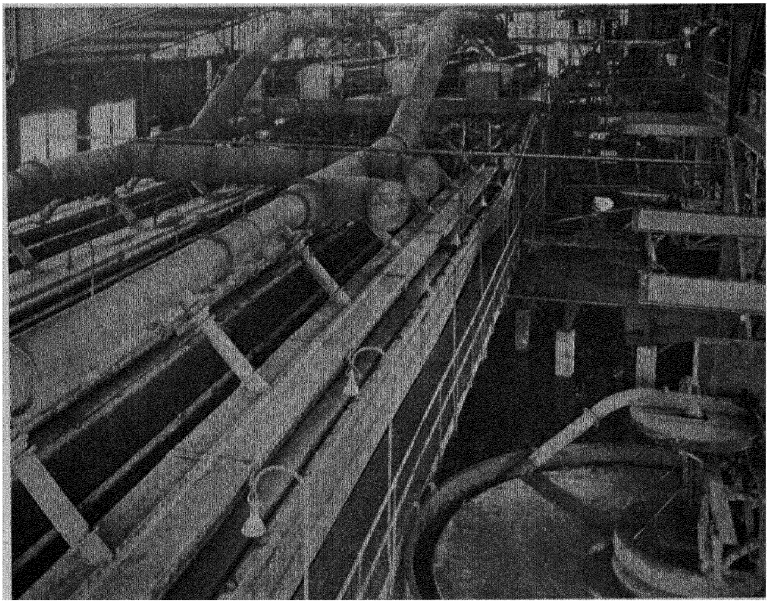
added reagents to either supplement or to overcome this depressant action, and on recirculation of various middling and tailing products in the flotation circuit. Subsequent smelting operations require an iron : cobalt ratio not exceeding 4 : 1, and it is this which represents the main problem in the differential separation of copper and cobalt to take care of fluctuations in cobalt grade and in types of mineralization. After thickening and filtering, the concentrates pass to the smelter. An analysis of the two concentrates is illustrated by:

	Cu	Co	Fe	S	SiO_2	Al_2O_3	CaO	MgO
Cu concentrate	56.81	0.64	10.37	23.93	4.21	1.18	0.12	0.43
Co concentrate	35.72	2.40	7.77	17.46	21.04	5.07	1.22	1.51

It is evident that the differential separation of copper and cobalt sulfides by flotation at present is far from satisfactory. A specific collector for cobalt, or a combination of collectors, depressants, and promoters similar to that which is so effective in the lead-zinc industry, is still awaited by cobalt metallurgists.

Smelting

The two concentrates are treated separately in reverberatory furnaces.



Courtesy Rhokana Corp., Ltd., Nkana, No. Rhodesia

FIGURE 14. Flotation section of concentrator at Rhokana Corporation, Ltd., Nkana.

Although the concentrates are called copper and cobalt respectively, the cobalt concentrate merely has less copper and more cobalt than the copper concentrate. The chemical reactions proceeding in reverberatories and converters accordingly differ only in degree. It will be convenient to discuss the smelting operations under two headings:

(1) Copper Section. The cobalt content of the reverberatory matte is increased by the circulating addition of returned copper converter slag. This returned slag, which is a subsilicate, picks up additional basic materials and has considerable value as a flux. It has been found that the reduction of the cobalt content of this material is improved by its addition

as a cold charge after granulation rather than as a hot charge direct from the converter. In this way less cobalt is lost in the furnace slag. The granulated return slag is mixed intimately with coal and concentrate to attain the necessary degree of reduction.

A typical charge to the copper reverberatory furnace is shown in Table 5.

At Rhokana the presence of cobalt introduces a complication into converter practice. Cobalt oxidizes before copper, so that an impure cobalt oxide can be removed as a slag from the converters and used as a feed to the electric furnaces for cobalt production. In practice, of course, this slag is a mixture of copper, cobalt, and iron, present as oxides, sulfides, and silicates, together with the silicates of aluminum, calcium, and magnesium.

Table 5. Charge to Rhokana Copper Reverberatory Furnace

	Wt. (%)	Cu (%)	Co (%)	Fe (%)	S (%)	SiO_2 (%)	Al_2O_3 (%)	CaO (%)
Nkana copper concentrate	66 1	50 7	0 73	13 7	24 7	4 4	1 4	0 1
Nchanga concentrate	18 2	38 3	—	3 1	7 0	28 7	4 5	0 1
Converter secondaries	4 8	5 0	4 6	36 0	—	18 0	—	—
Limestone	10 9	—	—	0 1	—	1.0	0 1	53 5
Total charge	100 0	10 9	0 67	11 1	17.6	8 6	1.7	5.9
Matte	76 9	59 6	0 99	13 1	22 0	—	—	—
Slag	23 1	0 8	0 16	9 5	—	11 9	10 6	23.7

(2) Cobalt Section. The operation of the cobalt reverberatory does not differ materially from that of the copper. The iron : cobalt ratio is regulated if possible not to exceed 4:1 to produce a suitable grade of cobalt converter slag.

The cobalt reverberatory matte at Rhokana consists principally of two mineral phases, copper sulfide and iron sulfide. The minor mineral phases are metallic copper and metallic iron, while in the mattes produced from a reducing charge, crystals of metallic cobalt-iron appear. The cobalt of these mattes is present in solid solution in copper sulfide, iron sulfide, and metallic iron. Some iron is also present in solid solution in the copper sulfide. Cobalt sulfide as such does not crystallize out in any of these mattes. In the normal cobalt matte produced at the Rhokana smelter, approximately two-thirds to four-fifths of the cobalt is in solid solution in the copper sulfide.

Such mattes will only give a low extraction of cobalt on leaching with sulfuric acid, since the copper sulfide and with it the cobalt in solid solution will not dissolve in this acid. The problem of producing a leachable matte is therefore that of lowering the amount of cobalt in solid solution in

the copper sulfide to negligible proportions. This can be achieved in the following manner:

(1) By increasing the amount of iron in the charge and thus increasing the amount of iron sulfide formed. More cobalt is then taken up in solid solution in the iron sulfide.

(2) By increasing the amount of iron in the charge and at the same time reducing by the addition of coal, so that besides increased solution of the cobalt in the iron sulfide cobalt will also be held in solid solution in a metallic cobalt-iron alloy.

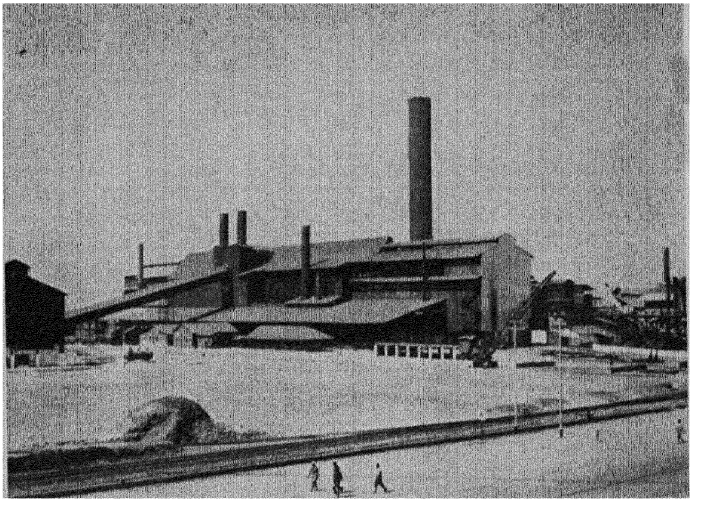
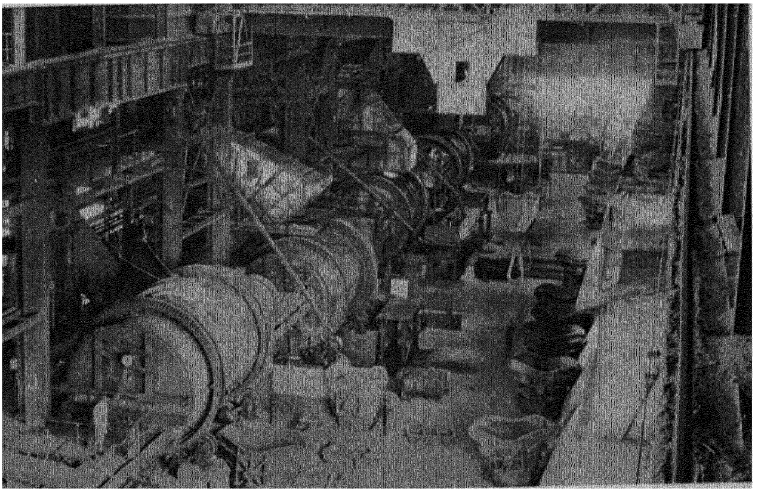


FIGURE 15. Smelter of Rhokana Corporation, Ltd., in Nkana, Northern Rhodesia.

In order to obtain a matte which will give a satisfactory extraction on leaching, a volume percentage of over 3.5% metallic cobalt must be given by the microscopic count, or over 40% of the total cobalt must be given as metallic cobalt by chemical analysis.

With regard to their crystalline structure the elements cobalt and iron fall into the same group, while copper lies in the adjacent group. Iron and cobalt sulfides have the same crystalline structure which differs from that of copper sulfide. It is known that elements of the same groups will more easily form solid solutions in each other than in elements of other groups. Provided there is sufficient iron present, therefore, cobalt will preferentially go into solid solution in the iron sulfide and metallic iron rather than in the copper sulfide.

Iron oxidizes before cobalt and this is shown in successive slag skims taken from the converter. It was a former practice to take advantage of this fact by circulation of the primary skims charged back cold to the reverberatory, but this resulted in high reverberatory slag losses. Present practice



Courtesy Rhokana Corp., Ltd., Nkana, No. Rhodesia

FIGURE 16. Converter aisle in smelter of Rhokana Corporation, Ltd., in Nkana.

Table 6. Charge to Rhokana Cobalt Reverberatory Furnace

	Wt. (%)	Cu (%)	Co (%)	Fe (%)	S (%)	SiO_2 (%)	Al_2O_3 (%)	CaO (%)
Co concentrate	57.9	32.4	2.83	10.5	20.5	18.6	5.1	0.1
Nchanga concentrate	12.9	38.3	—	3.1	7.0	28.7	4.5	0.1
Converter secondaries	14.3	6.0	4.5	36.0	—	18.0	—	—
Limestone	12.7	—	—	0.1	—	1.0	—	53.5
Coal in charge	2.2	—	—	—	—	—	—	—
Total charge	100.0	23.8	2.27	11.6	12.8	17.0	3.5	6.8
Matte	51.3	54.9	3.46	15.4	22.0	—	—	—
Slag	48.7	1.1	0.77	10.7	—	43.3	11.3	19.6

is to take the entire cobalt converter slag with the exception of skims which can be seen by visual inspection to contain a large quantity of copper.

A typical cobalt reverberatory furnace charge of Rhokana Corporation is given in Table 6 above.

The cobalt converter practice differs from the copper converter in that all of the slag from the latter is granulated and charged cold to the cobalt reverberatory for the recovery of its cobalt content.

High copper converter slags together with slag shell and reverts of high cobalt content are stock piled until sufficient quantity is accumulated for a separate run in the cobalt reverberatory. This material is mixed with concentrate and the copper content of the slag reduced so that it can be added to cobalt converter slag and treated in the electric furnace for alloy production. The unusual feature of Rhokana converter operation is the low copper content of the cobalt converter slags which must be regulated very closely in order that a stable product for the electric furnace may be maintained.

Slag from the converters is granulated by pouring in a thin stream into two superimposed jets of water operating at 60 lb per sq in pressure in a steel tank 10 ft in diameter by 5 ft deep. The granulated slag is removed by a bucket elevator to a system of conveyor belts that carries it to the stock dumps. The granulated cobalt converter slag generally runs Cu 2 to 3%, Co 5 to 10%, Fe 40%, SiO_2 20 to 25%.

The granulated slag is mixed with minus $\frac{1}{4}$ inch crushed coke for treatment in the electric furnace. For the most efficient recovery of cobalt it is advisable to make the percentage of coke in the charge equal to the percentage of cobalt in the granulated slag. When the iron content in the granulated slag exceeds 20%, silica is added to the charge to bring the iron content to this figure.

The charge passes through a mixer to a conveyor belt which carries it to the charge bins in the electric furnace building. Feed belts and chutes feed the electric furnaces from these charge bins.

It is interesting to note that, although the nickel content of Rhokana mill feed is extremely small, being less than 0.001% or $\frac{1}{1000}$ that of cobalt, there is more nickel than cobalt found in blister and electrolytic copper, and in tank house solutions. This is an illustration of the greater affinity of cobalt for oxygen and its consequent more complete removal in slagging operations at the smelter.

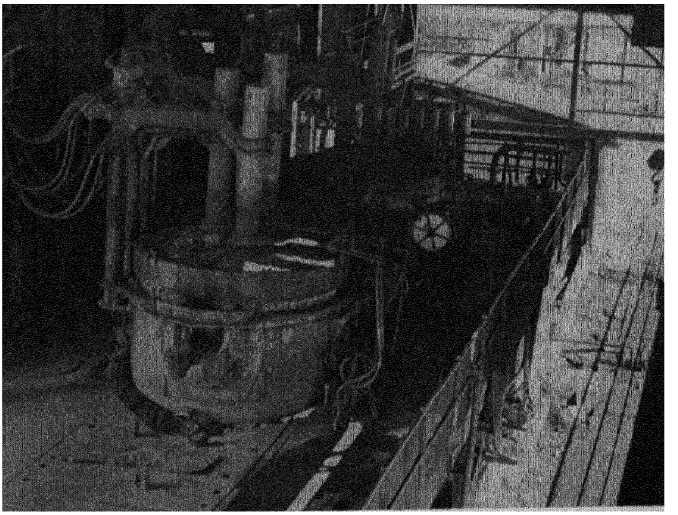
Electric Furnace Operation

The converter slags consisting of oxides, silicates, and sulfides of copper, iron, and cobalt, are melted in three Moore Rapid Lectromelt electric furnaces with coke. The object of the electric furnace operation is to obtain a differential reduction between cobalt and iron. This is regulated by the quantity of coke charged. A copper-cobalt-iron alloy and a slag are produced. The melting point of the alloy is so high that the electric furnace is the only practical unit for this purpose. The slag consists of

copper sulfide and a little cobalt sulfide, cobalt oxides, the silicates $2FeO \cdot SiO_2$, $3Al_2O_3 \cdot 2SiO_2$, $MgO \cdot SiO_2$, free SiO_2, and occasionally a little metallic cobalt. The reactions occurring in the electric furnace may be illustrated thus:

$$CuO + C \rightarrow Cu + CO$$
$$Cu_2O + C \rightarrow 2Cu + CO$$
$$CoO + C \rightarrow Co + CO$$
$$Co_2O_3 + 3C \rightarrow 2Co + 3CO$$
$$Co_3O_4 + 4C \rightarrow 3Co + 4CO$$
$$FeO + C \rightarrow Fe + CO$$
$$2FeO \cdot SiO_2 + C \rightarrow Fe + CO + FeO \cdot SiO_2$$

The alloy containing about 15% Cu, 40% Co, and 45% Fe is the final cobalt product at Nkana at present.



Courtesy Rhokana Corp., Ltd., Nkana, No. Rhodesia

FIGURE 17. Electric furnaces for cobalt production at Rhokana Corporation, Ltd., in Nkana.

The electric furnaces at Rhokana operate at 150 volts and 5,000 amperes. After a furnace has been skimmed it is returned to a horizontal position, about 1.5 tons of converter slag are charged, and this is levelled off by a steel rabble. A small quantity of alloy is placed on the surface of the charge to make contact between the electrodes, and the latter are lowered to press into the alloy. Current is switched on, an arc is struck between the electrodes, and the alloy and charge begin to melt. The

individual electrodes are raised or lowered to keep the phases balanced and all three are lowered slowly until the required amperage is reached, at which time the controls are put on the automatic basis. The electrodes are then raised or lowered automatically to keep the amperage in all three phases balanced at the required value as the electrodes are eaten away or as the level of the charge drops.

After an hour's run the electrodes are raised and the power switched off. At this time a layer of unmelted slag is left on the side walls of the furnace, protecting them from the molten charge. The unmelted charge is rabbled away from the skimming door into the furnace and the latter is tilted to allow the charge to run out in a thin stream into the skimming launder and hence to the slag pot. A flat steel paddle is passed through the slag stream and as soon as metal shows on the paddle the furnace is tilted back to the horizontal position, the furnace is charged again, and the cycle of operations is repeated. The operation of skimming and charging takes about 15 minutes.

The number of charges treated before granulating varies between 8 and 15, the operator judging when there is sufficient alloy present to granulate. The last charge before granulating is made much smaller than usual and is smelted for 30 minutes before skimming. Smelting is then continued for a further 15 minutes, any unsmelted material being poled down into the molten slag. During the last skim the granulating spout of the furnace is cleaned out and relined with clay. After the final heat a skimming pot is lowered under the granulating spout by an overhead crane, and the slag on top of the alloy is rabbled by hand into the pot using a wooden-headed rabble. When the surface of the alloy is clean the pot is removed and the water jets are opened. One jet is attached to the furnace under the granulating pot and the other is in the granulating tank. The jets operate at a pressure of 60 pounds per square inch. The furnace is tilted by hand, allowing a thin stream of metal to impinge on the upper water jet. The latter breaks up the stream of metal while the lower jet breaks it into smaller particles. The size of the metal stream and of the water jets is adjusted by the operator to give the coarsest size of granulated metal possible. When granulating is completed the furnace is returned to the horizontal position, the granulating spout is cleaned and the furnace is repaired if necessary. The cycle of smelting operations is then repeated.

French Morocco

The Moroccan ores are hand sorted where necessary to give a high cobalt product going directly to the blast furnace, the balance of the ore requiring concentrating operations. After crushing and grinding, the material is fed to air shaking tables and finally to Wilfley tables, where

the heavier arsenides are readily separated by gravity from the gangue. It is stated that flotation has not given satisfactory results on Moroccan ores, but the reasons are not forthcoming.

The cobalt oxide minerals are magnetic while the arsenides are non-magnetic. Where only a very small percentage of arsenides are mixed with oxides, magnetic separation is very simple and a satisfactory concentration of cobalt in oxides can be made. For mixed oxide-arsenide ores, an oxidizing roast is employed to remove a good deal of the arsenic as As_2O_3 and leave the rest as arsenates. The latter are magnetic and can be separated with the oxide cobalt.

A recovery of 93% of the cobalt and nickel, and 91% of the gold is reported[8].

These concentrates, together with direct smelting ores, are put in a blast furnace with limestone and coke, and smelted to a speiss. The latter is ground to 1 mm and roasted in a reverberatory or rotating hearth furnace to reduce the arsenic to that required for precipitation of iron as ferric arsenate. Arsenic trioxide is recovered in dust chambers and bag houses for refining.

The roasted speiss is ground to minus 100 mesh and dissolved in H_2SO_4 or HCl. Gold remains in the residue. The excess acid is neutralized and copper is precipitated on scrap iron. Iron is oxidized by blowing in air through the solution, or by adding chlorine. Limestone is added to precipitate iron as basic ferric arsenate. The liquid, containing only cobalt and nickel, is decanted into a vat and fractional additions of sodium hydroxide and bleaching powder are made. $Co(OH)_3$ is first precipitated fairly pure, then the rest of the cobalt comes down mixed with a little $Ni(OH)_3$. The latter is recirculated to obtain pure $Co(OH)_3$. The nickel in the solution is precipitated by adding sodium hydroxide, and the resulting $Ni(OH)_3$ purified by electrolysis or reduction to metallic nickel. $Co(OH)_3$ is roasted at 750° to give black cobalt oxide containing 70 to 71% Co.

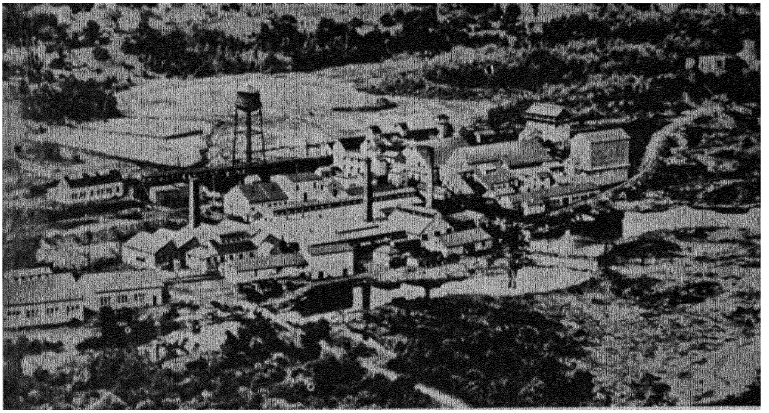
Canada

There have been a number of processes proposed for the treatment of the complex European and Canadian cobalt ores[1, 3, 4, 7, 13]. One of the principal procedures may be described here as illustrative of modern practice. It is representative of the treatment of Northern Ontario cobalt ores at the Deloro Smelting and Refining Company, Deloro, Ontario.

The crushed ore is charged to a blast furnace with coke, limestone, iron scrap, and return speiss. The products of the blast furnace are fume and dust, crude silver bullion, speiss, matte, and slag.

Gases, fume, and dust from the charge pass from the top of the blast

furnace through a downcomer to brick flues and chambers where most of the flue dust settles out. The fume and finer dust particles are blown by a fan into a bag house where arsenic is recovered. Since many cobalt ores contain 30% arsenic, large quantities of this element may be collected as a by-product if considerable tonnages of cobalt ores are treated. The bags in the bag house are of wool, and are shaken at intervals to collect the crude arsenic. The latter is sometimes contaminated with Sb_2O_3 and PbO, though usually the product of the arsenic bag house is 99% As_2O_3. It can be purified by sublimation in a small arsenic furnace, and the unsublimed residue which carries silver and lead, together with small quantities of cobalt and nickel, is charged back to the blast furnace.



Courtesy Deloro Smelting & Refining Co., Ltd., Deloro, Ontario

FIGURE 18. Aerial view of plant of Deloro Smelting and Refining Company, Ltd., Deloro, Ontario.

Bullion, the heaviest furnace product, is tapped from the crucible of the blast furnace into pots. It is obtained in the speiss pots when the furnace charge is sufficiently rich in silver to saturate the speiss and matte, and have silver left over to form bullion. By precipitation with metallic iron the speiss and matte can be freed of most of their silver. The silver collects in the bottom of the speiss pot and, on cooling, separates easily from the solidified speiss. Impurities in the bullion will depend on the charge to the furnace, but copper and lead are the principal ones for cobalt ores. The silver bullion is usually electrolytically refined to market requirements.

Speiss, an artificial arsenide or antimonide, in the case of cobalt ores usually is an arsenide. The charge must contain sufficient arsenic to combine with the cobalt and nickel, otherwise the latter will pass into the slag.

Nickel has the greatest affinity for arsenic, followed by cobalt, and then iron. Their affinity for oxygen is in the reverse order, iron being oxidized before cobalt and the latter before nickel. To prevent too much oxidation of cobalt compounds it is necessary to prevent excessive oxidation of the iron. The ratio of iron to arsenic in the speiss is generally kept about 18% Fe to 23% As, in order to facilitate the removal of arsenic by iron in a later stage of the process. A typical speiss might contain the following percentages: Co 20, Ni 12, As 23, Fe 18, Cu 2, Sb 1, Ag 2.7. The speiss contains all the cobalt together with nickel.

The matte formed in the cobalt blast furnace always contains some arsenic. In fact some mattes are very similar to a speiss since the arsenic is present to almost the same extent as sulfur. Matte forms a separate layer above the speiss in a pot, and generally contains a higher ratio of cobalt to nickel than speiss.

It is preferable to form as little matte as possible, as a different subsequent roasting treatment is required if any appreciable quantities are present. A typical matte might contain the following percentages: Co 9, Ni 4, As 5, Fe 27, Cu 12, S 23, Ag 6–24. When matte and speiss are formed at the same time in a furnace it is impossible to prevent Co, Ni, Ag, Fe, Cu, etc. dividing between these two. The use of large quantities of limestone in a charge encourages matte formation at the expense of speiss.

Slag is tapped into pots when it is to be returned to the furnace, otherwise it may be granulated and sent to a dump or transported in the molten state to the latter in small dump cars. The usual slag for cobalt blast furnaces is a bisilicate, containing SiO_2, FeO, Al_2O_3, CaO, and MgO. Occasionally PbO, ZnO, or MnO are found. The slag loss is usually kept under 1% for Ni plus Co.

The iron which is not required for a speiss and matte formation is oxidized and is then available for slag. The oxidation is of course dependent on the supply of coke and air. The charge usually contains about 12% coke, but this can be reduced slightly on material wherein heat is developed by oxidation of arsenic and sulfides to oxides. It is common practice to add a portion of return slag to the charge, especially if the latter is composed largely of fines and the slag losses are high.

The speiss from the blast furnace is crushed and ground to minus 20 mesh. It is roasted in Edwards roasters to eliminate a great deal of arsenic. At a temperature of about 400° the charge becomes self-roasting and external heat can be shut off. The roasted product may go 12% As, 13 to 26% Co, 16 to 22% Ni, 2 to 3% Cu, and the balance iron. It is mixed with about 15% sodium chloride and ground in a ball mill. Chloridizing is carried out in a Bruchner revolving oil roaster, requiring 12 hours for

about 5 tons. This treatment reduces the arsenic content to about 6 to 8%. If roasted speiss is not to be cyanided the chloridizing roast is usually omitted, and the material is reground and sulfated.

The chloridized product is now ball milled to 40 mesh and the water-soluble chlorides of cobalt, nickel, and copper are leached out. The insoluble silver chloride and cuprous chloride left are leached with sulfuric acid.

The residue is agitated with sodium cyanide and silver is recovered by precipitation with aluminum dust and caustic soda. Copper in soluble chlorides is precipitated out with scrap iron.

Insoluble chlorides of cobalt, etc. are pugged with sulfuric acid, 160 lb H_2SO_4 to 200 lb of residue, and the mixture is dumped into bins for a period of four weeks to complete the sulfation. Solution of the sulfated material is carried out in cone-bottom wooden tanks with air and steam agitation. The residue is washed and filtered. The nonsulfated portion returns to the blast furnace, while the solution passes to the iron-arsenic removal tanks.

Neutralization of the solution with lime to a pH of about 3.5, after oxidation of the iron by means of sodium chlorate or hypochlorite, gives a precipitate of ferric arsenate, ferric hydroxide, and calcium arsenate. Arsenic, if present in an amount not greater than that of iron, will be precipitated completely as $FeAsO_4$. Antimony, if present, will also be precipitated in this manner with iron. If the pH does not exceed 3.5 most of the copper will remain in solution, but at pH 5 a large proportion of the copper will be precipitated.

Filtration is carried out on an Oliver filter, with washing, and the cake is discarded. Final traces of copper are removed with scrap iron and the iron in turn precipitated with additional lime. The solution, containing cobalt and nickel, is then ready for the final-stage precipitation of cobalt.

The principle of the cobalt separation depends on the fact that in neutral solutions cobalt is more readily oxidized than nickel. The oxidized cobalt compound hydrolyzes and precipitates, leaving nickel in solution. The acid liberated by the hydrolysis must be neutralized to carry the reaction to completion.

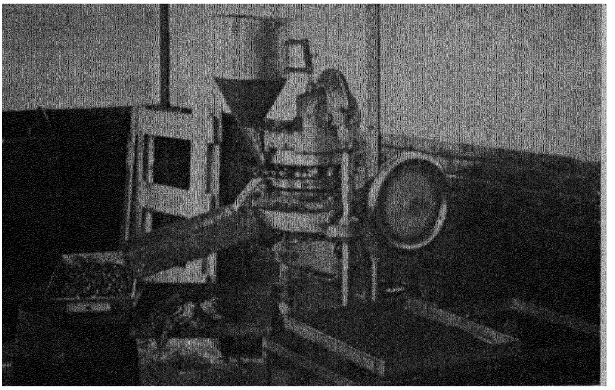
The solution with added sodium hypochlorite gives first a pure $Co(OH)_3$, and then a mixed hydroxide of $Co(OH)_3$ and $Ni(OH)_3$. By adding the hypochlorite in stages, a pure cobalt hydroxide is first obtained, and afterwards the mixed hydroxides are recirculated. Sodium hypochlorite is made by passing chlorine into a solution of caustic soda and soda ash. The reactions involved are not wholly understood, but probably the first step is the precipitation of a basic cobalt carbonate, $CoCO_3 \cdot Co(OH)_2 \cdot H_2O$. The sodium hypochlorite then reacts with cobaltous hydroxide to give

cobaltic oxide:

$$2Co(OH)_2 + NaOCl + H_2O \rightarrow NaCl + Co_2O_3 \cdot 3H_2O$$

Cobaltic oxide undergoes rapid oxidation and reduction in the presence of hypochlorite and a continuous evolution of oxygen occurs from the bleach solution.

A certain amount of free hydrochloric acid is liberated from the hypochlorite solution, and this reacts with $CoCO_3$ of the basic carbonate precipitate to form $CoCl_2$, from which cobalt is again precipitated by fresh bleach solution.



Courtesy Deloro Smelting & Refining Co., Ltd., Deloro, Ontario

FIGURE 19. Cobalt oxide pellet-making machine for compressing cobalt oxide with binder to form pellets for reduction to metal rondels.

Precipitation is stopped when nickel commences to come down with the cobalt. This can be observed by a change in the color of the solution.

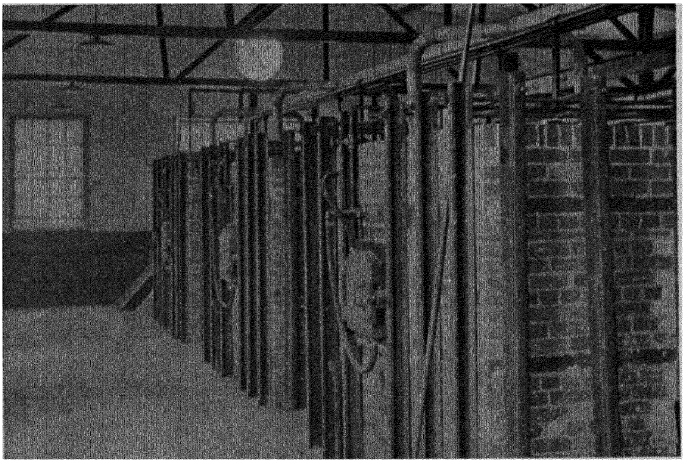
The cobalt precipitate is filtered off, calcined, and soda ash is added to transpose $CaSO_4$ to $CaCO_3$ and Na_2SO_4. Calcium carbonate is removed by a dilute hydrochloric acid leach, leaving fairly pure cobalt hydrate. This dried product now is ground in a Raymond pulverizer to minus 200 mesh and goes to the metal reduction plant.

The finely-pulverized cobalt hydrate is mixed dry with dextrin, water and aerosol are added, and the material is made into rondels in a pelletizing machine. The rondels are dried in ovens and then reduced with charcoal in a small reverberatory furnace at 1050°, with rabbling.

Reduction occurs in two stages. Cobalt hydrate goes to Co_2O_3, Co_3O_4, CoO, etc., the first heating driving off some oxygen. The next stage is the action of carbon monoxide on lower oxides with eventual reduction to

metallic cobalt. Slow heating and reduction are essential to avoid cracking in the rondels. The mesh size of cobalt hydrate and the pelletizing practice also have an influence on cracking.

The reduced rondels are cooled under charcoal in drums, passed over a magnetic separator, screened, inspected, and packed in small drums for sale. From cobalt-nickel ores the final product is usually 97 to 97.5% Co, with 1 to 1.5% Ni.



Courtesy Deloro Smelting & Refining Co., Ltd., Deloro, Ontario

FIGURE 20. Furnaces for reducing cobalt oxide pellets to cobalt metal rondels.

Treatment of Rhokana Cobalt Alloy at Deloro Smelting and Refining Co.

The copper-cobalt-iron alloy from the electric furnaces of Rhokana Corporation in Northern Rhodesia has until recently been refined at Deloro, Ontario. This product, approximating 15% Cu, 40% Co, 45% Fe, has only traces of nickel and no arsenic, so that its refining does not entail all of the steps detailed above for cobalt ores. The foregoing and following description is essentially correct for the treatment of cobalt alloy in Canadian, British, or Belgian refineries.

The alloy is dissolved in hot 20% sulfuric acid in copper baskets. Copper in the alloy does not go into solution, unlike cobalt and iron under these conditions, and the copper residue is shipped to a smelter. It is of interest to note that in spite of the very low content of gold in the Northern Rhodesian coppers, these residues contain in the neighbourhood of 0.03 oz of gold per ton.

The solution of cobalt and iron is treated with sodium chlorate and soda

ash, filter pressed and washed. The cake is dissolved in acid and reprecipitated to set free the occluded cobalt. The final precipitation of cobalt from solution is done with sodium hypochlorite to g ve cobalt hydrate. The latter goes to the metal reduction plant described above. The final cobalt product from Rhokana alloy goes 99.1+ % Co, 0.22% Fe, 0.18% CaO, 0.012% S, 0.06% C, 0.13% Si, 0.19% Co_3O_4, balance Mn, MgO.

Germany

Information has been obtained by the Combined Intelligence Objectives Sub-Committee[2] on cobalt refining in Germany.

Gebroders Borchers Plant. Gebroders Borchers plant at Goslar, Hartz., operated on Casablanca ore before the war, with an output of about 30 tons of cobalt per month. Later it operated on Mansfield slags. The Moroccan ore ran 15 to 16% Co, 10% Ni, 7 to 8% Fe, 30% As, and the balance SiO_2, Al_2O_3, etc.

After the usual blast furnace treatment and calcination of the resulting speiss, the oxides were leached with dilute sulfuric acid. Removal of iron and arsenic with sodium chlorate and limestone was followed by precipitation of the cobalt with sodium carbonate and hypochlorite. The cobalt hydrate was filtered off through wooden presses equipped with nitrocellulose cloths made by I. G. Bielefeld. These lasted for three months and would stand temperatures up to 60°, but above this temperature were liable to explode. Analysis of dried cobalt cake gave in percentages: Co 69.65, Ni 0.51, Cu 0.30, Fe 0.31, Mn 0.05, CaO 0.23, Na_2O 0.05, S 0.04, SiO_2 0.09.

Reduction of cobalt oxide was carried out in an electric furnace, using hydrogen, and maintaining an atmosphere of the latter during the cooling period of 24 hours. Analysis of the final cobalt metal was, in percentages: Co 98 to 98.25, Ni 0.6 to 1.5, Cu 0.05, Fe 0.2 to 0.4, S 0.1 to 0.2, Ca 0.06 to 0.1, As 0.006 to 0.03. Overall recovery of cobalt was about 80%.

Letmathe Cobalt Refinery. Letmathe cobalt refinery, Letmathe, Westphalia, was one of the largest in Germany, producing in 1938, 459 tons of cobalt metal from Rhokana and Katanga copper: cobalt: iron alloys.

The alloy was calcined at 700 to 800° for 6 hours in a rotary kiln. This converted some of the metal to oxide and assisted the leaching operation. Leaching was carried out with 25% sulfuric acid at 90° with mechanical agitation. When the acid strength had dropped to 2%, additional alloy was added. There were sufficient metallics in this to cement out practically all the copper, sodium sulfide being used to complete the precipitation. Acidity was kept lower than pH 2 by the addition of cobalt carbonate.

Iron was precipitated with sodium chlorate and sodium carbonate at pH 5.5 at 90°. A special type of filter press was used to filter the iron slurry.

The internal edges of the frame were sloped so that the cake when formed was like a wedge. It was claimed that when back-washing the press, the water travelled in the direction from the larger to the smaller section of the wedge, and any tendency of the cake to shrink was offset by the cake driving farther into the smaller section of the frame. No cracking occurred and with a very small flow of water complete washing could be obtained in 8 hours. This appears to the writer to be an excessive time for washing any cake on a filter press. The press was blown dry before opening and the cake had a moisture content of 15%. A loss of about 1% of the total cobalt occurred in this filtration.

Manganese, which occurs to an appreciable extent in Katanga alloy, was precipitated by the addition of potassium permanganate at a temperature of 95° and pH of 4.5 to 5.5. Since this precipitate contained considerable cobalt it was given an acid treatment, followed by smelting with sulfur and silica to slag off manganese and form a cobalt matte.

Cobalt was finally precipitated from the purified solution by the addition of soda ash. The slurry of cobalt carbonate was filtered, dried, crushed, mixed with 1 to 2% of its weight with soda ash and roasted at 1,000 to 1,050° for 8 hours in a strongly oxidizing atmosphere. The grey oxide (72 to 73% Co) was preferred to the black oxide (69 to 72% Co) for the subsequent reduction to metal. The oxide was pulverized and slurried with water. Calcium was removed with 10% HCl and the slurry was filtered and washed with water until free of sulfur and calcium.

From the dried and ground oxide two cobalt products were made:

(1) Metal fines containing about 6% oxygen, which were readily soluble in dilute acid and used for production of cobalt salts. The oxide was mixed with 13% charcoal and reduced in horizontal retorts at 950 to 1,000° for 5½ hours. The analysis of this material approximated, in percentages: Co 93 to 94, O_2 6, Cu 0.02, Fe 0.10, Mn 0.20, Ca 0.20, Mg 0.10, SiO_2 0.18, S 0.006.

(2) Rondels for alloy steel production. The oxide was mixed with potato flour, dried, crushed, and pressed into rondels. The latter were reduced in retorts at a gradually increasing temperature over 8 hours up to 1150°. The rondels were discharged into water to avoid discoloration, dried, and polished in a tumbling barrel. An analysis of this material gave, in percentages: Co (+Ni) 99.38, Cu 0.016, Fe 0.13, Mn 0.19, Ca 0.12, Mg 0.04, S 0.003, SiO_2 0.08.

Possible Developments of the Refining Process in Germany

The following developments had been apparently tried out on tests at the Letmathe refinery, according to Mr. Walter Voos, 48 Kirch Strasse, Letmathe[2].

(1) Purification of the precipitated cobalt carbonate could be carried out by decanting off the clear liquor above the cobalt carbonate slurry, adding a solution of sodium chloride at 60°, and blowing in carbon dioxide. The impurities are claimed to go into soluion and can be removed by filtering and washing.
(2) By using formic acid to dissolve the cobalt carbonate a cobalt metal of 99.8 to 99.9% purity can be obtained. Electrolysis is carried out at room temperature with pH 5.8 to 6.0, a current density of 100 to 250 amperes per square meter, and with an electrolyte containing 12 to 15 grams per liter cobalt.
(3) Mr. Voos claims that the cobalt cathode sheet can be ground to very fine powder without serious oxidation in a vibratory mill.

The Recovery of Cobalt from Roasted Pyrite

The recovery of cobalt, as well as other metals, from roasted pyrite was carried out extensively in Germany. Iron pyrites from Sweden, Finland, Spain, Cyprus, etc., after roasting for their sulfur content, were treated at some of the I. G. Farbenindustrie plants in the following manner: About 12% of sodium chloride was added to the material and it was given a chloridizing roast to render all the metals, except iron, soluble. The roasted material was leached with dilute HCl and H_2SO_4. The chlorides and sulfates of Cu, Zn, Co, etc. dissolve, and the fairly pure iron residue was sold to the blast furnaces.

Copper and precious metals are removed from the solution by scrap iron, and ultimately recovered by electrolysis. Air is blown through the liquid containing zinc, cobalt, and iron, to get the latter to the ferric state. Lime is added to precipitate iron as ferric hydroxide. To the clear solution containing zinc and cobalt is added bleaching powder and lime to precipitate $Co(OH)_3$.

Although the recovery of cobalt is only 50 to 60% and the quantities of cobalt present are generally very small, often only 0.05%, the very large tonnage of roasted iron pyrites treated contributed greatly to cobalt production in Germany.

United States of America

During World War II small quantities of cobalt were obtained in the United States from two principal sources. The Bethlehem Steel Company recovered cobalt from magnetite mined at Cornwall, Pa. According to the 1944 U. S. Bureau of Mines, "Minerals Yearbook", this ore, containing a little less than 0.05% cobalt, is separated magnetically to yield a magnetic concentrate and a nonmagnetic reject; the latter amounts to 36% of the ore and contains 5.6% pyrite and 0.086% cobalt. The reject is treated

by a selective flotation to produce pyrite and chalcopyrite concentrates that represent 5.94% and 1.58% of the heads, respectively. The pyrite concentrate contains 88.7% pyrite and 1.39% cobalt and represents a recovery

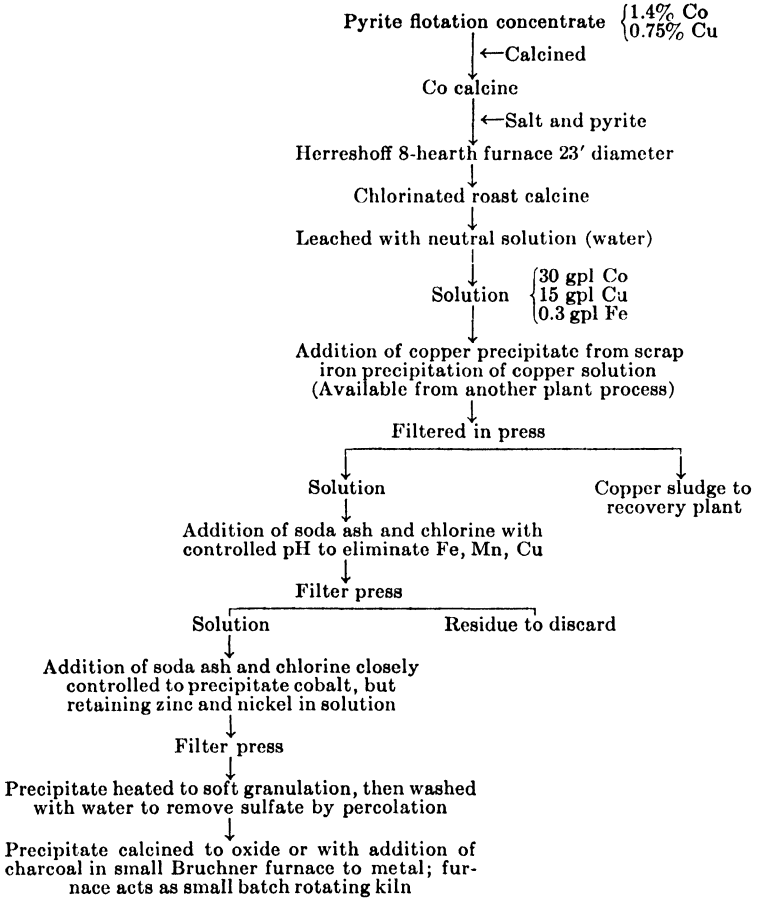


FIGURE 21. Flowsheet of cobalt production of Pyrites Corporation, Wilmington, Delaware, U. S. A.

of 64.7% of the cobalt in the ore. It is shipped to the Davison Chemical Co. at Baltimore where it is roasted and the SO_2 used to make sulfuric acid. The calcine is shipped to the Pyrites Co., at Wilmington, Del., where it is treated chemically to recover the cobalt. A flowsheet of this process is given in Figure 21. In addition to magnetic reject currently produced, the

Bethlehem Company has approximately 7,000,000 tons in dumps. This dump material is estimated to contain 0.086% cobalt; based on 50% recovery it would yield over 2,875 tons of cobalt.

The St. Louis Smelting and Refining Co. began producing cobalt commercially at its property near Fredericktown, Mo., in 1944. The complex lead-copper-nickel-cobalt ore is treated by flotation to yield a lead concentrate, a copper concentrate, and a nickel-cobalt concentrate. The roasted nickel-cobalt concentrate contains about 19% Ni and 13% Co. Production of nickel-cobalt concentrate was suspended in September, 1945. Recent reports from the Bureau of Mines indicate that this company shipped during 1946 some cobalt calcines averaging 2.3% Co.

Experiments of U. S. Bureau of Mines on Cobalt

Hydrometallurgy. A number of factors in the hydrometallurgy of cobalt have been recently studied by the U. S. Bureau of Mines[12].

A summary is given of the roasting of arseniferous cobalt ores alone and with added reagents. By direct oxidation at 600° to 700°, about 99.5% of the sulfur, but only about one half of the arsenic, can be removed. By the addition of one part coal or coke to 8 parts of ore, as high as 83% of the arsenic has been volatilized, but this procedure lowers the leachability of the contained cobalt. The use of oxidizing reagents such as sodium nitrate increases the acid solubility of the cobalt. Temperatures above 800° to 900° in the roast lower the cobalt solubility, which is attributed to the formation of cobalt ferrite. These cobalt ferrites are nearly insoluble in sulfuric acid, are magnetic, and exhibit other typical ferrite characteristics. The cobalt ferrites may be leached satisfactorily after being given a reducing roast above 700° by using fuel oils or gases as the reducing agents.

Cobalt can be leached from the calcines with hot 10 to 20% H_2SO_4 solutions in about 3 hours. Cold, moderately strong acids will leach up to 70% of the cobalt, but the residue, containing the cobalt arsenate, requires hot leaches of relatively high acidity.

Cobalt and arsenic can be separated satisfactorily by roasting the calcined cobaltite with soda ash and sodium nitrate at 700° to 900° to convert the arsenic to sodium arsenate. The soluble sodium arsenate is leached from the calcine with water and forms a recoverable by-product.

Cobalt and arsenic in solution may be separated satisfactorily by precipitation of the arsenic as ferric arsenate under exact pH control. Ferric iron must be present in excess of the stoichiometric requirements of ferric arsenate.

Cobalt carbonate may be precipitated from the arsenic-free solutions after proper secondary purification by soda ash under controlled pH conditions. Ordinarily the cobalt carbonate precipitated between a pH of 6.7 and 7.2 is used as the commercial product, and cobalt carbonate calcined at 600°

will yield the cobalt oxide of commerce, or the carbonate may be used to neutralize acid electrolytes for the electrowinning of cobalt metal.

Silver-lead anodes are to be preferred where iron- and manganese-free solutions are being used. However, if these two metals are to be partly removed at the anodes the use of pure lead is recommended.

The ease of stripping electrodeposited cobalt from stainless steel cathodes appears to be a function of the purity of the electrolyte. It is recommended that a solution of the required purity be limited to the following maximum content of impurities, in mg. per liter: Zn 10, Cd 1, As (trivalent) 3, As (pentavalent) 1, Sb 10, Hg 1, Ni 1000.

Cathodes are prepared by etching in a relatively concentrated solution of nitric acid containing 75% or more HNO_3 for 10 to 20 minutes, followed by thoroughly washing the cathode in pure water. New cathodes entering the cell for the first time should be roughened by grinding or abrasion, but it is not necessary to roughen the plates before each electrolysis if the etching procedure is followed.

Shelton[10] later reported that experimental work on cathode surface conditioning indicated a 7.5 minute etch in 50% aqua regia, or coating the slightly roughened cathode surface with a 5% solution of paraffin in gasoline and allowing the gasoline to evaporate, reduced the stripping difficulties materially.

Metallurgical Treatment of Goodsprings Ore. The following conclusions were reached by Shelton[10] in his report on the metallurgical treatment of cobalt ores from the Goodsprings mining district of Nevada, carried out by the U. S. Bureau of Mines in World War II.

The cobalt oxide mineral stainierite, $Co_2O_3 \cdot H_2O$, is amenable to concentration commercially by flotation in hot pulps of finely ground ore. Satisfactory reagents are barium sulfide, sodium silicate, American Cyanamid Reagent 301, and pine oil. Gravity concentration by tabling followed by flotation of the table middlings and tailings is successful on relatively high-grade cobalt ores.

Stainierite concentrates are leached most satisfactorily with combinations of sulfuric and sulfurous acids in aqueous solutions. Sulfur dioxide is a good solvent when used alone, as are certain other reducing reagents.

Copper in impure cobalt solutions is removed by cementation on iron or precipitation as sulfide. Oxidation of iron and sulfur dioxide, usually by aeration, and addition of pulverized calcite removes the iron from the cobalt solution.

Cobalt carbonate precipitates from the purified solution by treatment with aqueous solutions of soda ash within certain narrow pH ranges to produce relatively high-grade hydrated cobalt carbonate. The purified cobalt carbonate may be calcined successfully at 600° to the commercial oxide, Co_3O_4.

Electrolysis of cobalt is discussed by Shelton, Churchward, Stahl, and Livingston[12], and Shelton, Churchward, Stahl, and Davis[11]. Electrolytic cobalt metal deposits satisfactorily from an electrolyte containing 50 gm per liter of cobalt sulfate, 50 gm per liter of boric acid, and 50 gm per liter of sodium fluoride. A current density of 45 amperes per sq ft and an electrolyte pH of 1.8 to 2.0 is recommended. Precipitated cobalt carbonate is used to neutralize the spent electrolyte.

An alternative method of producing electrolytic cobalt metal involves the use of 50 grams per liter of cobalt sulfate and 50 grams per liter of ammonium sulfate in the electrolyte, and deposition of the metal at 50 amperes per square foot at an electrolyte pH of 1.9 to 2.1.

Stainless steel cathodes and lead anodes prove satisfactory for cell electrodes.

Oxides of cobalt and lead are deposited at the anode, especially at the higher current densities.

Sodium and nickel sulfates accumulate in the electrolyte during cobalt electrodeposition and must be removed periodically. We do not see why nickel will not deposit with cobalt on the cathode under these conditions, but apparently these workers found that codeposition did not occur.

Wetting agents aid in increasing the current efficiency of cobalt electrodeposition.

The fluoborate electrolyte for electrowinning of cobalt has been tested successfully over a relatively long period of continuous operation.

Recovery of Cobalt from Manganese Ores. The recovery of cobalt from manganese ores in the production of electrolytic manganese has been reported by Schlain[9] and by Jacobs, Shelton, and Knickerbocker[5], in the *U. S. Bureau of Mines Report of Investigations*, 3866.

Analyses for manganese and cobalt in 197 samples of manganese ore from 27 states are tabulated Many conta n 0.1 to several per cent cobalt. It is probable that the cobalt occurs as asbolite, a form of wad containing cobalt oxide. Cobalt in concentrates up to 0.1 gram per liter can be removed from manganese solutions by the standard method of purifying manganese electrolytes. Purification is sufficiently complete to permit electrodeposition of manganese at a current efficiency of 60%. The sludge residue from the manganese-electrolyte purification contains cobalt that is recoverable by differential solution with H_2SO_4. Over 99% of the manganese and about 10% of the cobalt can be dissolved from the sludge material by extracting for 36 hours with 2% H_2SO_4. The cobalt in solution from this operation can be removed by precipitating as sulfide at pH 3.5 to 5.5. About 99% of the cobalt can be recovered from the acid-leach residue by roasting at 600° and leaching at boiling temperatures with 5% H_2SO_4. The copper, iron, and a small amount of manganese remaining in the solu-

tion can be removed by various precipitation methods. The cobalt can be precipitated as the hydrated carbonate with soda ash; the pH should be 6.7 to 7.2 during precipitation. The cobalt carbonate can be roasted to the oxide by calcination at 600°. The metal can be obtained by reduction of carbonate or electrodeposition.

Other Processes

Though the processes described above represent typical modern cobalt smelter and refinery practices, variations of certain steps in procedure may be expected in some cases. Some of these are discussed by Liddell[6].

Oxidized cobalt ores may be treated directly, after fine grinding, with sulfuric or hydrochloric acid to bring the cobalt into solution. Heat, time of contact, agitation, and particle size are the main factors influencing solution.

Unoxidized ores can be melted with soda ash, niter, and salt in a cast iron container at about 700°. By pouring the melt into a rapid stream of water it is disintegrated. Arsenic goes into solution as sodium arsenate, and sulfur as sodium sulfate. The metals, with silica and alumina, remain in the residue. After filtering, the cake is dissolved in hydrochloric acid to give the metals as chlorides.

Another procedure for unoxidized ores involves digestion in a glass-lined vessel with hydrochloric acid and niter. In the final solution the metals are present as chlorides, the arsenic as arsenic acid, and sulfide sulfur goes to elemental sulfur.

Copper precipitates arsenic in a similar manner to iron, forming a copper arsenate. Digestion of ferric arsenate or copper arsenate with hot caustic soda gives sodium arsenate. The extracted arsenic can be readily converted to calcium arsenate. If there is insufficient iron and copper to combine with arsenic in the calcium carbonate precipitation of a speiss, the metal deficiency can be made up by adding copper hydroxide slurry. The whole is precipitated by calcium carbonate at about pH 5, filtered, and washed. The cake is repulped with water, extracted with caustic soda, and again filtered and washed. Almost all the arsenic passes into the filtrate. The cake from the caustic filtration is repulped with water and run to storage tanks. This slurry provides the copper hydroxide added at the first precipitation.

Copper can be separated from cobalt and nickel in many ways. Hydrogen sulfide in acid solution has been used, as well as electrolysis in acid sulfate solution. Copper may be removed by cementation on metallic nickel or cobalt. When neutral copper solution is agitated in the presence of air at about pH 6 or slightly higher, and a small quantity of lime or soda ash is added, a basic copper carbonate is formed. Some cobalt and nickel

will also be precipitated, particularly if they are present in much larger quantities than copper. Lead is also carried down by this reaction and completely removed.

In some cobalt ores where manganese is present in appreciable quantities, cobalt and nickel are precipitated by means of sodium sulfide. Manganese remains in solution.

A great deal of study has been given to the separation of cobalt from nickel by the addition of hypochlorite. It has been found that the process is only successful when the ratio of cobalt to nickel is about 3 to 1, and when the solution is dilute. Otherwise a number of fractional precipitations must be carried out, and even under the most favorable conditions small quantities of nickel will be present in the final cobalt residue.

Liddell[6] mentions the Herrenschmidt separations wherein a slurry of cobalt and nickel hydroxides is added to a sulfate or chloride solution of nickel + cobalt. The following reaction occurs:

$$Ni(OH)_3 + CoCl_2 \rightarrow NiCl_2 + Co(OH)_3$$

Liddell is quite right in stating that this separation is not very satisfactory.

Iron and copper may also be separated from cobalt by the addition of cobalt or nickel hydroxides. This is probably useful when one does not wish to introduce calcium or other ions into the solutions or resulting residues, but large quantities are required when the acidity is high and large amounts of iron are present.

Production of Cobalt Metal from Cobalt Compounds

Cobalt hydroxide or carbonate obtained by processes described above is calcined at 750° to give black cobalt oxide containing 70 to 73% cobalt. This is undoubtedly a mixture of oxides but according to Perrault[8] corresponds roughly to Co_3O_4, whose theoretical formula is 73.4%. In our experience it has been chiefly Co_2O_3 with some Co_3O_4.

Another commercial cobalt oxide is grey oxide, containing about 75% cobalt. This is made by incomplete reduction of the hydroxide at about 900°. It is also unquestionably a mixture of oxides, but according to Perrault is composed largely of CoO which, when pure, contains 78.6% Co. We have found this grey oxide to be chiefly CoO with some Co_3O_4 invariably present.

Cobalt may be produced from black oxide by several methods of reduction:

(1) *Carbon.* This is the common procedure in industry.

$$2Co_2O_3 + 3C \rightarrow 4Co + 3CO_2$$
$$Co_3O_4 + 2C \rightarrow 3Co + 2CO_2$$

With an excess of carbon, complete reduction can be secured at 900°.

(2) *Hydrogen.* This method is also used industrially, particularly for the production of cobalt powders in powder metallurgy, giving a very pure product. Reduction commences below 500° and is rapid at 700° to 1100°. It is preferable to cool the reduced cobalt in a hydrogen atmosphere to avoid oxidation.

(3) *Carbon Monoxide.* Reduction occurs rapidly above 600° and is complete below 900°.

(4) *Aluminum Powder.* The thermit process for reducing metallic oxides with aluminum can be employed, if required, to yield metallic cobalt.

Cobalt is made into rondels in the following manner. Black oxide is mixed with 10% of pulverized wood charcoal and an organic binder, and compressed into small pellets in a machine. These pellets are placed in graphite powder in a crucible, and the latter placed in a reducing furnace heated with gas or electricity. The rondels are cooled in a reducing atmosphere, separated magnetically from the adhering carbonaceous powder, and polished in a tumbling barrel.

Electrolysis of a cobalt sulfate or chloride solution attained considerable importance in Germany before World War II. This gave a product of 99.5% Co or better. With the present production of electrolytic cobalt in the Belgian Congo, and the interest displayed by other producers in electrolytic refining, it will probably not be many years before most of the world's cobalt is produced as an electrolytic product.

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Chapter 4
Chemical Properties of Cobalt

The important chemical properties of cobalt and its principal compounds will be discussed briefly here. More complete information and references to the original literature prior to 1935 may be obtained from Mellor[9].

Cobalt, Co: Atomic weight 58.94; atomic number 27; melting point 1480°; boiling point 2900°; specific gravity 8.9; valence 2 or 3.

Cobalt in the finely-divided form occludes considerable quantities, 50 to 150 volumes, of hydrogen. The metal in the compact state is not attacked by oxygen or water at ordinary temperatures, but at elevated temperatures or in a finely-divided form cobalt is oxidized in moist air. The halogens combine with cobalt to form the respective halides. Hypochlorous acid in contact with cobalt gives oxygen, chlorine, cobalt hydroxide and chloride.

Cobalt is readily dissolved by sulfuric, hydrochloric, and nitric acids, but only very slowly by hydrofluoric acid, to form cobaltous salts. Cobalt dissolves with difficulty in ammonium hydroxide, forming a nitrite, and is slowly attacked by sodium hydroxide.

There does not appear to be as yet any evidence of atomic disruption by bombardment of cobalt with alpha particles. The electronic structure of the cobalt atom is usually represented on the assumption that the electrons present are 2 for the K-shell; (2,2,4) for the L-shell; (2,2,4,3,4) for the M-shell; and (2) for the N-shell.

Cobalt Compounds

Carbides

At atmospheric pressure and 226–230°, carbon monoxide and finely-divided cobalt react slowly to form a product whose composition corresponds to the formula Co_2C. Hofer and Peebles[8] found that the difficultly hydrogenated carbon is in the form of finely-divided carbon crystallites, and that there was no evidence of solid solution of carbon in α-cobalt in a partly carburized sample.

The carbides of cobalt are of importance in the Fischer-Tropsch synthesis of hydrocarbons, discussed in Chapter 11.

Carbonates

Cobaltous carbonate, $CoCO_3$, is found in nature as sphaerocobaltite. It can be prepared by the action of alkali carbonates on cobaltous salts, and

is the carbonate formed in many industrial processes for the recovery of cobalt when soda ash or lime are added to a cobalt salt.

Cobaltic carbonate, $Co_2(CO_3)_3$, is produced by the oxidation of cobaltous carbonate. A number of ammines are known.

Carbonyl

At a pressure of 100 atmospheres, finely-divided cobalt reacts with carbon monoxide if heated to about 200°, forming orange red crystals of cobalt carbonyl, $Co_2(CO)_8$. These crystals decompose above 60° in the air into cobalt and carbon monoxide. This reaction differs from that of nickel with carbon monoxide in that the latter reaction proceeds at atmospheric pressure and low temperature, forming the basis for a commercial separation of nickel from cobalt.

Halides

Bromides. Cobaltous bromide, $CoBr_2$, can be produced by the action of hydrobromic acid on cobaltous hydroxide, or bromine on cobalt.

Cobaltic bromide has not yet been isolated, but many of its complex ammonium salts are known.

Chlorides. The aqueous solution of cobalt chloride is readily formed by dissolving the metal, oxide, hydroxide, or carbonate in HCl. If the aqueous solution is evaporated, crystals of the hexahydrate, $CoCl_2 \cdot 6H_2O$, are formed. Cobaltous chloride is one of the most important salts of cobalt, and its reactions with many other substances are recorded in Mellor[9].

Cobaltic chloride, $CoCl_3$, has not been isolated, but its complex salts are well-known. Cobaltous hexamminochloride, $[Co(NH_3)_6]Cl_3$, is prepared by oxidizing an ammoniacal solution of cobaltous salt by exposure to air. An enormous number of complex ammonium compounds with cobalt are described by Mellor. These cobalt ammines include:

(*A*) *Compounds with one cobalt atom in the nucleus.*

(1) Hexammine family, or compounds of the tervalent basic group (CoA_6), *e.g.*, $[Co(NH_3)_6]X_3$

(2) Pentammine family, or compounds of the bivalent basic group (CoA_2X), *e.g.*, $[Co(NH_3)_5OH]X_2$

(3) Tetrammine family, or compounds of the univalent group. (CoA_4X_2)′, *e.g.*, $[Co(NH_3)_4(OH)_2]X$

(4) Triammine family, or compounds of the null-valent group. (CoA_3X_3)′

(5) Diammine family, or compounds of the univalent acidic group (CoA_2X_4)′, *e.g.*, $M[Co(NH_3)_2(NO_2)_4]$

(6) Monammine family, or compounds of the bivalent acidic group. (CoA_5X)′′, *e.g.*, $Na_2[Co(NH_3)(NO_2)_5]$

(7) Hexa-acid family, or compounds of the tervalent acidic group. $(CoX_6)'''$, *e.g.*, $H_3[Co(NO_2)_6]$

(*B*) *Compounds with more than one cobalt atom in the nucleus.*

(1) Dicobaltic salts, with two cobalt atoms in the nucleus, *e.g.*, $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]X_4$

(2) Tricobaltic salts, with three cobalt atoms in the nucleus, *e.g.*, $[(H_2O)(NH_3)_3\ Co{-}{-}(OH)_2(H_2O){-}{-}{-}Co{-}{-}{-}(OH)_3{-}{-}{-}\cdot Co(NH_3)_3]X_4$

(3) Tetracobaltic salts, with four cobalt atoms in the nucleus, *e.g.*, $[Co(OH)_2{-}{-}Co(NH_3)_4]_3X_6$

Fluorides. Cobaltous and cobaltic fluorides are described by Mellor[9]. Cobaltous fluoride, CoF_2, is a red crystalline solid generally obtained in a hydrated form. A number of complex salts and cobalt aminofluorides have been described in inorganic literature.

Cobaltic fluoride, CoF_3, forms brown crystals in the anhydrous state. On heating in air it forms red cobaltous fluoride and finally black cobalt oxide.

The role of cobalt fluorides in the synthesis of fluocarbons is discussed in Chapter 11.

In view of the increasing importance of the metallic fluorides in industry, the properties of simple and complex cobalt fluorides might well repay further investigation, quite apart from their role in fluorocarbon synthesis.

Iodides. Cobaltous iodide, CoI_2, is made by the action of iodine on powdered cobalt at elevated temperatures.

Cobaltic iodide has not been isolated, but a large number of its complex ammine salts have been prepared.

Hydrides

The hydrides of cobalt are discussed by Ray and Sahai[12].

Hydroxides

When an alkali hydroxide is added to a solution of a cobaltous salt, cobaltous hydroxide, $Co(OH)_2$, is formed. This compound is blue, green, or red depending on the grain size, presence of adsorbed ions, temperature, etc. It is slowly oxidized by air to cobaltic hydroxide.

One of the most important methods of separating cobalt from nickel depends on the fact that if cobalt is oxidized to the cobaltic state by means of chlorine, hypochlorites, or peroxide in neutral solution, the cobaltic salt formed immediately hydrolyzes and precipitates as cobaltic hydroxide.

Nitrates

When dilute nitric acid is added to cobalt metal, oxide, hydroxide, or carbonate, an aqueous solution of cobaltous nitrate is formed, which on evaporation yields red crystals of the hexahydrate, $Co(NO_3)_2 \cdot 6H_2O$.

Cobaltic nitrate has been prepared by the electrolysis of a concentrated solution of cobaltous nitrate in a partitioned cell, but is very unstable and is known only in aqueous solution. As with other cobaltic compounds, a large number of stable ammino salts have been described.

Cobalt reacts with ammonia gas at 470° to form a cobalt nitride, Co_4N_2, which decomposes at 600°.

Broughton, Laing, and Wentworth[2] report a violent explosion when a filtrate containing only sodium acetate, acetic acid, sodium nitrite, sodium nitrate, and a trace of cobalt was heated. They suggest that the purple color appearing on heating this solution represents the formation of a new nitro- or nitritocobalt complex which explodes on continued heating.

In view of the frequency with which this combination of reagents might be encountered in analytical work it is of the utmost importance that this matter be investigated thoroughly.

Oxides

Cobalt, like iron, has three well-known oxides: the monoxide or cobaltous oxide, CoO, cobaltic oxide, Co_2O_3, and cobaltosic oxide, Co_3O_4.

Cobaltous Oxide. Cobaltous oxide is formed slowly when cobalt metal is heated to redness without free access of air. Cobalt monoxide is readily dissolved by dilute hydrochloric acid, forming a pink solution; in the concentrated acid it gives a deep blue solution. Pure cobaltous oxide is a difficult compound to prepare, since it readily absorbs oxygen to form Co_3O_4. The higher the temperature of calcining, the less oxygen is absorbed. Cobaltous oxide is usually prepared by heating Co_2O_3 or Co_3O_4 at a high temperature. Cobaltous oxide is a catalyst for the oxidation of ammonia. It is also a catalyst for the oxidation of drying oils and is employed extensively for the rapid-drying paints and varnishes.

Cobaltous oxide varies in color from olive green to red, depending on the grain size, but is usually dark grey. It is insoluble in water, soluble in acids, in alkali hydroxides, and very slightly soluble in ammonia in the presence of air. Cobaltous oxide is easily reduced to metal by carbon or carbon monoxide. When heated at high temperatures with SiO_2 and Al_2O_3 it forms colored silicates and aluminates of importance in the ceramic industry. It contains 78.65% Co. Cobaltous oxide is the principal constituent of the grey cobalt oxide of commerce.

Cobaltic Oxide. Cobaltic oxide, Co_2O_3, is formed when cobalt com-

pounds are heated at a low temperature in the presence of an excess of air. This black compound contains 71.06% cobalt. At a higher temperature, Co_2O_3 goes to Co_3O_4. Oxidation of cobaltous salts in acidic or alkaline solution gives hydrated cobaltic oxide. Cobaltic oxide is amphoteric, forming unstable salts with both acids and bases. Cobaltic oxide forms cobaltites when it unites with an oxide of other metals, such as $ZnO \cdot Co_2O_3$. Carbon monoxide slowly reduces Co_2O_3 above 500° and very rapidly at 900° or above. It is the principal constituent of the black cobalt oxide of commerce, together with a little Co_3O_4.

Cobaltosic Oxide. When cobalt salts are heated at temperatures not exceeding 850°, the stable black oxide Co_3O_4 is formed. This oxide can be reduced to the metal by carbon, carbon monoxide, and hydrogen. It is soluble in acids. It contains 73.43% Co. Cobaltosic oxide is stated by Mellor to be the chief constituent of grey oxide, but most commercial firms[6] list the latter as CoO. We have found the grey oxide of commerce to be largely CoO, with some Co_3O_4 invariably present.

Other Oxides. Various workers have reported the existence of cobalt dioxide, CoO_2, and of other higher oxides, but the evidence is rather contradictory. Shelton[13] found an anode deposit on electrolyzing cobalt, corresponding to a mixture of PbO_2 and Co_2O_3 or possibly CoO_2. Other workers[10, 15, 16] have discussed this oxidation of cobalt at the anode.

Oxide Films. An electron diffraction and electron microscope study of oxide films formed on cobalt and other metals at moderate temperature has been reported from the Westinghouse laboratories[4, 5, 7, 11]. Films of CoO and Co_3O_4 were found at temperatures ranging from 200° to 500° to consist of small oxide crystals varying from 450 Å at 200° to 1000 Å at 500°. The oxides formed during the oxidation of aluminum, tungsten, and chromium gave the smallest average crystal size. The largest crystals are formed during the oxidation of copper, iron, molybdenum, nickel, and cobalt. The first group probably form the more protective films against oxidation under the conditions of the experiment. If the materials are compared at the same temperature, nickel and cobalt would be included in the first group and not in the last. In further work the same authors worked with a number of alloys of iron, nickel, chromium, and cobalt, including the refractory alloy K 42 B, a magnetic cobalt-iron alloy containing 30.4% Co, and the sealing alloy Kovar. K 42 B contains 41.7% Ni, 22.5% Co, 20.0% Cr, 12.0% Fe, 1.89% Ti, 0.21% Al, 0.57% Mn, and 1.21% Si, while Kovar consists of 54% Fe, 18% Co, and 28% Ni. Cobaltous oxide was not observed on the surfaces or in the body of an oxide even when the percentage of cobalt is as high as 30%; there may, however, be a solid phase reaction between CoO and Fe_2O_3 to form the spinel, $CoO \cdot Fe_2O_3$.

Phosphates

A number of cobaltous phosphates can be produced by heating a cobaltous salt with phosphoric acid or alkaline phosphates. Many cobaltic ammine phosphates have been described by Mellor[9].

Silicates

Cobaltous *ortho*silicate is a violet crystalline compound, Co_2SiO_4, found in slags and some glazes. Cobalt silicates and aluminates, in all shades of blue and violet, are found in small quantities on the slag dump of Rhokana Corporation, a sight unique among the black and grey slag dumps of copper smelters.

Silicides

There are a number of cobalt silicides. The Climax Molybdenum Company has patented a procedure for making additions of cobalt and silicon to molten iron or steel in the form of exothermic silicides such as Co Si or $Co\,Si_3$[3].

Sulfates

Cobaltous Sulfate. When cobalt oxide, hydroxide, or carbonate is dissolved in dilute sulfuric acid, an aqueous solution of cobaltous sulfate is obtained, which crystallizes out as the pink heptahydrate, $CoSO_4 \cdot 7H_2O$. This important cobalt compound shows less tendency to alter in composition by deliquescence or dehydration than the corresponding chloride or nitrate, and is hence preferred for many commercial uses. A number of double salts of cobaltous sulfate are described by Mellor[9].

Cobaltic sulfate. Cobaltic sulfate, $Co_2(SO_4)_3$, is an unstable salt which can be prepared by electrolysis of a standard solution of cobaltous sulfate in dilute H_2SO_4 in a platinum dish as anode and with a platinum wire in a porous cell containing dilute H_2SO_4 as cathode. It goes to the cobaltous sulfate almost instantaneously on the addition of water. Many of its complex ammonium salts have been described[9].

Sulfides

Cobaltous sulfide, CoS, is a black powder formed when H_2S is passed into an alkaline cobalt solution. It is the most common sulfide of cobalt. It occurs to a small extent as jaipurite, a natural sulfide found in India.

Cobaltosic sulfide, Co_3S_4, has been prepared by heating together compounds of cobalt and sulfur for a long time. Cobaltic sulfide, Co_2C_3, and cobalt disulfide, CoS_2, have also been prepared by heating compounds of sulfur and cobalt under varying conditions.

It is probable that the cobalt sulfides found in metallurgical products like mattes are mixtures of these. In such complex sulfides of copper, iron, cobalt, etc., it is not possible to determine by linking sulfur to the metals the exact sulfide present. A number of cobalt sulfides are found in nature as carrollite, linnaeite, etc.

Solomon[14] has described the use of cobalt salts as indicators of humidity and moisture.

Structural Chemistry of Cobalt Compounds

The structural chemistry of many cobalt compounds has been recently discussed by Wells[17].

In the hexamminocobaltic ion $[Co(NH_3)_6]^{34}$, the 36 electrons of the cobalt atom are made up as follows:

		3s	3p	3d		4s	4p
(2)	(8)	2	6	6 +	4	2	6

those within the rectangle being the 12 shared electrons forming the six d^2sp^3 bonds.

The octahedral radii of Co^{II} equals 3.32 Å and of Co^{III} equals 1.22 Å. CoF_2 possesses a symmetrical structure while $CoCl_2$, $CoBr_2$, and CoI_2 assume layer structures.

The familiar changes in the color of solutions of halides such as $CoCl_2$ on heating or on acidification in concentrated solution with HCl are due to the formation or breaking up of complex ions such as $[CoCl_4]^{2-}$. In a dilute pink solution of $CoCl_2$ there are hydrated Co^{2+} ions, but in the blue solutions $[Co\ Cl_4]^{2-}$ ions. If a hot concentrated solution containing CsCl and $CoCl_2$ in the proportion of two molecules of the former to one of the latter is allowed to crystallize, blue crystals with the composition Cs_2CoCl_4 separate from the deep blue solution. The structure of these crystals has not been analyzed, but there is no doubt about the existence of the $[CoCl_4]^{2-}$ ions, for they have been shown to exist in crystals of the closely related salt $Cs_3(CoCl_4)Cl$ which can be grown from a solution containing $3Cs:1CoCl_2$. If the concentrated blue solution of either of these salts is diluted, it turns pink owing to the dissociation of the $[CoCl_4]^{2-}$ ions.

A concentrated solution of cobalt chloride in water has a deep rose color, but on heating becomes deep blue. This change is attributed to the formation of $[CoCl_4]^{2-}$ ions.

A cubic close-packed structure may be converted into the hexagonal structure by sliding certain of the layers over one another, a process termed gliding. In view of this simple relationship between the two arrangements, it seems remarkable that a metal like cobalt should exist in the two distinct forms, and that the regular sequence ABAB . . . or ABCABC . . .

should be maintained throughout the whole of the crystal. Cobalt is apparently the only metal in which a crystal may occasionally possess a mixed cubic-hexagonal close-packed structure.

The magnetic moments of cobalt in aqueous solution are as follows:

Ion	No of 3d Electrons	No. of Unpaired Electrons	Calc. Spin Moment (In Bohr magnetons)	Observed Moment
Co^2	7	3	3.88	5.0–5.2

$[CoF_6]^{3-}$ and $[Co(H_2O)_6]^3$ contain ionic bonds, but $[Co(NH_3)_6]^3$, $[Co(NO_2)_6]^{3-}$, and $[Co(CN)_6]^{3-}$ possess covalent bonds.

In crystals of CoF_3, the fluorine ions are approximately close-packed and the cobalt ions occupy certain of the octahedral holes between them.

The constitution of compounds like $[Co(NH_3)_5Cl]Cl_2$ was at first difficult to understand since they could be represented as the normal halide plus a number of NH_3 molecules, and in some cases there was a series of compounds with different numbers of ammonia molecules, as in: $CoCl_3 \cdot 6NH_3$, $CoCl_3 \cdot 5NH_3$, and $CoCl_3 \cdot 4NH_3$.

Their formulation as six-coordinated complexes is due to Werner, who wrote them in the form:

$$[Co(NH_3)_6]Cl_3,\ [Co(NH_3)_5Cl]Cl_2,\ \text{and}\ [Co(NH_3)_4Cl_2]Cl$$

Conductivity measurements, for example, showed that $CoCl_3 \cdot 5NH_3$ yields only two, and $CoCl_3 \cdot 4NH_3$ only one, chlorine atom per "molecule".

The crystal radius of Co^2 equals 0.72 Å.

CoS crystallizes with the NiAs structure, as do CoSe and CoTe. The nonmetal atom is surrounded by six cobalt atoms at the apices of a trigonal prism. The immediate neighbours of a cobalt atom are six nonmetal atoms arranged octahedrally, but there are also two cobalt atoms sufficiently near to be considered bonded to the first cobalt atom.

In the Co-Te system the phase is homogeneous over the range 50 to 66.7 atomic per cent Te, using quenched samples, and at the latter extreme the composition corresponds to the formula, $CoTe_2$. The explanation of this unusual phenomenon, a continuous change from CoTe to $CoTe_2$, is as follows: The compound $CoTe_2$ crystallizes at high temperatures with the CdI_2 structure which is retained in the quenched specimen. This CdI_2 structure is quite similar to the CoTe structure, the tellurium atoms in both cases being arranged in hexagonal close-packing. In the CoTe composition all the octahedral holes are occupied by cobalt. As the proportion of cobalt decreases, some of the positions become vacant, and finally at the composition $CoTe_2$ only one-half are occupied.

Cobalt forms two carbonyls, $[Co(CO)_4]_2$ and $[Co(CO)_3]_4$, a carbonyl hydride $Co(COH)CO_3$ and several carbonyl halides, $Co(CO)X_2$, where X

may be Cl, Br, or I. Unlike carbonyls of cobalt and other metals, nickel carbonyl is prepared by the action of CO at atmospheric pressure on metallic nickel. This explains why nickel from the Mond process is virtually cobalt-free.

Cobalt, with an odd atomic number of 27, forms no mononuclear carbonyls but only $Co_2(CO)_8$ and $Co_4(CO)_{12}$. The metal atom acquires a share in sufficient additional electrons to possess an inert gas configuration.

The cobalt salts usually encountered are cobaltous, Co^{++}, salts, which are not readily oxidized to simple cobaltic salts. The latter have to be prepared by special methods such as electrolytic oxidation, by which means CoF_3 and $Co_2(SO_4)_3 \cdot 18H_2O$ are made. In coordination complexes, however, cobalt prefers the trivalent state. The $[Co(CN)_6]^{4-}$ ion is readily oxidized to $[Co(CN)_6]^{3-}$, and many cobaltic complexes possess remarkable stability.

The explanation of the facts that certain atoms and groups do not coordinate with cobalt and that others form coordination complexes with certain cobalt compounds probably lies in the different electronegativities of the metal and coordinating atoms. Cobalt is fairly electropositive and tends to form positive ions. It accordingly forms fluoro-complexes with ionic Co-F bonds but shows little tendency to form complexes with the other halogens. In such complexes as $[Co(NH_3)_6]^{+3}$ and $[Co(NH_3)_6]^{3-}$ having a set of 12 shared electrons around the metal atom and a total of 36 orbital electrons, the cobalt atom with atomic number 27 has effectively acquired a negative "formal charge" which is inconsistent with the tendency of such a metal to lose electrons and form positive ions. Accordingly only strongly electronegative atoms are found attached to cobalt in such complexes.

The demonstration of the optical activity of a compound such as $K_3Co(C_2O_4)_3$ was a striking confirmation of the octahedral arrangement of the bonds from the cobalt atom.

The chemistry of the cobaltammines is extremely complex; nine compounds of the empirical formula $Co(NH_3)_3(NO_2)_3$ are said to have been prepared.

The cubic close-packed form of cobalt is stable over an intermediate range of temperature, above and below which the element crystallizes with the hexagonal close-packed structure.

The absorption spectra of cobalt compounds are discussed by Brode[1]. Brode and his coworkers have concluded that in the blue cobalt complexes a direct bond exists between the cobalt and the halogen atoms. The light absorption is influenced by the strength and nature of the bond, together with the size and atomic weight of the anion. The color change of alkali borate glasses is not caused by a simple shift of the absorption band, but the band characteristic of the red form of cobalt decreases in intensity and

at the same time a new group of bands is formed characteristic of the blue color centers. Light absorption can only be interpreted by assuming intermediate stages rather than only two stable types of color centers. Brode studied the effect of alkali atoms on the blue color of cobalt glasses. The difference between soda and potash glasses is not due to sodium-cobalt or potassium-cobalt compounds. The blue cobalt centers are due to Co^{++} and oxygen, with oxygen shared between cobalt and alkali ions. Depending on their sizes, different alkali ions exert characteristic influences on the oxygens which reflect on the Co—O bond strength.

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Chapter 5
Physical and Mechanical Properties of Cobalt

Cobalt when polished is silver-white with a faint bluish tinge. Cobalt exists at ordinary temperature in a stable, close-packed, hexagonal lattice, α-cobalt. In this it differs from nickel and iron which crystallize in the cubic system. At the transition temperature, about 440°, the stable form is β-cobalt which possesses a face-centered cubic lattice. Both forms may exist together at ordinary temperature, but at the latter β-cobalt is unstable.

There is still some confusion about the transformations of cobalt and more work would be desirable in this field. The transformation of pure cobalt from the close-packed hexagonal lattice to the face-centered cubic has been reported by various investigators to occur at temperatures ranging from 399° to 475°[1, 10]. The transformation is very sluggish, a property probably associated with the small heat of transformation, 0.1 calorie per gram. The generally accepted temperature of transformation is 440°.

Some investigators have reported another transformation at a higher temperature, wherein the face-centered cubic lattice reverts to the hexagonal close-packed structure in the range of 800 to 1000°[2, 8]. Other workers have failed to confirm the existence of a second transformation[4, 9], and at present majority opinion favors only the one point at 440°.

Both α- and β-cobalt are ferromagnetic. Cobalt becomes paramagnetic at about 1115°.

The specific gravity of cobalt is 8.76 as cast, 8.81 after annealing, and 8.93 after swaging.

Cobalt has a hardness of about 5.5 on the Mohs scale. The Brinell hardness of cast cobalt is 124 to 130, and of electrodeposited cobalt varies from 270 to 311. It is therefore harder and more tenacious than iron or nickel. Pure cobalt may be readily machined in a lathe, although it is somewhat brittle. Cobalt containing a small proportion of carbon is machined like mild steel. Pure cobalt cannot be swaged down to fine wire without special heat-treatment, but the metal containing carbon can be readily swaged or rolled from the hot condition.

The tensile strength of cobalt varies from about 34,000 lb per sq in for cast and unannealed metal to 61,000 lb per sq in for cobalt with 0.06 to 0.30% carbon. The tensile strength increases with rolling, and may attain

100,000 lb per sq in when swaged down to wire. The compressive strength of purified cobalt, cast and unannealed, is about 122,000 lb per sq in and annealing lowers this slightly. The addition of carbon increases the compressive strength.

The melting point of cobalt is 1480° and the boiling point about 2900°.

Cobalt salts in aqueous solution exhibit remarkable color phenomena, well known to analytical chemists. For instance, solutions of cobalt chloride can be red, violet, or blue, depending on the temperature, concentration, and the presence of other ions.

A number of theories have been advanced to explain the color changes of cobalt salts. One group of workers maintains that these are caused by a change in hydration or solvation. Certainly the state of solvation exerts a marked influence on the optical properties of ions. A strongly solvated cobalt ion is pink, whereas a decrease in solvation is assumed to lead to the formation of blue color centers.

Other workers have concluded that the number of groups surrounding the cobalt ion is more important than their chemical composition. The type of spectrum is determined solely by the degree of saturation of the residual valencies of the cobalt ion. The saturated compounds having six groups around each Co^{++} are pink or red, while the unsaturated compounds with only four groups are deep blue.

Another theory attributes the colors to the presence of cobalt complexes. The pink and red colors are due to cobalt acting as a cation, and the blue color is due to complex cobalt ions like $CoCl_4^{--}$ which are considered anions. In an electric field the blue cobalt complexes migrate to the anode.

Recent work[11] tends to reconcile to some extent these opposing views by indicating that two different processes must take place. One corresponds to a change in hydration or solvation, the other to the formation of a new complex.

In its electrochemical behavior cobalt occupies a position between iron and nickel.

Under certain conditions cobalt becomes passive in acid or alkaline solution. In most cases the production of the passive state is accompanied by the formation of an oxide film on the metal[5].

Cobalt is magnetic at all temperatures up to about 1150°. After iron, cobalt is the most magnetic metal. A great deal of work on the magnetic properties of cobalt was done by Honda and associates[5].

Hume-Rothery[3] summarizes the data on the atomic radii of cobalt thus:

		α-Co	β-Co
Type of structure		Close-packed hexagonal c/a = 1.624	Face-centered cube
Lattice constants	a	2.50 (7)	3.54 (5)
	c	4.07 (2)	

		α-Co	β-Co
Interatomic distances	d_1	2.49 (9)	2.507
	d_2	2.507	
Goldschmidt's atomic diameter for co-ordination No. 12		2.50	2.507

Pauling[6] has recently discussed the atomic radii and interatomic distances in a number of metals, including cobalt.

Young's elastic modulus has been reported by various workers, ranging from 1.471×10^{12} to 2.038×10^{12}.

The coefficient of thermal expansion of cobalt varies between 0.00001236 to 0.0000181, depending on the temperature and impurities present. The thermal expansion of the metal changes in the neighborhood of 400° to 450°, corresponding to an allotropic change which occurs around 447° on the heating curve and 403° on the cooling curve.

The specific heat of cobalt is given by various authorities as 0.0822 to 0.1234 for temperatures ranging from 100° to 1570°. The value of 0.103 given by Perrault[7] is probably a fair average for ordinary temperatures.

The latent heat of fusion of cobalt has been reported to be 67 to 68 calories per gram.

References to the flame spectrum, spark and arc spectrum, absorption spectrum, ultraviolet and infrared spectrum, Zeeman and Stark effects, and x-ray spectrum are given in Mellor[5].

The electrical resistance of cobalt has been reported all the way from 5.5×10^{-6} to 11.8×10^{-6} ohms per cm cube. These variations are caused by the presence of impurities, effect of preheating or annealing, the atmosphere used in annealing, etc. For instance, one worker reported for purified cobalt, heated 4 hours at dull redness *in vacuo*, $R = 6.85 \times 10^{-6}$ ohm at 20°; and when not so preheated, 8.07×10^{-6} ohm. The effect of annealing in an atmosphere of carbon dioxide is at first to increase the resistance, and afterwards as the temperature rises to 800°, the specific resistance falls. A drop from 10.1×10^{-6} to 9.35×10^{-6} ohm per cm cube occurs in the specific resistance of cobalt wire of a high degree of purity annealed in an atmosphere of carbon dioxide at 600° compared with one similarly annealed at 500°. As little as 0.5% impurity triples the resistivity. The value of 8.96×10^{-6} ohm per cm cube at 18° is probably a satisfactory constant for this property.

In its electrochemical behaviour cobalt occupies a position between iron and nickel. The electrode potential of cobalt has been variously reported as 0.237 to 0.278 volt for $Co \rightarrow Co^{++}$ and 1.8 volts for $Co^{++} \rightarrow Co^{+++}$; 0.22 volt for 0.1 *N* $CoSO_4$, 0.21 volt for 0.1 *N* $Co(NO_3)_2$, and 0.15 volt for 0.1 *N* $CoCl_2$.

The hydrogen overvoltage, or minimum voltage for the first visible

appearance of hydrogen, with a cobalt electrode in normal H_2SO_4 at 20° was found by Harkins to be 0.22 volt[5]. The hydrogen overvoltage with current densities from 2 to 400 milliamperes per sq cm in normal solution is:

$CoSO_4$	0.48–0.51 volt
$Co(NO_3)_2$	0.26–0.73 volt
$CoCl_2$	0 30–0.53 volt

depending on the current density. At high-current densities sudden increases of overvoltage often occur; since cleaning the electrode restores the normal overvoltage, the effect must be a surface one as a result of the formation of a cobalt alloy or compound.

Much of the earlier data on the magnetic properties of cobalt was obtained on material which to modern standards was grossly impure. For instance some of the pioneer work of Honda was reported on 93% cobalt. The influence of the magnetic field, H, on the intensity of magnetization, I, is shown by the table below:

H	2.4	20.7	43.2	75.9	129.0	151.8
I	8.5	136.7	238 4	350.2	451.5	493.2
H	200	400	600	800	1000	1200
I	856	988	1032	1056	1080	1090

The coercive force of cobalt decreases with increase of temperature, for example from 12 at 0° to 5 at 400°.

The variation in magnetization of cobalt in a weak magnetic field rises at first, gradually reaching a maximum at about 400°, and then decreases slowly to vanish at the critical temperature.

The Curie point, or temperature at which cobalt passes from the ferromagnetic to the paramagnetic state, is given by various authorities as 1050° to 1150°. It is probably about 1115°.

Under weak magnetic forces the permeability of cobalt is increased by compressed stress but when the magnetic force is large the reverse is the case.

The thermal conductivity has been given as 0.1299 calorie per degree per cm per second at 30° by Masumoto, 0.1653 calorie per degree per cm per second at 30° by Honda, and 0.172 by Barrett[5].

Adsorption of hydrogen by electrolytic cobalt occurs to the extent of 35 times its volume, whereas powdered cobalt obtained by reduction of oxide at 300 to 400° adsorbs up to 100 to 150 times its volume of hydrogen.

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Chapter 6
Cobalt in Ferrous Alloys

Cobalt alloys readily with iron. These alloys are malleable and weldable, and cobalt raises the elastic limit of iron. Alloys with up to 6% cobalt can be forged at normal temperatures without difficulty. The equilibrium diagram has been worked out by various investigators[1], [30] and is reproduced in Figure 22. Cobalt has only a slight effect on the melting point of iron.

Additions of cobalt to a steel slowly raise the tensile strength and elastic limit, while decreasing the elongation and reduction of area These mechanical properties are changed gradually, without sharp alterations.

When cobalt is added to iron, Young's modulus decreases slightly, reaches a minimum with 10% cobalt, then rises to a maximum at 27%, and finally decreases to a second minimum at 82%. Beyond this concentration the modulus then rises to the value for cobalt alone. The change of the modulus of rigidity with concentration gives a similar graph with one maximum and two minima.

Bain[5] stated that in large amount cobalt is a most extraordinary accelerator of reaction rate in hardening steel. Unlike nickel in this respect, it produces a steel of shallow hardening characteristics. He quoted his experience of finding a 15% Co, 0.60% C steel soft after an oil quench, while a quench into brine produced only a fine pearlite structure. Houdremont has secured quantitative information on the depth of hardening of a series of cobalt steels of two different carbon contents. Cobalt slightly elevates the critical points of the steels to which it is added. Houdremont shows a consistent and pronounced grain size diminution effect with increasing cobalt content.

Cobalt, like tungsten, diminishes depth of hardening and both elements greatly reduce the grain growth tendency in the austenite. Bain suggests that cobalt may by solid solution alone raise the temperature for grain growth above that employed in his experiments, 1040°.

Davenport, in his Campbell Memorial Lecture, discusses cobalt in relation to isothermal transformation in steels[11]. Since the alleged influence of cobalt in promoting shallow hardening appeared to be at variance with the effect of other alloying elements in steel, the question was investigated by the isothermal transformation technique. A series of high carbon steels (0.95% C) was prepared containing 0, 1, 2% Co and the portion of the

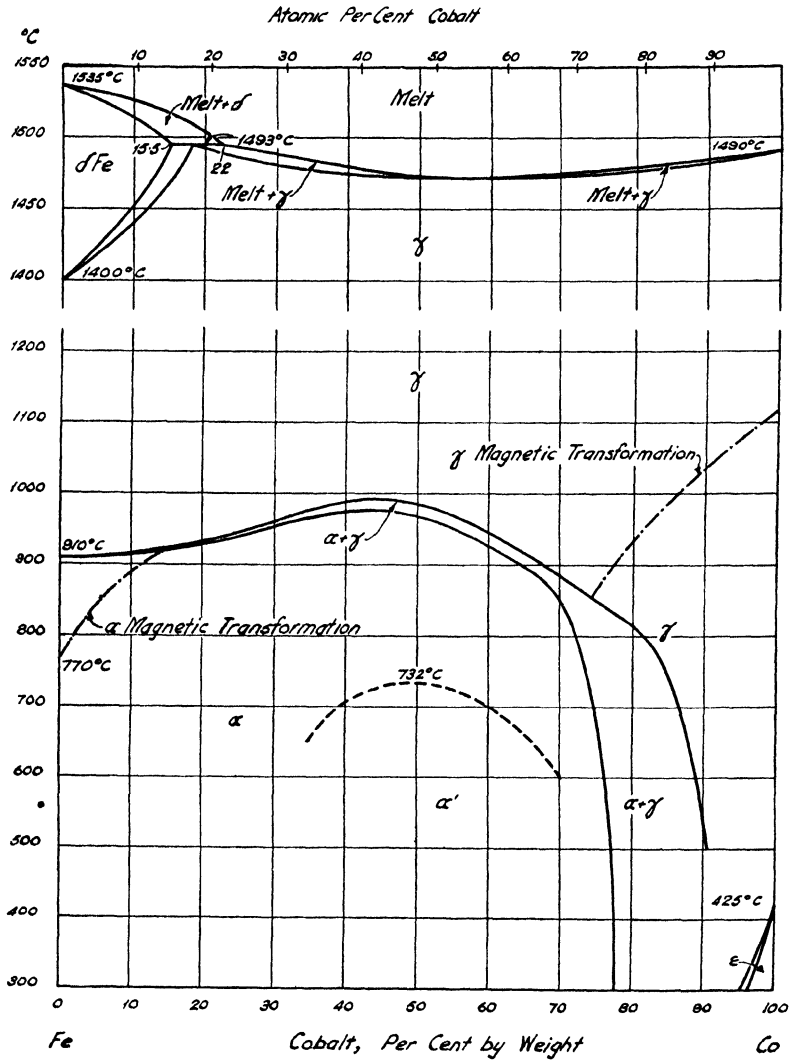


FIGURE 22. Iron-cobalt diagram.

S-curve between 370 and 650° was determined for each. Davenport's results show clearly that cobalt actually accelerates the transformation of austenite in the Ar′ range. There is no ready explanation for what appears

to be the unique influence of this element, although it has been suggested that it may be related in some way to the fact that cobalt undergoes an allotropic transformation of its own, in a temperature range not far from that in which iron transforms.

The thermal conductivity of iron-cobalt alloys first decreases with increasing proportions of cobalt, attaining a minimum at about 10% cobalt. It then rises to a maximum with about 65%, falls to a second minimum with about 90%, and finally rises to the value for cobalt alone.

The electrical conductivity of iron-cobalt alloys follows the curve for thermal conductivity very closely.

Tool Steels or High-Speed Steels

Cobalt is one of the principal constituents of a group of tool steels of enormous economic importance. It was only about 40 years ago that "high-speed" steels were developed, *i.e.* tool steels which were capable of cutting or shaping other steels or nonferrous metals for long periods of time at high speeds. These high-speed tools retained their cutting edge and hardness even at a dull red heat, and effected great savings in time and material in shop practice and general industrial economy. These high-speed steels consisted basically of 18% tungsten, 4% chromium, 1% vanadium, and from 0.50 to 0.80% carbon. The addition of from 5 to 12% cobalt to these steels allows greater red hardness and enables the tools to be used to better advantage on hard materials and at high speeds.

The carbide-forming tendency of cobalt is less than iron and it is largely dissolved in solid solution. Cobalt appears to increase hot hardness directly through its strenthening effect on the iron matrix. Cobalt when added to steel in the 1% carbon range raises the M-point (point at which austenite-martensite transformation begins) 20 to 25°F for each 1%. Cobalt under these conditions forms only the carbide Co_3C with an atomic radius of 1.25 Å. Smaller amounts of W, Mo, V, are required to combine with one carbon atom than is necessary with Cr, Mn, Co, or Ni.

A simple classification of high-speed steels is given in the excellent work on "Tool Steels" by Gill *et al.*[15] Table 7 illustrates these types

Cobalt is added to high-speed steels to improve the cutting efficiency at elevated temperatures. Where deep cuts and fast speeds are required the use of cobalt-containing tools is indicated. These steels are very widely used for single-point cutting tools; they are also very satisfactory for cutting cast iron or nonferrous metals giving discontinuous chips.

Cobalt in high-speed tools raises the melting point and permits the use of higher heat-treating temperatures without appreciable grain growth. A greater solution of tungsten, chromium, vanadium, and carbon in the austenite is thereby allowed. This, with the cobalt present in the matrix,

results in a greater amount of retained austenite, larger quantity of secondary hardness and a greater amount of red hardness.

The beneficial effect of cobalt on the cutting endurance of lathe tools is greatly increased by the use of higher quenching temperatures, around 1320°.

Cobalt when added to high-speed steels slightly increases the brittleness after quenching and tempering, but not to any extent detrimental for tool use.

Table 7. Classification of High-Speed Steels

Steel Type	C	W	Mo	Cr	V	Co
Tungsten	0.50–0 95	14 00–18 00	0 –0 80	4.00	1.00–3.00	—
Tungsten-cobalt	0.75	14 00–20.00	0 –0.80	4 00–4.25	1.00–2.00	5.00–12 00
Molybdenum	0.75–0.80	0 – 1.50	8.25–8.50	4.00–4.25	1.00–2.00	—
Molybdenum-cobalt	0.80	1.50	8 50	4.00	1.25–2 00	5.00–8 00
Tungsten-molybdenum	0.80–1 25	5 75	4.50–4 75	4.00–4 25	1.50–4 00	—
Tungsten-molybdenum-cobalt	0.80	5.75	4.74	4.00	1.50	5 00– 8.00

Table 8. Heat-Treating Temperatures for High-Speed Steels in Semi-Muffle Furnaces

Steel Type	Hardening Temperature (°F)	Tempering Temperature (°F)
Tungsten	2300–2350	1050–1075
Tungsten-cobalt	2325–2375	1000–1050
Molybdenum	2200–2220	1025
Molybdenum-cobalt	2200–2220	1025
Tungsten-molybdenum	2220	1050–1075
Tungsten-molybdenum-cobalt	2220	1025

Cobalt and molybdenum both increase the tendency towards decarbonization during the heating cycle and most cobalt tool steels should be ground to a considerable depth before use.

The effect of cobalt upon the amount of austenite retained in a high-speed steel has been estimated from magnetic saturation values by Houdremont and Schrader[20], but Gill *et al.* believe these results are high. It would be advisable to confirm these figures quantitatively.

The following data, abstracted from the work of Gill and associates, are given in Tables 8–11 to illustrate the differences in heat-treatment and physical properties between various high-speed steels.

Guillet[18] studied cobalt tool steels. Perrault[27] mentions the difficulties

encountered in France during World War II when cobalt was in very short supply for high-speed steels. It was found, for example, that machining of certain railroad equipment was possible only with cobalt-containing tools, and the regulations prohibiting the use of cobalt for anything but permanent magnets had to be revised to allow the production of tools containing 10% cobalt for these purposes.

A typical cobalt high-speed steel for cutting applications requiring maximum wear resistance is illustrated by a product of Atlas Steels Limited,

Table 9. Static Torsion Tests on Quenched and Tempered High-Speed Steels

Steel Type	Hardness at Room Temperature (Rockwell C)	Ultimate Torque (inch-lb)	Ultimate Deformation (degrees)
Tungsten	64 3–66.0	455–475	145–160
Tungsten-cobalt	64.9–65 8	420–430	100–135
Molybdenum	65.5	460	150
Tungsten-molybdenum	65.5–66 3	425–465	125–180

Table 10. Hot Hardness (Mutual Indentation). High-Speed Steels Treated for Maximum Hardness before Testing

Steel Type	1100°F Test (Brinell No)	1200°F Test (Brinell No)	Room Temperature (Rockwell C)
Tungsten	440–480	337–355	65.5–66.0
Tungsten-cobalt	520	400	65.0
Molybdenum	458–475	308–313	65.0–66.8
Tungsten-molybdenum	465	342	65.5
Tungsten-molybdenum-cobalt	500	390	66.0

Welland, Canada, which contains the following in percentages:

C	0 78
Mn	0.25
Co	8.00
W	19.00
Cr	4.00
V	2.00
Mo	0 80

This steel is recommended for heavy cuts and feeds at high speeds on hard, gritty, or scaly metals, as well as machining of material like austenitic stainless steels which work-harden under any form of stress. Typical uses are heavy duty turning, boring, form cutting, planing, and slotting on rough castings, car wheels, locomotive tires, heat-treated alloy steels and die blocks, and machining of stainless steels.

The company's recommendations for forging, annealing, hardening, and tempering are summarized below[2]:

Forging. Heat slowly to 1950° to 2050°F and soak at this temperature until steel is heated through. Do not continue forging below 1650° to 1700°F. High-speed steel will crumble and check in forging if too hot, and burst or crack if too cold. Repeated heating is recommended where a large amount of reduction or working is necessary, but adequate working after each heating is required to prevent a flaky or coarse structure. After forging, cool slowly away from water or drafts, preferably in a furnace, although dry ashes or other heat insulating material can be used. It is necessary to anneal after forging to remove strains and make the steel machinable.

Annealing. Heat slowly to 1600° to 1650°F, soak thoroughly, allowing 1 to 2 hours per inch of thickness, then cool very slowly in furnace. To

Table 11. Hot Hardness by Hot Rockwell Method

Steel Type	Hardness at Room Temperature before Testing (Rockwell C)	Hot Hardness		
		(1000°F)	(1050°F)	(1100°F)
Tungsten	64.0–66.3	58.0–60.2	56.5–57.8	54.5–56 2
Tungsten-cobalt	66.2–67.2	60.2–62.0	59.5–61.4	58.7–59.6
Molybdenum	65.3	58.0	57.0	55.5
Tungsten-molybdenum	65.3–65.4	58.0–59.0	57.0–57.5	55.9–56.7

prevent decarburization, pack steel in a mixture of charcoal with sand, lime, fine dry ashes, or ground mica. A good mixture is one part of charcoal to six parts of sand by volume.

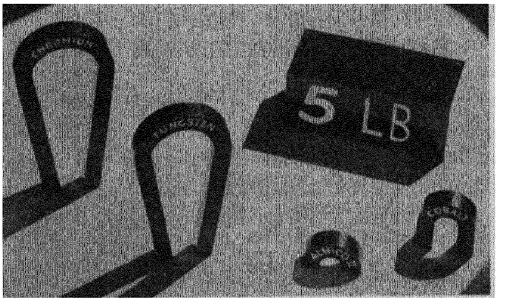
Hardening. Preheat carefully to about 1500 to 1600°F, preferably in a separate furnace, then bring up rapidly to hardening temperature of 2375° to 2425°F. Quench in oil or dry air blast. Good furnaces with accurately controlled temperature and atmospheric conditions are essential, since cobalt high-speed steels are particularly subject to decarburization and special care must be taken to minimize this condition. All tools should be ground after hardening.

Tempering. Tempering is necessary to develop red hardness, to relieve hardening strains, and to increase toughness. It should be carried out immediately after quenching, and a high draw of 1075 to 1125°F is recommended. Accurately controlled temperature in a good muffle or tempering bath is essential. A long draw or a double draw is recommended, using two hours per inch of thickness as a basis for calculating drawing time.

A short section on composition and heat-treatment of cobalt high-speed steels is given in the 1939 edition of "Metals Handbook"[1].

Magnets

Until 1916 the plain tungsten steels were the best for permanent magnets. In this year the remarkable magnetic properties of steels containing high proportions of cobalt were discovered by Honda in Japan[19, 23]. His KS magnet steels contained, in percentages, C 0.4 to 0.8, Cr 1.5 to 3.0, W 5 to 9, Co 30 to 40. These materials, although possessing approximately the same residual induction as the lower-alloy steels, exhibit vastly improved values of coercive force. These steels are oil-hardening and usually are quenched from temperatures of 1700 to 1800°F.



Courtesy General Electric Co., Schenectady, N. Y.

FIGURE 23. Comparative sizes of equivalent magnets of G-E sintered Alnico II, tungsten, chromium, and cobalt. Each is capable of suspending the five-pound weight shown.

Iron-cobalt alloys containing about 50% cobalt are important for magnetic purposes because of the high values of flux densities obtained with medium magnetizing forces. With magnetizing forces from 5 to over 1500 oersteds, the intrinsic induction is greater than that obtained with iron. In addition to the maximum in intrinsic induction, the electrical conductivity in this region at room temperature is greater than that of either of the components. Further work is needed to explain this anomalous behaviour. The binary alloy can be worked hot but is extremely brittle when cold. This imposes definite limitations where thin sheet produced by cold rolling is required. The limitations can be overcome by adding a few per cent of vanadium to the composition. This alloy can be worked hot, and after a quench from a high temperature can also be cold-rolled to thin sheet. The magnetic characteristics are not greatly affected by the vanadium, provided the addition is small.

In the iron-cobalt-nickel system, the alloys exhibit an unusual and useful property—constant permeability in low fields. Because of this characteristic, alloys in this region have been named "perminvars". A typical alloy contains 45% Ni, 25% Co, and 30% Fe. A low-temperature bake results in the extension of constant permeability to higher magnetizing forces.

The best permanent magnet steel in commercial use is the 35% cobalt steel, a complex alloy which contains tungsten, chromium, and carbon in addition to the cobalt. Typical values of coercive force and residual induction for this material are 220 oersteds and 9500 gauss. Although this material is decidedly superior in properties to the other magnet steels, because of high cost its use is limited to applications where space curtailment and apparatus requirements eliminate the cheaper steels.

A very useful earlier survey of magnetic materials in relation to structure has been made by Ellis and Schumacher[12].

The curve of intensity of magnetization of cobalt-iron alloys has a maximum at about 35% cobalt.

Cobalt carbide decomposes very readily so that in steels which contain much carbon, cobalt is only used in conjunction with chromium. The alloy corresponding to Fe_2Co has a saturation value of magnetization 10 to 13% higher than that for iron alone. The most important property of the Fe_2Co alloy is its permeability in medium fields, that is for a magnetizing force of 50 to 200 gilberts per cm. Through this range the permeability of the Fe_2Co alloy is approximately 25% greater than that of iron alone or of commercial grades of transformer steel or iron. The hysteresis loss of the Fe_2Co alloy is considerably less than for the best grades of commercial transformer steel at densities of 10,000 gauss and about the same as for commercial iron at corresponding densities—about 15,000 gauss.

By increasing the density in armature teeth 25%, the armature may be shortened a corresponding amount. Since the increased density in the teeth means also an increase in the density of the air gap, the latter may be shortened so as to keep the field ampere turn for the air gap and the teeth the same as before. The inside diameter of the armature core may also be increased to give a smaller core cross section. The shortening of the armature also shortens the pole pieces, and if a high permeability alloy is used in the field magnetic circuit as well as in the armature, the cross section of the field core and yoke may also be reduced. From the above reasoning it follows that the armature, besides requiring less iron will also require less copper, and the field spools, while containing the same number of ampere turns as before, will also require less copper. The total reduction of iron and copper may thus amount to as much as 25% each. The I^2R loss is also reduced in direct proportion to the reduction in copper used. Furthermore, as the hysteresis loss is lower per pound for the Fe_2Co alloy than for ordinary iron, and since the eddy current loss is about the same, the total

core loss should be considerably less than with ordinary iron, in spite of the increased density. It is for these reasons that dynamo machinery has become lighter and more efficient since the advent of the iron-cobalt alloys.

Cobalt metal is costly, however, and the high cobalt steels are very hard and brittle, and require such extreme care in forging that a certain amount of chromium is often substituted for cobalt. The chromium also serves to prevent carbide decomposition during hot-working and annealing.

Typical analyses of such steels are as follows:

C	Mn	Cr	Co	Mo
0.9	0 4	9.0	6.0	0.5
1 0	0 4	9 0	15.0	1.0

The following treatments are recommended for 6, 9, and 35 per cent cobalt magnet steels.

Forging: Between 950° and 1100°.

Annealing: Between 700° and 720°.

Hardening: (1) Heat to 1150° and cool in air.

(2) After standing for several hours, reheat to 700° and again air-cool.

(3) Reheat to 970° to 1000°, cool in air blast until black-hot, and then quench in oil.

Magnetization of permanent magnets is carried out by placing the magnets in a magnetic field of sufficient strength. The length of time that the magnets remain in this field does not appear to have any pronounced influence, but the intensity of the magnetizing field is of the utmost importance as will be observed from the following figures for a tungsten steel:

H_{max}	95	130	165	210	250	CGS units
H_c	59.4	69	74	75	75	CGS units
B_r	4800	7600	8400	9200	9200	CGS units

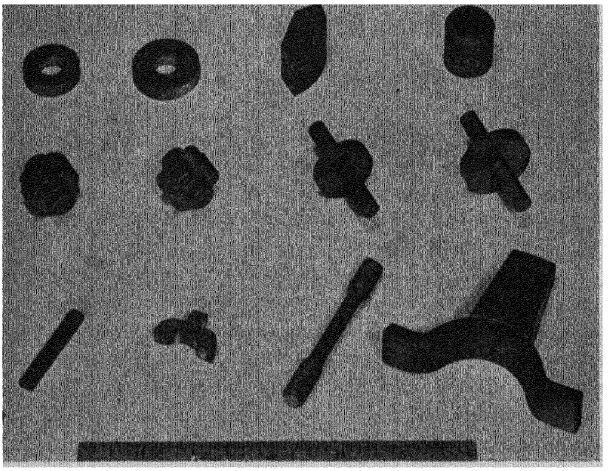
Thus, in order to obtain the maximum efficiency from a magnet, the magnetizing force must be sufficient to saturate the steel. A field strength of at least 400 gausses is recommended for tungsten steel, but a field of 1500 gausses is required for cobalt steel magnets.

Rough handling and vibrations in transit may seriously impair the properties of a finished magnet, and it is always advisable to remagnetize the steel immediately before use.

The magnet steels are hardened by quenching in oil or water according to size and composition. They may be tempered at 100° to relieve some of the internal stress, but this temperature should not be exceeded. After magnetization they should be aged so that they will withstand temperature

changes, vibration, impact, accidental demagnetizing forces, etc. This is accomplished by allowing them to stand for a long time, by mechanical jarring, heating in boiling water for about 10 hours, or by partial demagnetizing and remagnetizing followed by slight demagnetizing.

In 1930, Mishima in Japan discovered another remarkable series of permanent magnet alloys which contain about 25% nickel and 12% aluminum[24]. A large amount of work has since been done on alloys of this type to discover the relations between composition, treatment, and magnetic properties. The addition of 0.5 to 40% cobalt to an alloy containing 5 to 40% nickel, 1 to 20% aluminum, and the balance iron, decreases the grain



Courtesy General Electric Co., Schenectady, N. Y.

FIGURE 24. Several precision-cast* Alnico magnets.

size and consequently increases the coercive force and residual magnetism. These are known as the Alnico type magnets. The range of composition of the alloys now being made is within the limits Ni 14 to 30%, Al 6 to 12%, Co 5 to 35%, and the remainder iron. These alloys may, under proper conditions, produce good magnets in the cast condition without heat-treatment, but in general they are subjected to a high-temperature solution treatment followed by oil quenching and precipitation heat-treatment. These alloys cannot be worked or machined and magnets have to be cast to shape and subsequently ground.

*For details of precision investment casting, see Cady, E. L., "Precision Investment Casting", New York, Reinhold Publishing Corp., 1948.

Zumbusch[36, 37] concludes that one of the most satisfactory Alnico types from both quality and price is an alloy containing Co 20 to 22%, Ni 14 to 16%, Al 8 to 10%, Fe balance.

Oliver and Shedden[26] observed that the addition of cobalt to Ni-Al-Fe magnets entirely overcame previous difficulties encountered with scaling when these alloys were ground on refractory wheels at high speed.

For Alnico magnets containing copper, the Curie point increases with the cobalt and decreases with the nickel content. It is preferable to have less than 18% Ni and more than 12% cobalt.

Preliminary magnetization during the thermal treatment in the production of magnets is now common practice. The following composition is particularly well suited for this procedure: Ni 14 to 15%, Co 21.5 to 23.5%, Al 7.8 to 9.2%, Cu 3 to 4%, Ti 1%, Fe balance.

Permanent magnets are now being made by powder metallurgy[31]. Aluminum is introduced in the form of an iron aluminum alloy previously obtained by fusion and finely ground. The metal powders are intimately mixed with a synthetic resin, and pressed in a heated mold.

Ruder[29] reviews permanent magnet material and provides a table giving details of composition and of magnetic and physical properties. This is reproduced as Table 12.

Western Electric Company uses 36% Co steels for permanent magnet applications. "Remalloy" is a hot-rollable alloy used in handset receivers and contains 12% Co, 17% Mo, with the balance Fe.

"Permendur", which is 50% Co, 50% Fe, cannot be cold-worked. It is used in such magnets as pole pieces and pole tips. Permendur has a high saturation. A soft magnet containing 49% Co, 48 to 49% Fe, 2% V, and called a "vanadium permendur" can be hot- and cold-worked to thin sheet. Its major use is in diaphragms in telephone handset receivers.

Western Electric "Perminvar", 45% Ni, 25% Co, balance Fe, has a constant permeability over a wide range of magnetizing force. It is still a laboratory product. There are several "perminvars"; one with 77% Pt, 23% Co, is a magnet with the highest coercive force of any permanent magnet.

"Vicalloy" is a permanent magnet alloy which can be cold-worked. It is a Bell Telephone Laboratory product for high fidelity sound recording, with unusual working as well as magnetic properties[25]. Specimens that have been cast or subjected to a slight amount of hot reduction by rolling or swaging may be machined, punched, tapped, or drilled. After being either quenched, annealed, or given the usual cold finishing passes and then heated for 2 hours at 600°, such materials have a magnetic energy product of 1.0×10^6, about the same as Honda steel. The preferred composition for Vicalloy I is 38.5% Fe, 52% Co, 9.5% V. Vicalloy II is produced by severe cold reduction of the material after hot swaging. Following a cold

Table 12. Properties of Permanent Magnet Materials

Magnet Material	Nominal Composition (%)	Form	Residual B_r (gausses)	Coercive Force H_c (oersteds)	External Energy B_dH_d (max)	Weight (lb per cu in)	Mechanical Properties	Commercial Method of Fabrication
36% Cobalt Steel	Co 36 Cr 3.5 W 3 C 1 Fe Bal.	Bar	9,000	210	936,000	0.296	Hard, relatively strong	Hot-forge, machine
Comol	Co 12 Mo 17 Fe Bal	Bar	10,000	225	1,100,000	0 295	Hard, relatively strong, but brittle	Cast, hot-forge, machine, punch (thin sections)
Alnico 1	Al 12 Ni 20 Co 5 Fe Bal	Cast	7,100	400	1,400,000	0 249	Hard, brittle	Cast, grind
Alnico 2 (cast)	Al 10 Ni 17 Co 12.5 Cu 6 Fe Bal	Cast	7,200	540	1,600,000	0 256	Hard, brittle	Cast, grind
Alnico 2 (sintered)	Al 10 Ni 17 Co 12.5 Cu 6 Fe Bal.	Sintered	6,900	520	1,430,000	0.245	Hard	Sinter, grind

Alinico 4	Al 12 Ni 28 Co 5 Fe Bal.	Cast	5,200	700	1,300,000	0.253	Hard, brittle	Cast, grind
Alnico 5	Al 8 Ni 14 Co 24 Cu 3 Fe Bal.	Cast	12,000	575	5,000,000	0.264	Hard, brittle	Cast, grind
Alnico 12	Al 6 Ni 18 Co 35 Ti 8 Fe Bal.	Cast	5,800	950	1,750,000	0.260	Hard, brittle	Cast, grind
Cunico	Cu 50 Ni 21 Co 29	Strip, rod, wire, cast	3,400	710	850,000	0.300	Ductile, malleable	Cast, cold-roll, machine, punch
Vectolite	Fe_2O_3 30 Fe_3O_4 44 Co_2O_3 26	Pressed pieces	1,600	900	500,000	0.100	Low strength, brittle	Sinter, grind
Vicalloy I	Co 52 V 9.5 Fe 38.5	Wire, rod, sheet	8,800	290	1,100,000	0.296	Ductile	Cold-roll, machine
Vicalloy II	Co 52 V 13 Fe 35	Wire, strip	10,500	450	3,300,000	0.293	Ductile, machinable	Cold-roll, machine, wire-draw

reduction of 75 to 95% and a subsequent simple heat-treatment, the energy product is 2.0 to 3.5 $\times$ 10^6. The preferred composition for Vicalloy II is 35% Fe, 52% Co, and 13% V.

Hiperco is an iron-cobalt alloy marketed by Westinghouse containing 35% Co, 64% Fe, and 1% Cr. It has a high magnetic saturation value and unusually high permeability for magnetizing forces in the range $H = 10$ to $H = 400$ oersteds. Hiperco has been extensively used in the aircraft industry where a saving in weight or volume is important. It can be forged or rolled at 1000 to 1200° and can be cold-worked after hot reduction to 0.05 inch. In the unannealed state the alloy is soft and easy to machine. After annealing Hiperco becomes quite brittle.

Brittleness of Hiperco can be avoided either by quenching the alloy in cool water, or by continuous rolling while the hot metal cools. With the quenching method ingots are rolled into slabs 2 to 3 in thick, reheated to a high temperature, and rolled again to a thickness of $\frac{1}{10}$ inch. As the strip emerges from the last set of rolls, it passes into a trough of cooling water. The sudden cooling makes the metal so strong and workable it can be coiled like wire, whereas previously it could not be bent at all. The cool metal then undergoes a cold rolling process which can further reduce its thickness if necessary to 0.002 inch.

During World War II, an Advisory Committee on Metals and Minerals of the National Research Council in the United States reported on uses and possible substitutes for cobalt[22]. A useful relation between cobalt content and magnetic properties of cobalt steels is presented in Table 13, taken from this report.

It was concluded that it is almost impossible to find a substitute for cobalt in magnet steels. Some conservation could be effected by utilizing complex steels having less cobalt. For instance, low- and medium-cobalt steels carrying tungsten, chromium, and molybdenum can replace plain cobalt steels up to 30% Co. There is no known substitute for cobalt in high-coercive-force magnet steels, either in the 35 to 41% cobalt steels where machined magnets are essential, or in alloys of the Alnico or "new KS" types.

Developments in the production of cast and sintered Alnico magnets in Germany during wartime were recently published by the British Intelligence Objectives Sub-Committee[7].

Alloy Steels

Apart from its use in magnet and tool steels, cobalt is alloyed with iron for the following purposes:

(1) To furnish high strength at elevated temperatures.

(2) To provide resistance to oxidation and corrosion at high temperatures.

(3) For glass-to-metal seals.
(4) For dies, gages, etc., where wear resistance and heat resistance must be combined.
(5) For alloys possessing a zero coefficient of expansion.

The addition of cobalt to steel has a slight effect in retarding rusting in the atmosphere, and a pronounced effect in decreasing attack by acids.

Houdremont and Schrader[20] studied the effect of cobalt in steels. Cobalt up to 2% in cast iron has not a marked effect on the mechanical properties but increases its resistance to corrosion by dilute H_2SO_4.

Table 13. Relation between Cobalt Content and Magnetic Properties of Cobalt Steels

Cobalt (%)	Remanence B_r (gausses)	Coercive Force H_c (oersteds)	$(B_rH_c \times 10^{-6}$ (gauss-oersteds)
6	9000	120	1.08
10	9000	150	1.35
15	8000–10000	ca. 100	0.9
15	8200	200	1.6
20	8050	160	1.32
20	8000	158	1.27
20	8250	190	1.57
30	7950	203.5	1.62
30	8000	220	1.76
35	7500–9500	ca. 200	1.70
35	9000	240	2.16
35	8500	250	2.13
35	9000	240	2.16
36	9000	250	2.25
42	10700	240	2.52

Kovar A is an iron alloy marketed by Westinghouse containing 29% Ni, 17% Co, and 0.3% Mn. It has a yield point of 50,500 psi and a tensile strength of 89,700 psi. It has high resistance to amalgamation with mercury and withstands high thermal shock. Another useful property is the ease with which it may be soldered to other parts such as lids, terminals, and leads. Kovar A is ideal for any application demanding a vacuum-tight, metal-to-glass joint to conduct power into a glass vessel or to insulate electrodes from metal-walled vessels. Such uses include small rectifiers, grid-glow tubes, and Ignitrons.

Redston and Stanworth[28] suggested specifications for Fe-Ni-Co alloys for sealing to borosilicate glass as follows: Ni 29 ± 0.5, Co 17, Mn 0.3, Si 0.15, C 0.05 max., P 0.01 max., S 0.01, Ni + Co 46 ± 0.5.

The alloy "Fernico" of General Electric, which has the same coefficient of expansion as glass, rendering it very suitable for glass-metal seals, contains 18% Co, 28% Ni, and 54% Fe.

Scott[32] discusses the principles of glass-to-metal seal design, and includes the characteristics of the Kovar type, 54% Fe, 29% Ni, and 17% Co.

Westinghouse K-42-B alloy, containing 42% Ni, 22% Co, 18% Cr, 14% Fe, 2% Ti, possesses remarkable strength at elevated temperatures. It also has resistance to oxidation and corrosion. This alloy can be hardened by a precipitation-hardening heat-treatment.

Grant[17] discusses research on high temperature alloys for gas turbines carried out at Massachusetts Institute of Technology over a three year period. This is reviewed in the next chapter under cobalt in nonferrous alloys.

Knight[21] discussed heat-resistant materials developed during the war and listed the cobalt-containing alloys presented in Table 17, page 101.

Badger[4] in discussing metallurgical development of materials for turbo-superchargers and aircraft gas turbines, also gives the chemical compositions of heavy materials used for these purposes. He points out that the

Table 14. Composition of Cobalt-Containing Valve Steels

	C	Si	Cr	Co	Mo	V	Ni
(1)	0.95	0.4	18 5	2.0	1.0		
(2)	1-1.5	—	11-14	2.5-3.5	0.5-0.9	0.2-0.3	—
(3)	1.21	0.31	13.16	4.88	0.64	—	0.59
(4)	1.78	0 40	13 06	2.40	1.14	—	0.11
(5)	0.40	3-4	2-10	0.5-3.0	—	—	—

supercharger wheel may be exposed to a temperature of 1300°F at the rim and 500 to 600°F at the center. The design stresses at and near the center demand a material with a high yield strength, about 80,000 psi, at 600°F. The rim stresses require a material with a high rupture strength at 1200°F. The wheel materials must be readily forgeable, machinable, weldable, resistant to oxidation from exhaust gases, and not subject to brittleness or ageing.

Cross and Simmons[10], Browne[8], Bollenrath[6], Gordon[16], Sweeney[33], Freeman, Reynolds and White[14], Epremain[13], and Wilson[35] also consider cobalt alloys used for high-strength, high-temperature service.

Cobalt is an important constituent of alloy steels used for valves. For this use it is necessary that the steel retain its structure and mechanical properties up to 950° and resist corrosion and oxidation from exhaust gases. Perrault gives some typical compositions of valve steels[27], shown in Table 14.

Cobalt has occasionally been used for construction steels, but the tonnage is insignificant compared to the use of nickel for this purpose.

A high-carbon nonforgeable steel of the following percentage composition·

C	2–3
Si	0.1–0.6
Mn	0.2–1
Cr	25–30
Co	3.5–4

has been used in Germany for hot wire-drawing gages, pyrometer sheaths, and other purposes where wear resistance and heat resistance are required.

The addition of cobalt to chromium tungsten steels used for dies and other hot-working applications increases the wear resistance and hardness at high temperatures. Such steels may contain C 0.65, Cr 4.0, W 10.0, and Co 2 to 3%.

For a long period the nickel steel containing 36% Ni, called invar, had the lowest coefficient of expansion of any alloy. In 1929 Masumoto replaced some of the nickel with cobalt to give an alloy of Fe 63.5, Ni 31.5, and Co 5, which had an even lower coefficient of expansion than invar. Several years later Masumoto developed a "stainless invar" with the following composition: Fe 36.5, Cr 9.5, and Co 54% The coefficient of expansion of this alloy is practically zero. It is interesting to note that by slightly altering this composition to give Fe 37, Cr 9, and Co 54%, a negative coefficient of expansion is obtained, the alloy contracting very slightly at elevated temperatures.

There are a number of iron-nickel-cobalt alloys in use for high-strength, high-temperature service. Examples are Hastelloy A and Konel of Haynes Stellite Company. These alloys have the following composition:

	Hastelloy A	Konel
Co	19.5	19.5
Ni	56.0	76.0
Fe	22.0	7.4
Mn	2.5	—
Ti	—	2.8

An iron:cobalt:tungsten alloy has been studied by Sykes[34], containing 50% Fe, 30% Co, and 20% W. This material hardens by precipitation on ageing, and possesses a Brinell hardness of around 400 at 700°.

The scaling of hard surfacing alloys with various cobalt contents was studied by Cornelius[9]. The resistance to scaling at 900°, 1000°, and 1100° in air, lead-free fuel, and fuel containing 1.8% tetraethyl lead was investigated for six alloys. These were of the type used for valve seats in combustion engines. They contained 1 to 2.2% C, 0.84 to 2.41% Si, 0.18 to 0.45% Mn, 0.0 to 60% Co, 22 to 29% Cr, and 0.0 to 7.6% W. A new apparatus was used which permitted impingement of the hot gases im-

Table 15. Cobalt-Containing Alloys Used in Construction of Chemical and Metallurgical Equipment

Material	Manufacturer	Essential, Nominal, Chemical Composition (%)	Forms Available†	Primarily For*
Haynes Stellite 1	Haynes Stellite Co., Kokomo, Ind	Co; 28–34 Cr; 11–15 W	*R* (cast)	*C, H, A*
Haynes Stellite 3	Haynes Stellite Co., Kokomo, Ind.		*C*	*C, H, A*
Haynes Stellite 6	Haynes Stellite Co., Kokomo, Ind.	Co; 25–31 Cr, 3–6 W	*C, S, R* (cast)	*C, H, A*
Haynes Stellite 12	Haynes Stellite Co., Kokomo, Ind.	Co; 26–32 Cr, 6–10 W	*C, R* (cast)	*C, H, A*
Haynes Stellite 21	Haynes Stellite Co., Kokomo, Ind	Co; 25–30 Cr; 5–6.5 Mo, 5–3.5 Ni; 2 max Fe; 0.2–0.35 C	*C, S*	*C, H*
Haynes Stellite 23	Haynes Stellite Co., Kokomo, Ind.	Co, 0 35–0.5 C; 23–29 Cr, 1 5 max Ni,4–7, W; 2 max Fe	*C, S*	*C, H*
Haynes Stellite 27	Haynes Stellite Co , Kokomo, Ind	Ni, 0.35–0 5 C, 23–29 Cr; 5–7 Mo; 2 max Fe; 30 min Co	*C, S*	*C, H*
Haynes Stellite 30	Haynes Stellite Co., Kokomo, Ind	Co, 0 35–0 50 C, 23–29 Cr, 13–17 Ni, 5–7 Mo; 2 max Fe	*C, S*	*C, H*
Haynes Stellite 31	Haynes Stellite Co., Kokomo, Ind	Co, 0 45–0 6 C; 23–28 Cr, 9–12 Ni, 6–9 W; 1.5 max Fe	*C, S*	*C, H*
Haynes Stellite 93	Haynes Stellite Co , Kokomo, Ind	Fe, 15–19 Cr, 4–7 Co, 0 5–3 V, 13–17 Mo	*C, R*	*H, A*
Haynes Stellite 98M2	Haynes Stellite Co., Kokomo, Ind.	Co; 27–31 Cr; 16–19 W	*C*	*C, H, A*
Haynes Stellite Multimet	Haynes Stellite Co., Kokomo, Ind.	20 Cr; 20 Co; 20 Ni; 3 Mo, 2 W; 1 Cb, 0.14 N; 0.1–0 35 C	*B, C, CR, HR, D, P, S, R, T, W*	*C, H*
Haynes Stellite Star J	Haynes Stellite Co., Kokomo, Ind.	Co; 29–34 Cr; 15–19 W	*C*	*C, H, A*

Haystellite, Hard Grade	Haynes Stellite Co., Kokomo, Ind.	90–96 W; 0.5–2 Co; 3.5–4.5 C	*R* crushed grains	*A*
Haystellite, Tough Grade	Haynes Stellite Co., Kokomo, Ind.	79–85 W; 8–11 Co; 3.5–4.5 C	Cast inserts, crushed grains	*A*
K42B	Westinghouse Electric Corp., Pittsburgh, Pa.	42 Ni, 22 Co; 18 Cr; 14 Fe; 2.2 Ti	*B, CR, R, W, F*	*H*
Kanthal Alloys	C. O. Jelliff Mfg Corp., Southport, Conn.	Fe; 20–25 Cr, Co; Al	*W*, ribbon	*H*
Stoody 1	Stoody Co., Whittier, Calif.	Co; 25 Cr; 13 W; 2 C	*C*, welding rod	*C, H, A*
Stoody 6	Stoody Co., Whittier, Calif.	Co; 25 Cr; 5.5 W; 1 C	*C*, welding rod	*C, H, A*

* Primarily for: *C*, corrosion; *H*, heat; *A*, abrasion.
† Forms available: *B*, bars; *C*, castings; *CR*, cold rolled; *D*, drawn; *E*, extrusions; *F*, forgings; *HR*, hot rolled; *P*, plates; *R*, rods, *S*, sheets; *T*, tubes; *W*, wire.

mediately after combustion with the specimens suspended in the combustion chamber. The specimens having smoothly ground surfaces were exposed to the hot gases for ten 5-hour intervals with intervening cooling periods in the chamber. The weight loss determinations demonstrated that the cobalt content has no effect upon the resistance to scaling in air of either type of fuel. Differences in behaviour were traced to other causes, notably the carbon content. The formation of carbides depletes the alloy of chromium, which particularly in the absence, or low content, of tungsten would be essential for the scaling resistance of the alloys.

The materials listed in Table 15 have been used for the construction of chemical equipment. This table has been assembled from data appearing in the November, 1946, issue of *Chemical Engineering*.

Austin and Samans studied the metallography and certain physical properties of some alloys of cobalt, iron, and titanium[3]. Alloys containing 4.15 to 13.17% Fe, 1.15 to 4.70% Ti, and 81.11 to 94.15% Co were employed in the work. The following conclusions were drawn:

(1) The alloys investigated are susceptible to precipitation hardening.
(2) A favorable ageing temperature is 600° regardless of the solution treatment used.
(3) With the 1150° and 1300° solution treatments, some precipitation hardening occurs even at temperatures apparently in the solid solution range.
(4) Tensile deformation rates at high temperature are affected by the oxidation resistance and by the amount and degree of dispersion of the precipitates.
(5) Both 600° and 700° appear to be within the strain-hardening temperature range of the two richer alloys for the stresses studied. However, the alloy containing the smallest amount of ferro-titanium strain hardened only at the lower temperature.
(6) Ni_3Ti seems more prone to precipitate discontinuously at the grain boundaries while Fe_2Ti occurs more frequently as a general precipitate within the grains.
(7) From microexamination it is concluded that at the higher test temperatures (700° to 800°) stress may have accelerated the precipitation reactions.

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Chapter 7
Cobalt in Nonferrous Alloys

Cobalt and Other Elements

Aluminum. The freezing point curves of the cobalt-aluminum alloys have a maximum at 1628° and 68.5% cobalt, corresponding with cobalt aluminide, CoAl. They have two breaks at 1165° and 38% cobalt, and at 940° with 20% cobalt. There is a minimum in the curve at 1375° and 90.5% cobalt. There are two series of solid solutions containing respectively 68.5 to 80% and 90.5 to 100% cobalt. The alloys with 82 to 90% cobalt do not become homogeneous when heated for three hours at 1250 to 1270°. At 1165° the cobalt monoaluminide reacts with the fused mass to form cobalt hempentaluminide, Co_2Al_5, and at 940°, to form cobalt triatridecaluminide, Co_4Al_{13}. The hypoeutectic liquidus is a straight line extending from the freezing point of aluminum to the eutectic. Less than 0.02% cobalt dissolves in solid aluminum at 655°. The intersection of the hypereutectic liquidus with the eutectic horizontal occurs with 1% of cobalt.

Alloys with 9 to 12% cobalt have the best mechanical properties, although the tensile strength is very little greater than that of aluminum. The alloys with 75 to 80% cobalt are brittle and as hard as hardened steel.

More work needs to be done on the effect of the addition of other alloying elements on the properties of the cobalt-aluminum alloys. The cobalt-aluminum diagram reproduced from Sachs and Van Horn[17] is given in Figure 25.

Beryllium. It may be noted that beryllium copper usually contains about 0.5% cobalt in addition to 2% beryllium.

The addition of 4% beryllium to cobalt gives an alloy which, after quenching in water at 1150° and annealing a few hours at 400°, has the remarkable Brinell hardness of 660.

Boron. Cobalt boron alloys have been prepared[14].

Cadmium. Alloys of cobalt and cadmium have been described[14].

Chromium. Cobalt and chromium are miscible in all proportions in the liquid and solid states. The hardness attains a maximum with about 70% chromium, the tensile strength with 30% chromium. Alloys with 15% chromium possess the greatest magnetic intensity.

The cobalt-chromium alloys are quite resistant to corrosion, and were the basis for the development of stellite. These alloys are discussed sep-

arately under Stellite. Other chromium-cobalt alloys are considered under Vitallium.

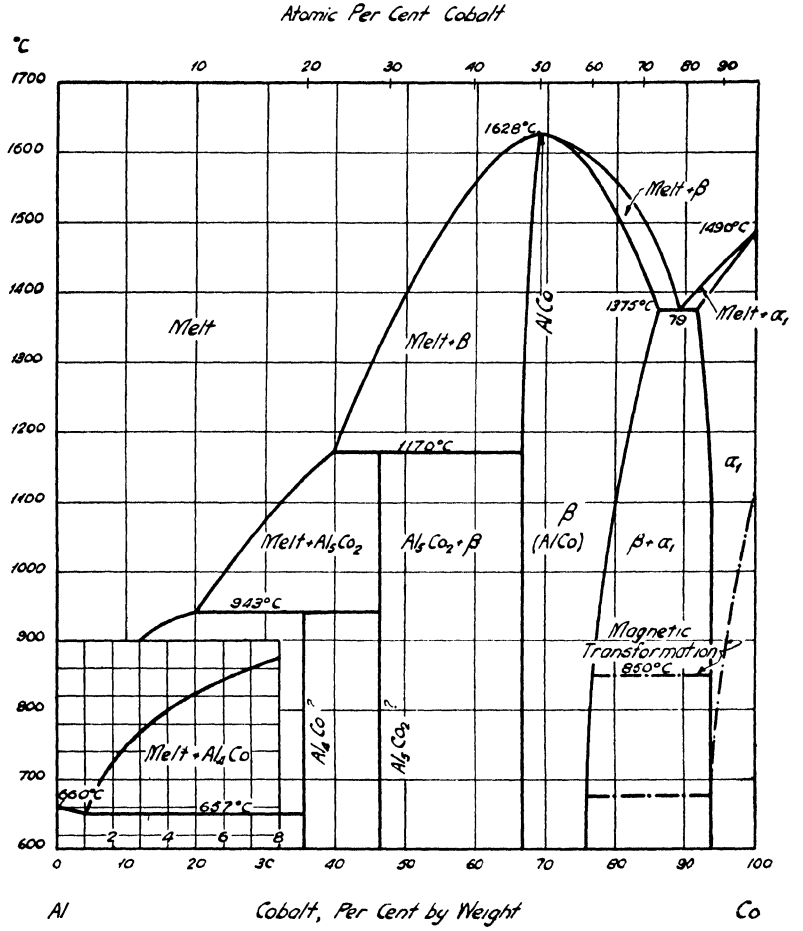


FIGURE 25. Cobalt-aluminum diagram.

Cobalt chromate banding is discussed by Liesegang in connection with its significance in ore deposits[18].

Copper. Copper and cobalt form two series of solid solutions with 0 to 10%, and 95.5 to 100% copper respectively. There is a break in the cooling curve at 1100° with alloys having 10 to 95% copper, below which

the alloy solidifies completely to a conglomerate of two series of solid solution. Alloys with 99% cobalt are still magnetic.

The effect of small quantities of cobalt on the electrical properties of copper was found to be nearly as great as that of manganese and considerably greater than that of nickel. The conductivity of copper: cobalt alloys is illustrated diagrammatically in Desch's "Metallography"[7].

Smart and Smith[18] found that cobalt enters solid solution in oxygen-free copper and is responsible for a sizable decrease in conductivity, 0.43% per 0.001% of cobalt. Up to 0.05% cobalt has only a minor effect on softening temperature. Oxygen completely precipitates cobalt as an oxide.

Lead. Cobalt and lead are partially miscible in the liquid state, but in the solid state neither compounds nor solid solutions are formed.

Magnesium. It has been reported that magnesium-cobalt alloys could not be obtained by melting a mixture of the component metals. In view of the present importance of magnesium, more work needs to be done on the possibility of magnesium alloys with cobalt and other metals.

Manganese. Cobalt-manganese alloys form a continuous series of solid solutions with a flat minimum at about 30% cobalt and 1150°.

Mercury. Cobalt forms an amalgam when sodium amalgam is mixed with solutions of cobalt compounds.

Molybdenum. The cobalt-molybdenum system has been studied by Sykes and Graff[20].

The freezing point curve of cobalt-molybdenum alloys has a eutectic at 1335° and about 38% molybdenum. Solid solutions are formed with up to 28% molybdenum. The curve rises from the eutectic and suffers a break at 1484° corresponding with cobalt molybdite, CoMo, which does not form solid solution. There is no indication of the formation of any other compound. The compound is nonmagnetic but the solid solution rich in cobalt is magnetic.

Nickel. Nickel-cobalt alloys form a continuous system of solid solutions. The solid alloys, when heated above a critical temperature which increases with the cobalt content, become nonmagnetic[1].

The Co-Ni diagram, from Sachs and Van Horn[17], is presented in Figure 26.

Complex nickel-cobalt surgical and dental alloys are discussed in *British patent 578,097* of Deloro Smelting and Refining Co.[6]. A preferred composition is Cr 18, Ni 15, V 10, Mo 4, B 0.25, C 0.30, Si 0.30, Mn 0.35, remainder Co (51.80%).

A large number of alloys containing nickel and cobalt as major constituents are described by various workers [8, 10, 12, 22] and listed in Tables 12 and 15.

Silicon. Cobalt silicide is a remarkably inert material even in hot strong acid solutions. There are probably at least five silicides: Co_2Si,

CoSi, Co_3Si_2, $CoSi_2$, and $CoSi_3$. Those richer in silicon are more resistant to strong acids, while those high in cobalt are more inert to alkaline solu-

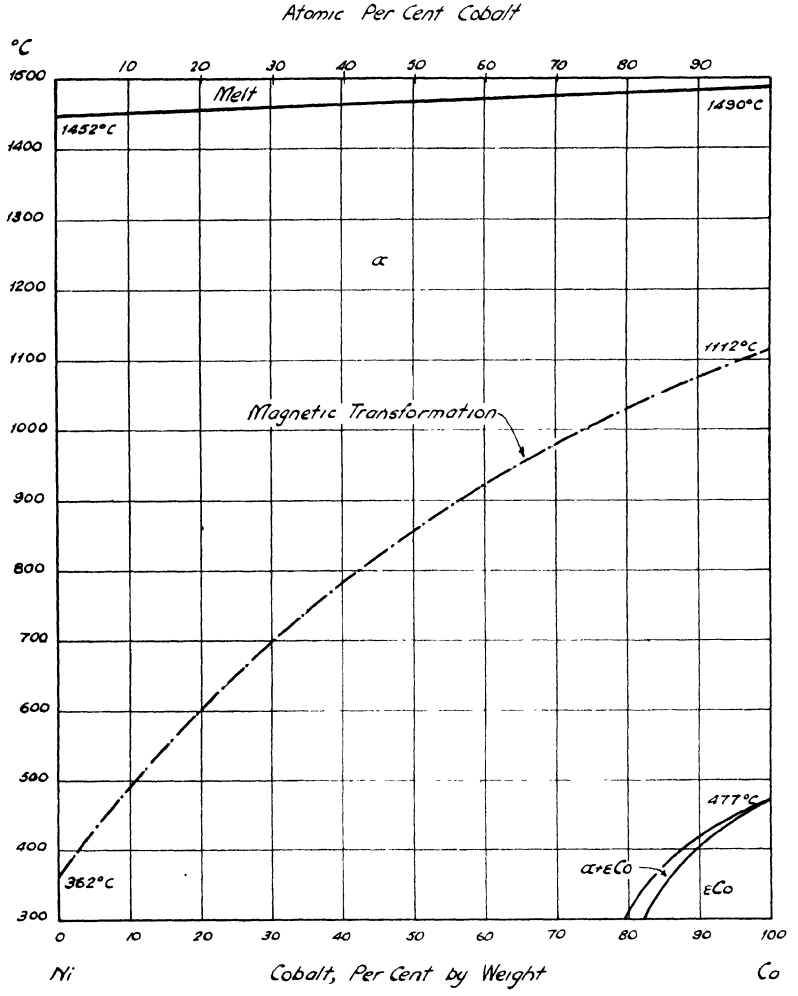


FIGURE 26 Cobalt-nickel diagram

tions. Reference has already been made on page 61 to the addition of cobalt silicides to steel.

Silver and Gold. Cobalt and silver are practically insoluble in each

other. Molten cobalt and gold can be mixed in all proportions. The freezing point curves have two branches meeting at a eutectic at 997° and 90% gold. Solid solutions containing 0 to 5.5% and 96.5 to 100% of cobalt are formed. Cobalt whitens gold, but much less than nickel. A French patent[16] employs 4% Co, 75% Au, 10% Ag, and 11% Cu, for certain jewelry purposes where hardness and ease of polishing are important.

Tin. Cobalt and tin are miscible in all proportions in the liquid state. In the solid state the maximum amount of tin dissolved by cobalt is 3.5%. Their properties have been studied by numerous workers, but as yet no economic use has been found for them.

Titanium, Thallium. Alloys of cobalt with titanium and thallium have been described, but they are not of economic importance[14].

Tungsten. The cobalt-tungsten system was studied by Sykes[19]. Alloys with 0 to 40% W consist of a series of solid solutions, and those with 40 to 70% W, of a mixture of the eutectic and solid solutions, or of eutectic and monotungstide, CoW, depending on whether the alloy contains less or more than 45% W. The eutectic is at 1400° and 44.5% W. Alloys of cobalt, tungsten, and chromium are discussed later under Stellites.

Vanadium. A permanent-magnet alloy of iron, cobalt, and vanadium under the name of Vicalloy has been developed. This alloy containing 35 to 38.5% Fe, 52% Co, and 9.5 to 13.5% V, has excellent working properties. It is discussed in Chapter 6.

Zinc. Zinc and cobalt alloy together, but the resulting substances have undesirable physical and chemical properties, oxidizing readily in air or water.

The cobalt-zinc-copper alloys, or cobalt brasses, are white, brittle, and hard. The addition of cobalt raises the tensile strength of brass wire considerably.

Stellites

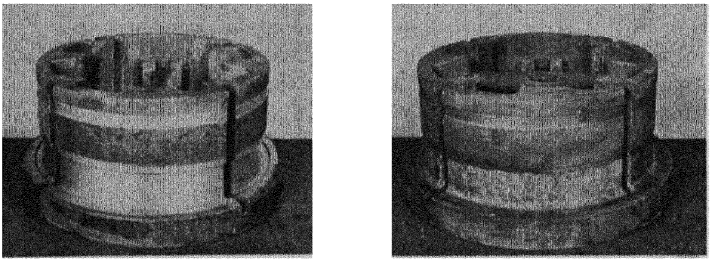
Chromium-tungsten-cobalt alloys, sometimes modified by the addition of iron, molybdenum, and nickel, are called stellites. They are very hard, resistant to corrosion, and take a high polish. An example of a stellite composition is Co 55, Cr 28, W 15, C 2.5. The hardness increases with increasing chromium and decreasing cobalt content, with tungsten having little influence on this property. The wear-resistance increases generally with decreasing cobalt content; tungsten and chromium have very little influence. Resistance to corrosion is apparently sensitive to the proportion of carbon, an alloy with about 2.5% being about the most satisfactory.

The stellites were developed by Haynes prior to 1914 but their commercial importance did not appear until some years later. They are very important cutting tools.

Stellites are used for exhaust valves in aircraft motors where freedom

from oxidation and distortion are necessary at temperatures up to 800°. They are also important for exhaust ports of Diesel marine engines where traces of sulfuric acid are present from the sulfur in the fuel oil.

The composition of stellites varies over a wide range, and many of the commercially available grades contain, in addition, appreciable quantities of Ta, V, Mo, B, etc. These materials are practically unaffected by heat-treatment and cannot be annealed. They range in hardness as cast from 50 to 60 Rockwell C, depending upon the particular combination of alloying elements present. The grades that are applicable for metal cutting are too hard and brittle to be hot rolled or forged. They must therefore be cast to shape and finished by grinding.



Courtesy Deloro Smelting & Refining Co., Ltd., Deloro, Ontario

FIGURE 27. A 22-inch diameter draw block for copper wire showing, *left*, preparation for stelliting, and *right*, Grade-12 stellite as deposited.

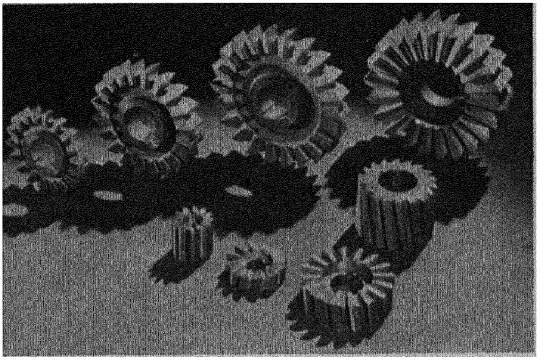
Compared to the standard types of high-speed steel, these cast nonferrous materials possess a greater red hardness, a lower coefficient of friction against steel and cast iron, and a greater ability to resist abrasive wear at elevated temperatures. Hardened high-speed steels are harder than the cobalt-chromium-tungsten cast materials at temperatures up to 1100°F, but above this point the cast materials are superior in hardness.

The hot hardness of the Co-Cr-W alloy is dependent to quite an extent, however, upon the actual composition of the material. It is quite probable that the tungsten content and carbon content are of considerable influence in this connection.

For relatively light cuts where the temperature at the nose of the cutting tool is less than 1100°F, high speed steel will prove superior, while for cuts at higher tool temperatures the cobalt-base cast materials will often be more satisfactory and may be used at higher cutting speeds under otherwise equivalent conditions.

Because of their lack of ductility the cast Co-Cr-W alloys must be well supported. They are generally used as cast tool bits in a tool holder or as

tips brazed or welded to a shank of tough steel. In operation, care must be taken to avoid sudden shocks caused by interrupted cuts, stopping the cutting with the tool in the work, chatter, excessive chip thickness, and extreme irregularity in the hardness of the metal being cut.



Courtesy Haynes Stellite Co., Kokomo, Ind.

FIGURE 28. Stellite milling cutters.

Table 16. Composition and Hardness of Typical Stellites Produced by Deloro Smelting and Refining Company Ltd.*

	Co	Cr	W	Fe	C	Si	Rockwell Hardness (C Scale)
No. 1 welding rod	50	33	13	2	2	1	54–56
No. 6 welding rod	64	25.5	4.75	2.5	1	1.75	39–42
No. 12 welding rod	58	29	9	1.5	1.85	1.5	48–51
Cutting alloys	42–48	30.5–35.5	15–19	1.5	1.75–2.7	1.5	59–68
Battery castings	50–65	28–35	5–15	1.5	0.5–1.25	1	35–50

* Courtesy of C. R. Whittemore, Research Metallurgist, Deloro Smelting and Refining Company, Limited.

These materials are also available in the form of welding rod by means of which hard wear-resistant layers may be built up on any number of engineering parts.

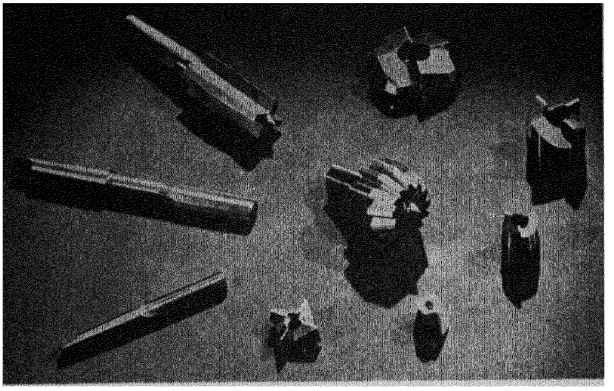
At the plant of the Deloro Smelting and Refining Company, Limited, Deloro, Ontario, stellite is produced in 250-lb Detroit electric furnaces. A charge of approximately 150 lb of cobalt, chromium, and tungsten is melted, and as the metals are pure no slagging is required. The power requirements are about 0.36 kw hr per lb of metal produced.

Melting is done at 1475 to 1500° and pouring of cutting tool stellite is

carried out at 1325 to 1425°, depending on the size of the bar and the type of alloy required. The metal is cast into graphite molds for both cutting tools and welding rods. Most casting at present is static, but it is anticipated that centrifugal casting will be practiced more and more in future stellite production.

Table 16 shows the characteristics of some stellites produced at Deloro.

Vitallium. A dental and surgical alloy containing essentially 65% Co, 30% Cr, and 5% Mo or W, was developed about 1936 in the United States and called Vitallium. It is not attacked by body liquids, does not give rise



Courtesy Haynes Stellite Co., Kokomo, Ind.

FIGURE 29. Special counterbores, spotfacers, and reamers made from stellite.

to any irritation to tissues, and is electrically neutral in the body. Since it cannot be cold-worked or drawn into wire, however, there are many uses in the medical or dental field for which it is not applicable.

Vitallium, owing to its resistance to high temperatures, has found extensive application in aircraft turbosuperchargers, buckets, nozzle vanes, etc. Vitallium with about 65% Co, 30% Cr, and 5% Mo, is used for the turbine buckets of both gas turbines and turbosuperchargers. In view of its limited hot formability and difficult machinability, this alloy is generally precision cast. Vitallium has over 65,000 psi tensile strength at 1500°F with 20% elongation. High strength at elevated temperatures and abrasion resistance are provided by this alloy.

Table 17 illustrates a variety of cobalt-containing heat-resistant materials used where strength at elevated temperatures is essential.

Grant[10] discusses at length research on high temperature alloys for gas turbines carried out at the Massachusetts Institute of Technology over a three-year period. In the Vitallium group the best all-round properties

at 1500°F (815°) were shown by an alloy in which 2% Ta was substituted for 2% of Co, giving a composition of C 1.11, Cr 23, Co 67, Mo 6, Ta 2, N 0.062%.

Examples of the best alloys in the cast nickel-chromium-cobalt-iron group were the following: C 0.99, Ni 30, Cr 20, Co 21, Mn 1.5, Si 1.0, Mo 3,

Table 17. Cobalt-Containing Heat-Resistant Materials

Alloy Designation	Co (%)	Maker	Parts Used in
Low-carbon N155 Multimet	20.00	Haynes Stellite	Wheels, bolting, gas turbine blades, tail cones and ship propulsion turbines
Low-carbon N153	13 00	Haynes Stellite	Experimental
S.590	20.00	Allegheny Ludlum	Wheels and buckets
S.816	44.00	Allegheny Ludlum	Buckets
K-42-B	20 00	Westinghouse	Turbosupercharger blades
Refractaloy	20.00	Westinghouse	
Hastelloy B	29.00	Haynes Stellite	Buckets
Vitallium	64.00	Austenal Laboratories	Buckets, turbosupercharger and jet buckets, nozzle vanes, liners, tail cones, heat exchangers.
6059	33.00	Haynes Stellite	
Vanadium Corp. NDRC Research	20 00–30 00	Vanadium Corp.	
HS-2361	approx. 65.40	General Electric	Blades for gas jet engine, engine, locomotive turbines
HS-30 442	49 50	Haynes Stellite	Blades for gas jet engine, locomotive turbine and hollow blades
19 NR 12	51.00	Haynes Stellite	Blades for gas jet engine, locomotive turbine and hollow blades
X-40	54 00–58.00	General Electric	Gas turbine and jet engine blades

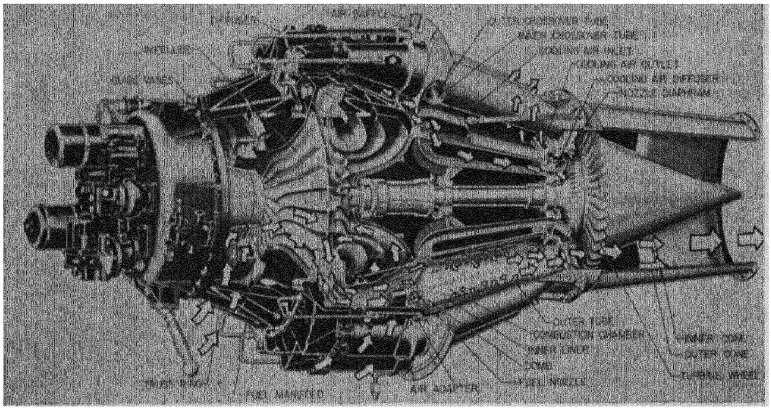
Ta 2, W 2.2; and C 1.21, Ni 30, Cr 20, Co 21, Mn 1.5, Mo 3.0, Cb 1.0, W 2.2, N 0.09%.

A round-table discussion at the American Society for Metals' National Metal Congress held in Cleveland, February 5th, 1946, was reported in *Metal Progress*, **50**, 97–122 (July, 1946). Haynes Stellite Alloy No. 21 (a modified Vitallium) was given as a cobalt base alloy containing Cr 27%, Mo 6%, Ni 2%, 0.2–0.3% C, and a trace of iron as an impurity. These cobalt-chromium alloys show a room temperature strength of 80,000 to

110,000 psi. Tensile strength of these alloys at 1350°F ranges from 66,000 to 80,000 psi. High strength, high temperature, nonferrous alloys have been reviewed by Epremain[8], Knight[12], Wilson[22], Browne[4], Bollenrath[3], Cross and Simmons[5], Freeman, Reynolds, and White[9].

Other Nonferrous Cobalt Alloys

Cobalt-tungsten-iron alloys containing little or no carbon rely upon a process of precipitation for their ability to harden. Consequently the heat-treatment consists of a "solution anneal" at an elevated temperature, preferably near the melting point, followed by quenching and reheating to a



Courtesy Allison Division, General Motors Corp., Indianapolis, Ind.

FIGURE 30. Cross-section view of turbo-jet engine. Cobalt-containing alloy is used in the blades of the turbine wheel.

temperature at which precipitation is allowed to take place. These alloys are an improvement over the precipitation-hardening iron-tungsten alloys, which can be aged to a hardness of only 52 to 55 Rockwell C. Substitution of cobalt for a portion of the iron in iron-tungsten alloys containing from 15 to 30% tungsten, results in a remarkable increase in the hardness in both the quenched and "aged" states.

The course of precipitation hardening as a function of reheating time and reheating temperature in iron-tungsten alloys and in several iron-tungsten-cobalt alloys is recorded in tables of the booklet of Molybdenum Corporation of America "Tungsten Steel"[15]. The latter materials, hardened to values in excess of 60 Rockwell C have received limited use in tool and die applications.

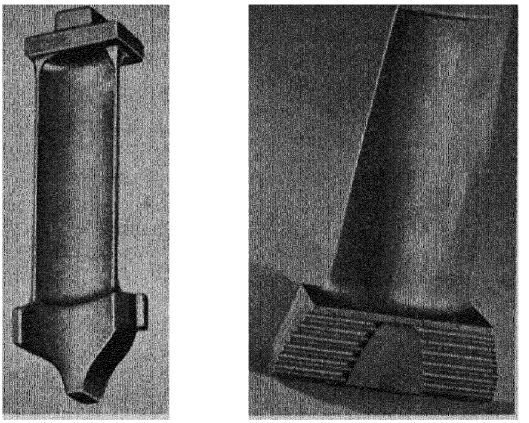
Cobalt brasses have been studied by Guillet[11]. Alloys with 2 to 3%

cobalt have superior hardness and this persists even when the temperature is carried to 700°. Such brasses at this temperature have a Brinell hardness of 90, strength of 55,000 psi, and elongation of 25%.

Small quantities of cobalt added to beryllium copper increase the hardness of the alloy and its electrical conductivity. This alloy is frequently used for conduction and welding electrodes.

Studies have been made on the effect of cobalt in "aluminum bronzes", the alloys containing 90% Cu and 10% Al[14].

A few alloys have been reported where cobalt is used with the light metals



Courtesy Haynes Stellite Co., Kokomo, Ind.

FIGURE 31. High-temperature alloy parts used in the aircraft industry. *Left:* Turbosupercharger bucket made of Haynes Stellite No. 21. *Right:* Gas turbine blade of same alloy used on turbine wheel of engine illustrated in Figure 30.

aluminum and magnesium[14, 21]. On the whole, however, these do not appear to have attained commercial importance.

Cobalt-containing alloys used in the construction of equipment in the chemical industries are listed in Table 15.

The Elgin National Watch Company has recently developed Elgiloy for watch springs[2]. This alloy, which is reported to contain 20% Cr, 40% Co, 15.5% Ni, 15% Fe, 7% Mo, 2% Mn, 0.15% C, and 0.03% Be, is nonmagnetic, has high corrosion-resistance, and excellent working properties hot or cold.

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Chapter 8
Cobalt in Powder Metallurgy

It is not surprising that cobalt is an important metal in powder metallurgy, for until very recently cobalt itself was produced for market only in the form of a rondel made by reduction of oxide by carbon at a temperature below the melting point—in other words a powder metallurgy operation.

Although Moissan at the end of the last century made tungsten carbide and pointed out its hardness, it was not until 1914 that tungsten carbide tools were produced, in Germany. In 1923 Schroter sintered tungsten carbide in a cobalt base[4], and about 1930 the cemented carbides began to attain great importance in industry. The cutting speed of machine tools has increased in the following manner. Before the advent of high-speed tool steels, a medium hard steel could be cut by carbon tool steels at the rate of 14 to 20 feet per minute before they became so hot that they lost their cutting edge. The introduction of high-speed tool steels containing cobalt increased this rate up to 120 to 180 feet per minute. With cemented carbides of tungsten, titanium, molybdenum, and tantalum, speeds can be increased to over 600 feet per minute.

The briquetted mixtures of tungsten carbide and of matrix metal, usually cobalt, are sintered at a temperature above the melting point of the latter. The cobalt melts and serves as a bond holding the hard carbides and adding the toughness and resistance to shock needed to make these carbides of practical value.

Cobalt is the most satisfactory matrix or binder for tungsten and other carbides. The cobalt grains sinter and dissolve the carbide to form a solid solution. Melting of cobalt around 1400° gives a liquid phase containing about 19% WC, representing around 8.5% of the sintered mass. This penetrates by capillarity between the grains of carbide and even diffuses partially into the crystals themselves. This partial solution of tungsten carbide in cobalt enables a lower sintering temperature to be employed than for tungsten carbide alone. On cooling, the carbide dissolved in the liquid phase crystallizes, for its solubility in the stable hexagonal form of cobalt is practically nil. The tungsten carbide appears as prismatic grains having a triangular base, with cobalt forming a thin border around the carbide.

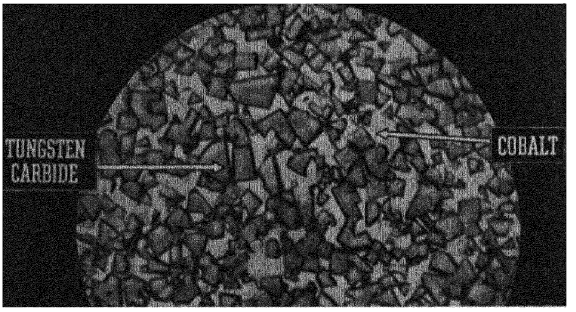
The normal carbide WC is preferred; W_2C is brittle, difficult to prepare,

and does not bond well with cobalt. About 3 to 15% cobalt is mixed with the carbide in powder metallurgy.

During the sintering period of cemented carbides the original compact shrinks about 25 to 30% from its initial size. This results in a great increase in density. There are many purposes for which a heavy metal is desirable, and cemented carbides have come into use for this purpose. A metal having a composition W 90, Co 5, Ni 5, has a specific gravity of 17, and is obviously better for many purposes than lead, which was formerly used, with its specific gravity of 11.

Production of Cemented Carbides

Cobalt powder, like W, Mo, Fe, Cu, and Ni, is made by reducing cobalt oxide with either hydrogen or one of the common reducing gases. It is



Courtesy Carboloy Co., Inc., Detroit, Mich.

FIGURE 32. Tungsten carbide particles cemented by cobalt in Carboloy.

an extremely flexible process and the product may be controlled closely by the temperature, pressure, and gas employed. The powder is, however, nearly always slightly porous, and if any oxide remains it is more significant than the oxide which is so frequently present in mechanically produced powders. The latter is primarily a surface oxide which does not materially reduce cohesion when the powder is used in a die. The oxide which may remain in a powder obtained by reduction is primarily that part of the original oxide which has not been reduced, and therefore lies in the center of the particle. Mechanical handling or the frictional attrition which may arise in the die during molding cannot reach this oxide, and its action is more objectionable.

In making cemented carbides, the nickel or cobalt in quantities from 3 to 15% and intimately mixed with the carbide, is subjected to a temperature which is high enough to melt it. It naturally flows to fill in cavities

between the carbide particles, and when the product has again reached room temperature, the once-liquid metal freezes in this new position. Thus it acts as a net in which the harder carbide particles are confined. When it is desirable to depend on this network phenomena it is very important to consider the physical affinity of the metal used to form the network. Cobalt clings closely when fused with tungsten carbide but it has little affinity for titanium carbide[1]. Therefore in tools made of tungsten carbide, cobalt is used as a binder, whereas in tools made of titanium carbide, nickel is employed since it has excellent affinity for titanium but a poor one for tungsten. Cobalt and nickel, however, are readily soluble in each other. Many modern tools are made of combinations of tungsten and titanium carbide, and it has been found desirable to use a mixture of cobalt and nickel as the cementing medium for these.

In making tungsten carbide, the aim is to form WC with no deficiency of carbon, since W_2C does not form a strong bond with the cobalt cementing medium. Carbides are mixed or milled with cobalt for a few hours or a few days until each carbide particle has been coated with a continuous layer of the softer binding metal. With a given binder content, which may range from 3 to 20%, a fine-grained cemented carbide is usually harder but not as strong as a coarse-grained one. Physical properties of some commercial cemented carbides are given in Table 18. Griffiths[3], in discussing the development of carbide detachable bits, states that tungsten carbide percussive drilling bits should not have more than 12% cobalt, since with further increase the durability of the carbide is offset by increased wear of the matrix.

Pressure is the least important factor in sintering cobalt powder, but the optimum pressure range to give maximum density of 8.7 is 20,000 to 80,000 psi. Temperature is the most important factor in bringing about maximum sintering, and time at this temperature is also important. A temperature of 1375° for 32 hours was shown[7] to be adequate for cobalt.

With tungsten carbide, nickel is a poorer binder due to absorption of gas and greater porosity. Nickel is not as poor a binder with tantalum carbide.

Additional light on what happens during the sintering of tungsten carbide-cobalt mixtures is thrown by some recently unearthed German work reported in *Metal Industry*, February 8, 1946. The results of sintering were studied, not by the conventional method of examining polished and etched surfaces, but by a leaching method in which thin sintered plates were boiled in hydrochloric acid to remove the cobalt. It was found that in materials with a cobalt content of less than 10 per cent, a strong network of firmly coherent tungsten carbide crystals is formed. With 20% cobalt no such network is formed, and on leaching the material broke down into small pieces. The strength of the carbide network after leaching was about the same as that of tungsten carbide sintered without cobalt.

Table 18. Properties of Cemented Carbides

Composition	Density (gm/ml)	Rockwell Hardness (A scale)	Transverse Rupture (psi)	Young's Modulus (psi × 10^6)	Compressive Strength (psi)	Proportional Limit in Compression (psi)	Impact Strength (psi)	Endurance Limit (psi)	Coefficient of Thermal Expansion
97% WC, 3% Co	15.25	92.7	170,000	97.5	815,000	780,000	—	—	—
95.5% WC, 4.5% Co	15.05	92.3	200,000	90.5	890,000	740,000	—	—	—
94% WC, 6% Co	14.85	90–92	225,000	88	750,000	600,000	0 73	95,000	5.0×10^{-6}
91% WC, 9% Co	14.60	89 5–91 5	275,000	—	685,000	540,000	—	—	—
87% WC, 13% Co	14.15	87.5–90	300,000	80	625,000	525,000	1 10	105,000	5.9×10^{-6}
80% WC, 20% Co	13.55	85–87	350,000	—	550,000	425,000	1.75	—	—
Predominantly WC, with TaC and 13% Co	13.90	87–88	275,000	—	610,000	475,000	—	—	7.25×10^{-6}
Predominantly WC, with TaC and 6% Co	14 70	91–92	220,000	—	752,000	670,000	0 65	85,000	—
Predominantly WC, with TiC and 6% Co	11.20	92–93	160,000	—	700,000	—	0.40	90,000	6.8×10^{-6}
Predominantly WC, with less TiC than above, 8% Co	12.80	91.5–92.5	250,000	—	570,000	560,000	0.60	90,000	—
Predominantly WC, larger amount of TiC, 7% Co	9.00	92–93	150,000	—	725,000	—	—	—	7.0×10^{-6}
Predominantly WC, with TaC and TiC, 8% Co	11.7	91.5–92.5	165,000	72	720,000	—	—	—	6.75×10^{-6}
Predominantly WC, with TaC and TiC, 11% Co	11.6	90.5–91 5	175,000	—	680,000	—	0 60	85,000	6.0×10^{-6}
Predominantly WC, with TaC and TiC, 15% Co	11.4	89.5–90.5	190,000	67	670,000	—	0.92	—	7.5×10^{-6}

Use of Cobalt-Containing Metal Powders

General Electric is producing "Fernico" for sealing vacuum tubes, and for other work where a metal having a similar expansion coefficient to glass is required. This is produced by the powder method and contains 16 to 18% cobalt.

The Austenal Laboratories in New York are turning out "Vitallium" for denture work. The powdered form of this alloy contains 25% Cr, 6% Mo, 3% Ni, 0.5% Mn, 0.5% Si, 0.25% C, and the balance cobalt.

The constituents, tungsten and cobalt, of cemented carbide tool steels are reducible with hydrogen in case the very fine powders have been oxidized slightly on their surfaces. Other elements like titanium, tantalum, and columbium form oxides which are not reducible by hydrogen during sintering, and consequently these powders must be protected carefully in handling.

A very useful cemented carbide is $WTiC_2$, with cobalt as a binder. It is used extensively for machining steels of tensile strength 80,000 to 270,000 psi or 167 to 552 Brinell hardness.

Tungsten-titanium carbides usually contain 6 to 8% cobalt.

Two general types of tungsten carbides in a cobalt base are known:

(*1*) *Cobalt content of 5 to 6% by weight, or 8.5 to 10.5% by volume.* These tools are used for cutting steels, nonferrous alloys, ceramic materials, glass, quartz, compressed graphite, rocks, plastics.

(*2*) *Cobalt content of 8 to 14% by weight, or 13 to 22% by volume.* Such tools are employed for mining drills, rough shaping of hard steels, machining of dies and matrices.

For wire-drawing purposes, as a general rule, the bigger the diameter of wire the greater the percentage of cobalt in the carbide tool. Below 10 mm diameter, tungsten carbide with 6% cobalt is used; above 10 mm diameter and for polygonal dies, 10 to 11% cobalt is employed. Larger wires require cobalt contents of 15% or more in the carbide.

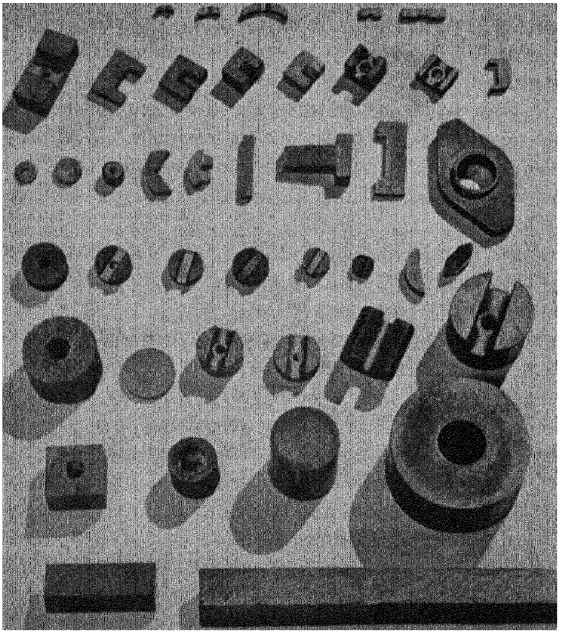
Standard relay contacts for telegraph transmission now consist of tungsten carbide bonded with cobalt. The Western Union Telegraph Company found that nickel was unsatisfactory for bonding. The introduction of tungsten carbide-cobalt polar relays to replace platinum-iridium alloys reduced the cleaning of contacts from a daily task to one not required during the two-year life of the contact.

In addition to machine tools, carbides are employed for dies, stamping matrices, circular saws, cartridge production, injection nozzles, valves for high pressure operations, etc.

Brown[2] discusses a tantalum-tungsten carbide tool with cobalt as a binder.

Diamond powder has been mixed with tungsten carbide and cobalt to form a very hard surface.

Carboloy is the trade name of a widely-used series of cemented carbides made by The Carboloy Company, Inc., a subsidiary of General Electric. The sintering temperature for Carboloy containing about 12.5% cobalt is 1375 to 1400°. The shrinkage on Carboloy is about 18 to 20% and the pressure employed is in the neighbourhood of 30 tons per square inch.



Courtesy General Electric Co., Schenectady, N. Y.

FIGURE 33. Numerous G-E sintered Alnico magnets.

The powdered cobalt used in Carboloy is produced from cobalt nitrate, and is minus 325 mesh.

The corrosion resistance of Carboloy decreases with increasing quantities of cobalt binder. The Rockwell hardness, compression strength, proportional limit in compression, and Young's modulus of elasticity decreases with increasing cobalt content in the carbide. Impact strength, endurance limit, and transverse rupture strength increase with increasing quantities of cobalt binder.

Some grain growth occurs during sintering. The smaller particles are absorbed into the larger ones, forming sharply angular forms required for cutting purposes. A coarse-grained sinter may have grains up to 15

μ diameter, while in a fine-grained carbide all grains may be under 6 μ in diameter.

Table 19. Characteristics of Cobalt Powder Produced in the United States
(*After Schumacher and Souden*)

How Produced	Purity or Composition	Available Meshes	Typical Applications	Powder Suppliers
Reduced	97.5–99%	−100 to −300	Electric tube materials, glass-to-metal seals, permanent magnets, tools, dies and wear-resistant parts	Chas. Hardy Inc., New York Reduction and Refining Co., Newark

Table 20. Powder Metallurgy Fabricators in the United States
(*After Schumacher and Souden*)

Material	Fabricator
Electronic tube materials	Callite Tungsten Co., Union City, N. J. Fansteel Metallurgical Corp., Chicago, Ill. General Electric Co., Schenectady, N. Y. Metroloy Co., Newark, N. J. North American Phillips, Dobbs Ferry, N. Y. Sirian Wire & Contact Co., Newark, N. J.
Glass-to-metal seals	Callite Tungsten Co., Union City, N. J. General Electric Co., Schenectady, N. Y. Others
Magnets	General Electric Co., Schenectady, N. Y. General Magnetic Corp., Detroit, Mich. Indiana Steel Products, Chicago, Ill. Stackpole Carbon Co., St. Mary's, Pa. Thomas & Skinner Steel Products Co., Indianapolis, Ind.
Tools, dies and wear-resistant parts	American Electro Metal Corp., Yonkers, N. Y. Callite Tungsten Co., Union City, N. J. Carboloy Co., Detroit, Mich. Firth-Sterling Steel Co., McKeesport, Pa. General Aircraft Equipment Co., S. Norwalk, Conn. Kennametal Inc., Latrobe, Pa. Metal Carbides Corp., Youngstown, Ohio New England Carbide Tool Co., Cambridge, Mass. Tungsten Alloy Mfg. Co., Newark, N. J. Tungsten Corp., Union City, N. J. Vascoloy-Ramet Corp., Chicago, Ill. Wesson Co., Ferndale, Mich. Willeys Carbide Tool, Detroit, Mich.

Production of small Alnico magnets by casting is much more difficult than by the powder method. The magnetic properties of the sintered magnets are comparable with those produced by casting. Since the grain size of the sintered product is much finer, the magnetic flux distribution is more uniform and its mechanical strength is higher than that of cast Alnico.

Alnico II, made by powder metallurgy at General Electric, has 12.5% cobalt, with 10% aluminum, 17% nickel, 6% copper, and the balance iron. Alnico V, known abroad as Ticonal, has 24% cobalt, with 8% aluminum, 14% nickel, 3% copper, and the balance iron. General Electric has also developed a higher cobalt Alnico magnet made by powder metallurgy, containing 35% cobalt, 6% aluminum, 18% nickel, 8% titanium, and the balance iron.

Howe of General Electric has contributed a brief chapter on sintered Alnico in Wulff's book[7].

A symposium on production and design limitations and possibilities for powder metallurgy parts was reported in *Am. Inst. Min. Met. Eng., Transactions*, Vol. **161,** 525–634 (1945).

Schumacher and Souden[5] in November, 1944, *Metals and Alloys** list metal powders and their suppliers, with powder metallurgy applications and manufacturers of parts and products. Tables 19 and 20 on page 111 are reproduced from their paper.

Steinitz[6] describes a permanent magnet "Permet" made from powder, consisting of Ni 25%, Co 30%, Cu 45%.

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* The name was changed in 1945 to *Materials & Methods*

Chapter 9
Electroplating of Cobalt

Cobalt Plating

Cobalt plating has not achieved the commercial importance it once promised to attain. Various factors are responsible for this failure. The other demands for the metal and its relative scarcity have kept the price high in relation to competing nickel and chromium. Since cobalt oxidizes more easily than nickel or chromium it is not suitable for heating appliances.

Electroplated cobalt has a similar pleasing appearance to nickel but with a slight bluish tinge. Considerably higher current densities can be used than in nickel plating. Careful pioneer work on cobalt plating was done by Watts[14], Kalmus and associates[7], and recent references to cobalt plating are given in Creighton and Koehler[3]. Cast or rolled anodes have been used successfully in cobalt electroplating. The bath composition below is typical for cobalt plating:

	Gm/liter	Oz/gallon
Cobalt sulfate, $CoSO_4$	278	37.0
or $CoSO_4 \cdot 7H_2O$	504	68 0
Sodium chloride, NaCl	17	2.3
Boric acid, H_3BO_3	45	6.0
Temperature, room		
Current density, 3.5–17.5 amperes per sq dm, or 33–163 amperes per sq ft		

The Brinell hardness of cobalt deposits may vary between 270 and 311, that of nickel between 180 and 420.

The electrical resistance of cobalt is approximately 8.96×10^{-6} ohm per cm cube at 18°. The temperature coefficient of the resistance is about 0.0036 between 0° and 100°. The specific resistance of cobalt is greatly increased by the presence of impurities.

In the electrochemical series cobalt occupies a position between thallium and nickel, the standard electrode potential for $Co \rightarrow Co^{++}$ at 25° being + 0.278 volts. The deposition potential of cobalt from solutions of sulfate and chloride in different acidities and temperatures has been noted by Mellor[9].

The cathodic or hydrogen overvoltage for a cobalt electrode in N-H_2SO_4

has been given as 0.22 to 0.29 volt at 20° by various workers. Table 21 gives the cathodic overvoltage of cobalt with varying current densities in normal solutions of the following salts.

Table 21. Cathodic Overvoltage of Cobalt

	Current Densities (milliamp per sq cm)							
	2	6	10	20	50	100	200	400
$CoSO_4$	0.50	0.48	0.48	0.48	0.50	0.51	0.51	0.49
$Co(NO_3)_2$	0.26	0.38	0.45	0.57	0.73	0.72	0.69	0.64
$CoCl_2$	0.31	0.30	0.31	0.32	0.35	0.38	0.44	0.53
H_2SO_4	0.27	0.28	0.28	0.27	0.27	0.26	0.26	0.25
NaOH	0.25	0.28	0.28	0.29	0.29	0.29	0.30	0.30

The cathodic overvoltage is similar to that of nickel but is more constant. At very high current densities, rapid increases of overvoltage take place occasionally. The effect is a surface one, since cleaning the surface restores the normal overvoltage.

Cobalt becomes passive under certain conditions of electrolysis. The literature on the passivity of cobalt in electrolysis is voluminous and confused. This is to be expected where voltage, amperage, nature and concentration of electrolyte, temperature, form of electrode, and other variables affect the oxide film or surface modification formed by metals under conditions of passivation. Cobalt does not become passive at the low current densities required by nickel and iron.

The oxygen or anodic overvoltage of cobalt for varying current densities in normal solutions of the following salts is given in Table 22.

Table 22. Anodic Overvoltage of Cobalt

	Current Density (milliamp per sq cm)							
	2	6	10	20	50	100	400	1200
NaOH	0.58	0.60	0.59	0.58	0.58	0.57	0.56	0.54
$CoSO_4$	0.02	0.03	0.03	0.04	0.05	0.06	0.06	0.08
$Co(NO_3)_2$	0.11	0.11	0.09	0.06	0.00	0.00	0.02	0.02
$CoCl_2$	0.03	0.02	0.00	0.02	0.03	0.02	0.03	0.07

A number of factors in the electrodeposition of cobalt were studied by the U. S. Bureau of Mines[4, 6, 10, 11, 12]. The conductivity-pH relationship of the standard electrolyte containing per liter about 20 gm of cobalt as cobalt sulfate, 50 gm of boric acid, and 5 gm of sodium fluoride, may be expressed by the equation:

$$2.44C = 10^{-pH} + 0.0640 + 0.00125\ (T\text{-}29.6)$$

where T is degrees Centigrade. The mole-per cent of hydrogen released at the cathode is approximately equivalent to the percentage of the total current carried by the H^+ ions.

The specific viscosity of a cobalt sulfate electrolyte containing about 50 gm per liter boric acid and 5 gm per liter sodium fluoride can be calculated from the formula:

$$u = 1.468^k$$

u being the specific viscosity at 30° and k the normality of the electrolyte in cobalt. For pure cobalt sulfate solutions at 25°, the same formula becomes

$$u = 1.353^k$$

The temperature coefficient of specific viscosity for a fluoborate electrolyte containing 5 gm sodium fluoride, 19.76 gm cobalt sulfate per liter, and boric acid to saturation or 50 gm per liter, whichever is smaller, can be estimated to 0.1% by Meyer's formula:

$$u = 1.231 + 2.043 \times 10^{-3}T$$

T being temperature in degrees Centigrade. The formula gives an estimate to within less than 1% of the specific viscosity of electrolytes over a fairly wide range of both temperatures and cobalt concentrations.

Churchward, Shelton, and Knickerbocker[2] found in electrolyzing a standard fluoborate electrolyte containing 20 gm/l cobalt as $CoSO_4$, 50 gm/l boric acid, and 5 gm/l NaF at 25 amperes/sq ft (2.7 amperes/dm²) using lead anodes and stainless steel cathodes, the maximum tolerance for the metallic impurities for the production of satisfactory 7-hour cobalt electrodeposits is, in mg/l: Zn 10, Cd 1, As (trivalent) 3, As (penta-) 1, Sb (tri-) 10, Hg (di-) 1. Tri- and hexavalent chromium in concentrations up to 100 mg/l were only slightly harmful, while nickel, copper, iron, and manganese were not found deleterious. The impurities may be removed by: (1) Recrystallization of $CoSO_4$ or $CoSO_4(NH_4)_2SO_4 \cdot 6H_2O$. (2) Precipitation of the impurities with H_2S under 20 lb/sq in (1.4 kg/cm²) in solutions of pH 4 followed by the familiar iron purification.

Torrance reported cobaltic oxide, Co_2O_3, can be deposited on the anode from a faintly acid solution[13]. The Sand revolving-diaphragm electrode was used to separate the cathode from the cobalt solution, thus inhibiting the deposition of cobalt as metal. Cobaltic oxide is not deposited from a solution with acidity much stronger than pH 3.5. The anolyte must be buffered with sodium acetate. The anolyte was cobalt solution, and the catholyte was $2N$ HNO_3. Adherent deposits could not be obtained much above 0.0556 gm cobaltic oxide.

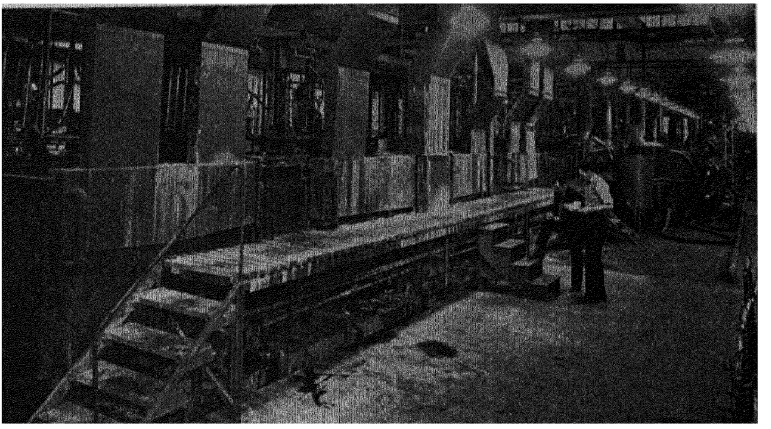
Kramer, Swann, and Bailar[8] studied the electrodeposition of cobalt from coordination compounds. A series of cobaltic and cobaltous ammines were

investigated, and the nature of the coordinating groups and the stability of the complex ions were more important in plating results than pH variations.

Cobalt-Nickel Plating

Although cobalt plating itself has not attained any commercial importance, the addition of cobalt to nickel for plating purposes has in recent years become widespread.

Weisberg in 1938 stated the electrodeposition of cobalt-nickel alloys had attained a significant commercial position within a little more than two years as a result of the discovery[17] that the presence of sodium formate and

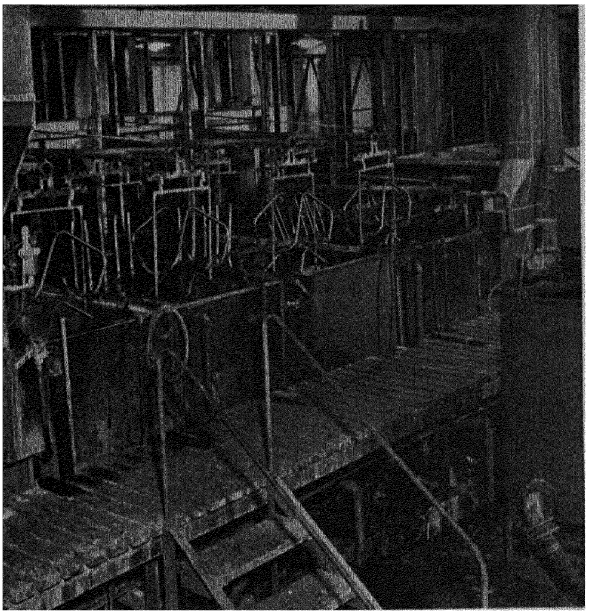


Courtesy Hanson-Van Winkle-Munning Co., Matawan, N. J.

FIGURE 34. Fully automatic electroplating conveyor for cobalt-nickel plating of tubular furniture.

formaldehyde in the sulfate bath renders it easy to obtain lustrous deposits of the alloy requiring no buffing or coloring after plating. The composition of the solutions used and the operating conditions necessary for producing such deposits are described[15]. The deposits are normally very ductile and can be bent or twisted without lifting or peeling. Pitting and double plate are rarely encountered. The presence of lead, copper, iron, zinc, and certain organic impurities reduces the brightness and also the throwing power. Brittleness when it does occur is caused by the presence of impurities. Methods of eliminating impurities to maintain optimum brightness and ductility are specified. Weisberg gave the following composition for a typical bath:

	Gm/liter
Nickel sulfate	240
Nickel chloride	45
Sodium formate	35
Boric acid	30
Cobalt sulfate	15
Ammonium sulfate	2.5
Formaldehyde	1



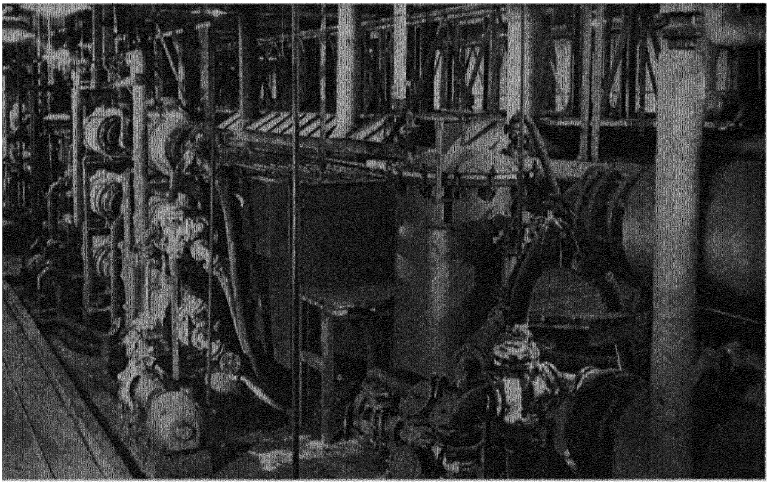
Courtesy Hanson-Van Winkle-Munning Co., Matawan, N. J.

FIGURE 35. Detailed view of middle section of Figure 34, showing work carriers leaving treatment tanks prior to cobalt-nickel plating.

The pH is 3.7 and the current density 4.3 amperes/dm^2. A temperature of 60°, and mechanical or air agitation are employed.

The solution of Weisberg and Stoddard is easily controlled. The anodes generally contain 1%, 5%, or 18% cobalt. Plated articles can be deformed severely without rupture of the coating. For example, cobalt nickel deposits can be applied to a $\frac{3}{8}$-inch diameter cold-rolled steel rod such as is used in making hand braces, the wooden handle slipped on, and then the braces bent to a 90° angle. The deposit does not flake off and presents a good appearance on the bend after this treatment.

In 1940 Weisberg reported that improvements in methods of removing impurities have made it possible to reduce the cobalt content of the deposit for some purposes as low as one per cent[16]. Substitution of nickel formate and formic acid for sodium formate, and use of less ammonium sulfate have resulted in deposits that are more ductile and easier to buff than those



Courtesy Hanson-Van Winkle-Munning Co., Matawan, N. J.

FIGURE 36. Equipment used in cobalt-nickel plating, showing purification tank (*center*), filter (*right foreground*), heat exchangers (*left foreground and extreme right*), and automatic electroplating conveyor (*background*).

formerly obtained. He gave the following composition for a satisfactory bath:

	Gm/liter
Nickel sulfate	240
Nickel chloride	30–45
Nickel formate	45
Boric acid	30
Cobalt sulfate	3–15
Ammonium sulfate	1–2.5
Formaldehyde	1

The pH is 2 to 4 and the temperature 60 to 70°. Impurities are removed by adding activated clay or alumina.

Cobalt-nickel plating solutions produce smooth, bright deposits, varying in color from white to blue-white. The coatings are hard but relatively ductile, non-laminated, of low porosity, and have exceptionally high

protective value. Cobalt-nickel baths can be continously purified without interfering with plating operations. Cobalt in the deposits can range from 1 to 18%. The 1% cobalt bath is widely used on a variety of automobile parts, such as bumpers. Typical present day formulae are given in Table 23, taken from trade literature of the Hanson-Van Winkle-Munning Co., Matawan, N. J.[5].

The process of bright nickel plating has also been reviewed recently by Brockington[1].

Agitation of the solution is essential to produce bright deposits. This may be achieved by mechanical means or air agitation. In the latter case the air must have any oil removed.

Table 23. Composition of Cobalt-Nickel Plating Solutions

	1% Co Deposit (oz/gal)	5% Co Deposit (oz/gal)	18% Co Deposit (oz/gal)
Nickel sulfate	32.0	32.0	32.0
Nickel chloride	4.0	4 0	4.0
Nickel formate	6 0	6 0	6.0
Cobalt sulfate	0 35	0 60	2 0
Boric acid	4 0	4 0	4 0
Ammonium sulfate	0 10	0 10	0.10
Formaldehyde	0 33	0.33	0.33
pH*			
(1) For maximum brightness and throwing power	3 7	3 7	3.7
(2) For semi-bright deposits with greatest softness and ductility	2 3	—	—

* Electrometric.

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Chapter 10

Cobalt Compounds in the Glass and Ceramic Industries

Cobalt is used to impart a blue color to glasses, enamel, pottery, and glazes. The color is stable at a high temperature and is unaffected by the presence of silicates. Cobalt oxide or smalt is used in preparing underglaze colors for the ultramarine blues. It is also employed for producing a matte or turquoise blue from cobalt aluminate. Soluble cobalt salts or cobalt oxide mixed intimately with clay are used to counteract the effect of traces of iron or other substances in the raw materials which give a yellow color to the latter. Cobalt is one of the most satisfactory coloring agents in the glass and ceramic industry, since oxidation and reduction in the melt have no effect on the color.

For several centuries a blue glass, called "smalt", has been prepared in many parts of the world by coloring fused potassium silicate with cobalt. In Saxony, where this product was developed about the sixteenth century, a crude crushed cobalt ore was roasted to produce a substance called "zaffre." This was mixed with potassium carbonate and sand, and fused to a glass. The blue glass was separated from the heavier impurities settling out at the bottom, crushed and ground to powder. The presence of oxides other than those of cobalt and potash, even in small quantities, markedly influences the color of the smalt.

Chinese porcelain for many centuries has depended on cobalt for the blue-and-white ware of the Ming dynasty (1368 to 1644) and of the Manchu dynasty (1644 to 1912). Throughout this long period there were generations when exceptionally fine porcelain was produced, followed by intervals characterized by a deterioration in coloring. These variations can probably be explained by changes in the character of cobalt ores, as well as by periods of artistic decadence and renaissance.

Cobalt violet, $2\ CoO \cdot P_2O_5$, has been used to give a violet color. It is made by calcining a cobalt salt with sodium phosphate. The same violet can be obtained by using zinc phosphate or sodium arsenate.

Cobalt yellow is potassium cobaltic nitrite. It can be used for oils or water colors. When used for painting porcelain it produces on baking the usual blue color.

Cobalt brown is prepared by calcining a mixture of cobalt, ferrous, and ammonium sulfates.

Cobalt bronze is a violet cobalt ammonium phosphate which has a bronze luster.

Cobalt magnesia pink is produced by a mixture of magnesium oxide and cobalt oxides and is generally formed by firing magnesium carbonate with cobalt nitrate.

Cerelcum or blue céleste is produced from oxides of tin and cobalt, and calcium sulfate or silica. It may also be prepared by precipitating a solution of cobalt nitrate with sodium stannate and heating the precipitate. Its composition may be expressed: tin oxide 49.7, cobalt oxide 18.7, calcium sulfate or silica 31.6. It is a light blue pigment of slightly greenish tinge, appearing violet under artificial light.

Thenard's blue, cobalt blue, cobalt ultramarine, azure blue, or King's blue is a fine ultramarine color. It is essentially cobalt aluminate. The presence of excess cobalt imparts a slightly greenish tinge. It is one of the most permanent blue pigments and is widely used.

The Thenard's blue colors include the range of blues known as "matte" blues. These are prepared by heating cobalt oxide with ammonium alum or potash alum and alumina with the addition of varying quantities of zinc oxide. From 20 to 30% of zinc oxide helps to weld the color to the body in the ceramic industry without destroying the blue.

New blue is a blue pigment varying in color from greenish-blue to deep turquoise, and is largely used for enamels. It consists of aluminates of cobalt and chromium produced by the action of alum on carbonate and hydroxides of cobalt and chromium, and the subsequent firing of the resultant precipitate. Turquoise green is made by firing a mixture of cobalt oxide, chromic oxide, and alumina.

Rinman's green or cobalt green is a fine permanent pigment varying from light to dark green. It may be prepared by mixing a solution of pure cobalt sulfate or nitrate into a paste with zinc oxide and heating in a muffle furnace for several hours. It may also be produced by the precipitation of a mixture of solutions of zinc and cobalt salts by means of sodium carbonate, phosphate, or arsenate, drying and heating the precipitate.

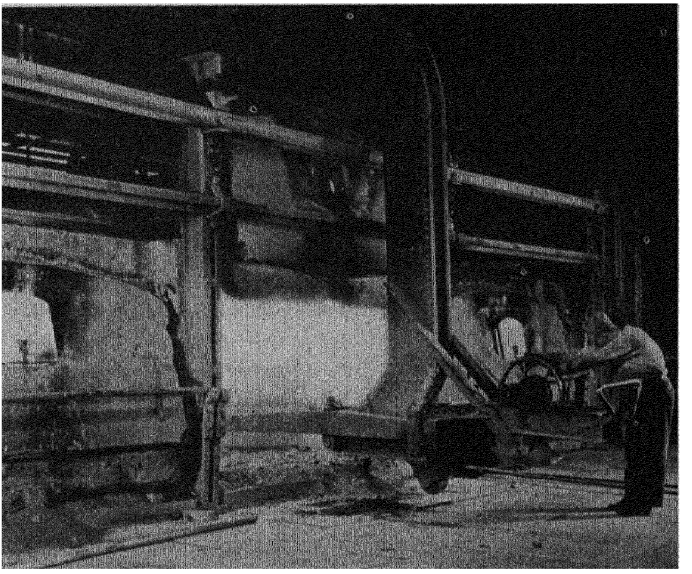
Cobalt in Glass

The presence of 0.005% cobalt oxide imparts a bluish tint to clear glass. The presence of other oxides has an injurious effect on the color produced, and for delicate work it is necessary to have very pure cobalt compounds. Copper, for instance, gives a greenish blue.

Glassmakers prefer finely-divided cobalt oxide powder to give uniform batches of colored glass.

A full description of the effect of cobalt on glass is given by Weyl[8].

From x-ray diffraction studies on crystalline substances it is found that pink or red colors result when the cobalt ion is surrounded by six oxygens. Blue colors occur when cobalt ions are surrounded by only four oxygen ions. When oxygen is replaced by other elements such as halogen or sulfur atoms, a more complicated behaviour results. In cobalt glasses the blue coloring center has such a strong absorption that whenever small concentrations of CoO_4 groups are present, the pink color of the saturated complex, CoO_6, is masked. As a result, the pink color of cobalt can only be



Courtesy Pittsburgh Plate Glass Co., Pittsburgh, Pa.

FIGURE 37. Pot-casting method for making small batches of special glasses, such as those containing cobalt.

obtained in glasses of unusual composition such as certain phosphates and borates where no formation of CoO_4 is possible.

Potash glasses give a purer blue than the corresponding soda glasses, and in borosilicates, reddish hues are obtained. All cobalt glasses have a high transmission in the red end of the spectrum, making them suitable for detecting traces of potassium in a flame test even in the presence of sodium. The intense yellow D-lines of sodium at 5889 and 5895 Å are strongly absorbed, whereas the characteristic lines of potassium at 7664 and 7688 Å are transmitted.

Alkali oxides have to be present in a cobalt-containing glass to supply

the oxygen ions necessary to form CoO_4 units. In the absence of alkali, cobalt is immiscible in glass melts. For instance, 90% SiO_2 and 10% CoO separate into two liquids on melting, and the same condition occurs with B_2O_3:CoO mixtures.

Most cobalt glasses which are pink at room temperature turn blue on heating, indicating that the average coordination number of cobalt decreases with increasing temperature. There is evidently an equilibrium between the two color centers which depends on the temperature, and on cooling, this will be frozen in by the increasing viscosity of the glass which makes atomic rearrangements difficult.

Cobalt ions in solution or in crystals cannot be excited to fluorescence, but many cobalt glasses when irradiated with ultraviolet light emit a brown to greenish fluorescence. The suggestion of Weyl, that neutral cobalt atoms are present in the latter case, should be investigated.

When removed from the melt the surface of cobalt-containing glass cools faster than that of a colorless glass. This is due to the increased infrared emission of cobalt-containing glasses. The faster cooling during the working range shortens the time available for certain moulding operations, producing the same effect as a higher temperature coefficient of viscosity. This, of course, is of consequence only when changing melts frequently in a glassworks.

The Pittsburgh Plate Glass Company reported the following uses for cobalt in their industry[6]:

(1) To impart a blue color to structural glasses. As much as 5 lb of cobalt per ton of glass may be used for this purpose.

(2) Ophthalmic glasses and optical filter glasses frequently employ cobalt. For example, the glass in the goggles used by furnacemen and welders may contain as high as 7 lb of cobalt per 1,000 lb of sand or 1,400 lb of glass.

(3) Cobalt is occasionally used for decolorizing purposes in plate and window glasses, to neutralize the yellow tint of iron and selenium, in quantities of 1 to 2 grams per ton of glass.

(4) Blue mirror glass sometimes contains a small quantity of cobalt.

The B. F. Drakenfeld Company of Washington, Pa.[1] gave the following uses for cobalt from the standpoint of a pigment manufacturer:

(1) *Glass Making*

(a) As a decolorizer to neutralize yellow and orange. Cobalt arsenate is frequently employed, and the cobalt content may range up to 3.3%.

(b) To produce blue glass. The quantities employed here depend on the shade of blue desired. For example a pastel blue is obtained by the use of 4 oz of cobalt per 1000 lb of glass.

(2) *Ceramics*
- (a) To produce blue pigments.
  - (I) As a silicate.
  - (II) As a zinc: cobalt compound.
  - (III) As an aluminate.
- (b) To mix with yellow to give greens.
- (c) To add to ground coat of enamel to enable the latter to adhere to steel.

The Maryland Glass Company, of Baltimore, is one of the largest users of cobalt in glass, and their observations on the subject are of interest[4]. Blue glass is popular for pharmaceutical, perfume, and decorative bottles. Cobalt has no light-protective properties for glass, but merely a sales appeal. Their dark blue bottle glass contains about 18 oz of cobalt oxide (70% Co) to 1 ton of batch, while a light blue shade is obtained with about 7.5 oz of cobalt oxide per ton of batch. Cobalt is preferably added as oxide to ensure uniformity of cobalt content, since many other cobalt compounds have a varying composition owing to water of crystallization. To kill the yellow color of many glasses, Maryland Glass Company uses about 1 part of cobalt to 20,000 parts of glass. Cobalt can be used as a color modifier, with copper and chromium, to give varying shades of blue and green. One disadvantage of cobalt is that appreciable differences in transmission result from small variations in thickness, imparting a spotty or streaked appearance to glass unless the latter is very uniform in thickness.

An interesting use for a very small quantity of cobalt is as a fused coating of blue glass on lamp bulbs for insect repellants.

Cobalt in Ceramics

Cobalt is used chiefly in the ceramic industry for the following purposes:

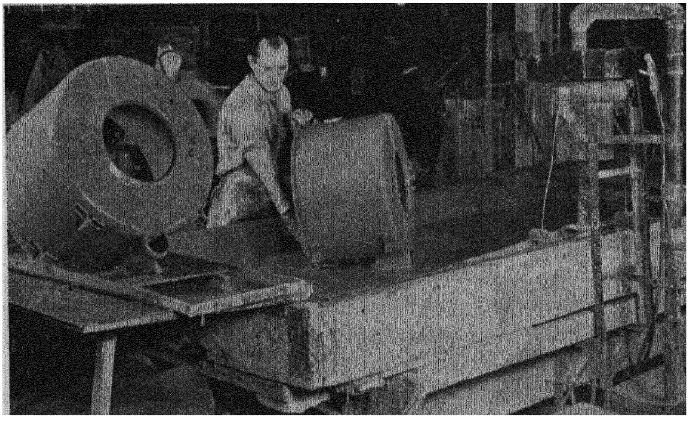
(1) *Body Stain.* Nearly all the clays used for pottery bodies contain iron which gives a yellow stain to the fired goods. This can be neutralized by the addition of the complementary blue color imparted by cobalt. Black cobalt oxide is mixed with about 10% of china clay, thoroughly ground with water, and passed through a 200-mesh sieve. The product is added to the pottery body in the next stage in the proportion of about 1 lb of cobalt oxide to 1 ton of dry pottery body. Sometimes cobalt is added as chloride. Cobalt oxides in larger quantities are used to color bodies various shades of blue. Other oxides such as those of manganese, nickel, chromium, etc. may be added to obtain different blues.

(2) *Glaze Stain.* A very rich blue color may be obtained by adding 5% cobalt oxide to a glaze of high lead content. The oxide may be added

either raw or after fusing with a soft frit in a crucible, running into water, and grinding with the necessary quantity of glaze. Addition of oxides of iron, manganese, nickel, copper, or chromium may be made to secure various shades of blue.

(3) *Under-Glaze or On-Glaze Stain.* For this purpose the usual stains are smalt or Thenard's blue. The latter gives a turquoise blue characteristic of cobalt aluminate, whereas smalt gives the typical violet blue of cobalt silicate.

(4) *Enamels.* Cobalt oxide is used in the production of white enamels to neutralize any yellow due to the presence of iron. Smalt is employed to



Courtesy Ferro Enamel Corp., Cleveland, Ohio

FIGURE 38. Ground-coat dipping.

color enamels blue. Cobalt oxide added to some mixtures gives an excellent black enamel.

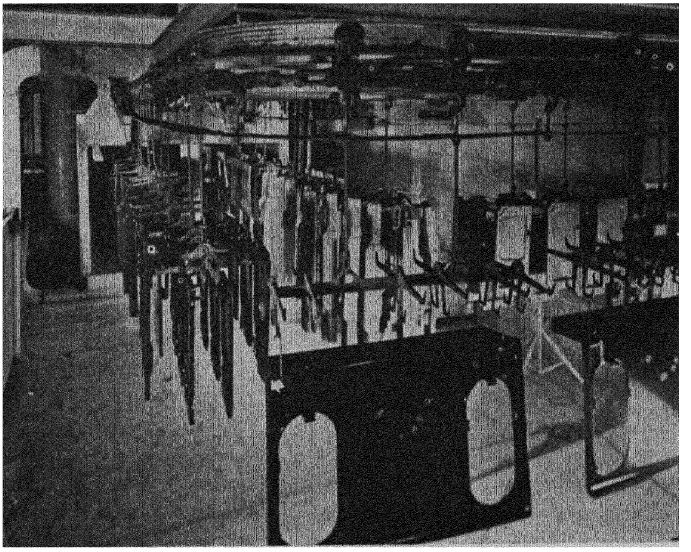
Cobalt oxide in quantities up to about 0.5% is used in ground enamels for iron vessels to increase the adherence of the enamel to the metal. From 0.2 to 2.3% cobalt oxide is used in enamel coats on steel [5]. Grey enamelled kitchen ware is usually made by a mixture of cobalt and nickel sulfates, singly or in combination.

Cobalt is the best metal to promote the adherence of enamel to steel. There does not seem to be any satisfactory explanation for this action. We need more information on this effect. Unfortunately, unless a blue tint is unobjectionable in the finished enamel, a second coat is necessary if white is desired. Tin oxide is a common source of white for enamels, but does not adhere to steel without the ground coat of cobalt oxide.

Priddey[7] discusses cobalt in enamel ground coats and concludes that no one theory offers an adequate explanation for the action.

The Ford Motor Company reported to the writer an interesting observation that white or light-colored alkyds, when cobalt is used as a drier, tend to yellow or darken, particularly if baked[2]. No explanation was given for this behavior, and it offers a field for investigation.

The Harshaw Chemical Company, of Cleveland, are large producers of cobalt compounds for a variety of uses. Their observations on the use of this element in the ceramic industry may be summarized as follows[3].



Courtesy Ferro Enamel Corp., Cleveland, Ohio

FIGURE 39. Ground-coat burning, showing stove parts entering the continuous furnace at right and leaving at left.

Cobalt blues are widely used in porcelain and pottery. For artists' pigments, the phosphate, arsenate, and aluminate are used. Cobalt aluminate is a good pigment for high temperature plastics where organic dyes are unsuitable. Cobalt arsenate is an artists' oil pigment, and is used in jewelry and enamel more than in glazes.

Cobalt stannate is "cereleum blue". A combination of cobalt, zinc, and chromium also gives an excellent color. Cobalt aluminum silicate is the compound generally formed in ceramics where cobalt is employed. Until very recently it was the only satisfactory blue color. Cobalt substitutes

for a ceramic blue were not found satisfactory in Germany during World War II. The range of cobalt in glazes and enamels is from 0.5% to 5%. Cobalt borate is a museum piece in ceramic art.

Cobalt is not used in water colors; the so-called "cobalt blue" of water colors is not a compound of cobalt.

Cobalt alkali silicate is a ground coat for enamel, 0.5 to 3% cobalt promoting the adherence of the next enamel coat to steel. There is no replacement for cobalt in this role. It is assumed that cobalt is a promoter of the oxidation of the surface layer of iron or steel to Fe_3O_4, giving greater adherence. All black oxide colors for enamels and glazes contain cobalt oxide. Usually these consist of chromium, iron, and cobalt, with a little manganese.

A standardization of nomenclature among producers of cobalt pigments and glasses would be very desirable. "New blue" and "turquoise green" for the same compound and color is confusing, and there are many similar instances where the science of ceramics and glass technology has not yet overcome the lack of logic in the art of these industries.

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Chapter 11
Catalytic Behaviour of Cobalt

The catalytic reactions of cobalt are in several cases, for instance in the drying of paints and varnishes, of great economic importance. In other instances the catalytic effect of this element is of considerable scientific interest. As a general rule the cost of a catalyst is of small importance compared to its efficiency, and further studies on possible substitution of cobalt for iron, nickel, etc., in many catalytic reactions may well show substantial economies.

Driers. A number of cobalt salts, particularly organic compounds, have been found to be excellent driers of paints and varnishes. Cobalt salts enable the low priced semi-drying oils such as fish, soybean, and cotton-seed oils to be used in place of higher priced linseed oil in paints. Cobalt driers are also used in the manufacture of waterproof fabrics, artificial leathers, linoleum, and other products.

When cobalt acetate is used for drying linseed oil, about 0.3% is required. The oil is heated to about 150 to 200° and the acetate is stirred in until dissolved. Soybean oil is treated with cobalt acetate in a similar manner.

Cobalt borate is prepared by adding a solution of cobalt sulfate to a cold solution of borax, and the precipitate is filtered, washed, and dried. Cobalt benzoate is prepared by adding cobalt carbonate to a solution of benzoic acid until neutral, filtering, drying and grinding the final product.

In the final production of cobalt resinate the best American water-white rosin is used, which should be completely soluble in turpentine and ether, having a melting point of 75 to 85° and a saponification value of 167 to 180. The resinate may be prepared by either the precipitation or the fusion method. For the precipitation method, the resin suspended in water, is heated to 100° and a 20% solution of sodium hydroxide is added with stirring. A solution of sodium chloride is then added to the clear brown solution. The precipitate of sodium resinate is dissolved in hot water and a 10% solution of cobaltous chloride is added to precipitate the green cobalt resinate which is washed and dried. The fused resinate is prepared by heating the resin to 140° and adding cobalt hydroxide with stirring. The temperature is then raised to 170 to 180° and the melt poured into pans and allowed to cool. The precipitated resinate contains about 7.5% cobalt and the fused product about 4.2% cobalt.

The fatty acid driers are generally made with linseed oil, although others such as soybean, tung, or walnut oil can be utilized. The linseed oil is completely saponified by gradually adding 10% sodium hydroxide to the oil heated to 100°. The clear brown solution is then diluted with hot water and a solution of sodium chloride added. The granular soap formed is removed, redissolved in water, and reprecipitated with brine. The purified soap is again dissolved in water and a 10% solution of cobaltous chloride is added. The precipitated cobalt linoleate is filtered, washed, and dried at 80°.

When 1.5% of a good drier is dissolved in linseed oil at a temperature of 120°, it should cause a thin film of this oil to dry at room temperature to a removable skin in 7 to 8 hours.

In recent years cobalt linoleates have practically supplanted resinates and oleates for drying agents in paints and varnishes. Linoleates may contain in the pasty or solid form about 6% of cobalt, and in the liquid state about 4% cobalt. For very rapid drying the naphthenates are preferred, containing around 12% cobalt. It usually requires approximately four times as much manganese as cobalt for the oxidation of drying oils. Cobalt linoleates are largely used in enamels and white paints. Cobalt naphthenate may be used everywhere. Cobalt acetate is also used as a drying agent for boiled linseed oil which is used as dressing on tarpaulins for railroad or marine service.

The Harshaw Chemical Company sells cobalt compounds for drying purposes and reports that in addition to the organic cobalt compounds the carbonate and sulfate are also used in paint driers[17]. Cobalt in any form will dry oil, but the physical state is the important thing, depending on the use. The printing trade, for instance, likes a heavy drier for ink.

Blue-colored cobalt is desirable for driers in paint to neutralize any yellow. In driers, cobalt ranges from 2 to 16%, resinates usually having 2%, while naphthenates run 12 to 16% cobalt. Cobalt is the best drying element, as it is fast and does not discolor as much as manganese, lead, or other metals.

The drying time for raw linseed oil with various driers is illustrated in Table 24[20].

Reference has already been made on page 127 to the darkening effect of cobalt driers on light-colored alkyds.

Ammination of Ethylene and Propylene. Cobalt catalysts are used for direct ammination of ethylene and propylene. This is described in a patent issued to the Sinclair Refining Co. in *U.S.P. 2, 381, 473*, cited in *Chemical Abstracts*, **39**, 5253 (1945).

Decomposition of Ethylene. When a cobalt catalyst prepared by calcining the nitrate on pumice followed by hydrogen reduction, is heated in a current of ethylene, no liquids are found up to 545°, while much carbon

is deposited. At 400° there is about 40% decomposition, yielding mostly hydrogen and a small amount of ethane. At 515° there is 97% decomposition into a gas containing principally hydrogen, a small amount of ethane, and 13% methane. Reduced cobalt has no effect upon ethylene at ordinary temperatures, but above 360° the gas is decomposed into hydrogen, ethane, carbon, and small quantities of benzene and its homologs. It is less active than nickel but acts similarly.

Desulfurization of Crude Oil. Cobalt and molybdenum mounted on alumina is used for catalytic desulfurization of crude oil by splitting out sulfur from the thiophene ring. This process is cited in a patent to Union Oil Co. of California in *U.S.P. 2, 369, 432*, recorded in *Chemical Abstracts*, **39**, 5451 (1945).

Fischer-Tropsch Synthesis. Although Sabatier[26] showed in 1902 that methane could be produced from carbon monoxide and hydrogen in the

Table 24. Drying Time for Raw Linseed Oil with Various Driers

Drier	Metal (%)	Drying Time (hours)
Cobalt linoleate	0.0494	11.5
Cobalt resinate	0.0483	10
Cobalt naphthenate	0.0494	12
Manganese linoleate	0.0316	18
Manganese resinate	0 0442	18
Manganese naphthenate	0 0499	17
Lead linoleate	0.3373	66
Lead resinate	0 3298	66
Lead naphthenate	0.3129	49

presence of a cobalt catalyst, it was not until 1925 that the synthesis of liquid hydrocarbons at ordinary pressure from water gas was demonstrated by Fischer and Tropsch. The investigations of Fischer and his coworkers have been reported in many publications[9, 10, 11, 12]. The success of their work depended on three main points; maintenance of a constant temperature of 190°, elimination of sulfur from the reacting gases, a catalyst such as cobalt, iron, or nickel. A very satisfactory catalyst is cobalt-thoria-kieselguhr; the usual proportions being $Co:ThO_2$:kieselguhr = 100:18:100. In time, the catalyst must be regenerated owing to the action of the traces of sulfur still remaining in the gases even after rigorous purification, to a crystallization of the metal which decreases the activity of the surface layers, and to a deposition of paraffin on the catalyst. For synthesis in the presence of cobalt catalysts, a mixture of two parts of hydrogen to one of carbon monoxide is required.

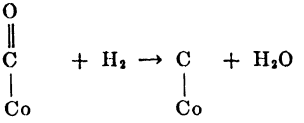
One mechanism of the catalytic action which has been postulated is the

formation of cobalt carbide by the action of carbon monoxide on cobalt, and the decomposition of this carbide by hydrogen to give the radical CH_2.

$$CO + 2H_2 + Co_2C \rightarrow Co_2C_2 + H_2 + H_2O$$
$$Co_2C_2 + H_2 + H_2O \rightarrow Co_2C + CH_2 + H_2O$$

Cobalt is generally held to owe its catalytic properties to the instability of its oxide.

Craxford[6] believes that the reaction for carbide formation is the reduction of a surface carbonyl:



and that the second step in the synthesis is the reduction of the carbide by molecular hydrogen leading to the production of CH_2 groups chemisorbed on the cobalt. When atomic hydrogen is present on the catalyst, the CH_2 groups are hydrogenated to methane. In the absence of atomic hydrogen, the groups link up with each other to form long paraffin chains.

Later work by Craxford[7] confirms the previous theory that oils are synthesized when the cobalt in the catalyst surface is in the form of carbide, whereas uncombined cobalt yields CH_4, allows the water gas-shift reaction to take place and is active for the hydrogenation cracking of hydrocarbons.

Craxford studied the function of promoters in the catalyst for the Fischer-Tropsch synthesis[8]. The following catalysts were equally active for the reaction:

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

(1) Cobalt
(2) Cobalt 100:thoria 18
(3) Cobalt 1:kieselguhr 1
(4) Cobalt 100:thoria 18:kieselguhr 100
(5) Cobalt 100:thoria 21:kieselguhr 100

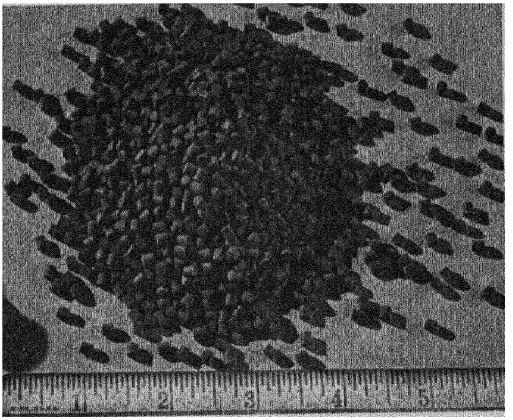
Both kieselguhr and thoria were powerful promoters for the reaction:

$$2CO + 2Co \rightarrow Co_2C + CO_2$$

They do not act primarily by increasing the available area of the cobalt but as specific promoters for the formation and reduction of cobalt carbide. For a satisfactory catalyst in the Fischer-Tropsch reaction one must have a high rate of carbide formation and a relatively slow rate of reduction of carbide for the formation of oils.

Since most steel metallurgists claim that cobalt forms only one carbide Co_3C, whereas Craxford holds the carbide is Co_2C, it would be desirable to have more information on the carbides of cobalt.

Herington[18] studied the mechanism by which the CH_2 groups link up. He calculated that an acetylene molecule can be adsorbed on the cobalt lattice across the 3.50 Å distance by the transformation of the triple into a double bond. Ethylene can only be adsorbed across the shorter 2.47 Å distance. If ethylene is present in the incoming gas it is found incorporated in the Fischer oil products, unlike acetylene which if introduced in the synthesis gas polymerizes independently. It is believed, therefore, that



Courtesy Harshaw Chemical Co., Cleveland, Ohio

FIGURE 40. Cobalt-thoria catalyst used in the Fischer-Tropsch process.

the combination of the CH_2 groups during synthesis occurs across the short spaces of the cobalt lattice.

A discussion of cobalt catalysts is included in Golumbic's review of the Fischer-Tropsch process[15]. The cobalt catalyst used in the large plants in Germany during World War II contained cobalt 100:thoria 5:magnesia 8:kieselguhr 200. The cobalt must be at least 99% pure with the remainder either copper or nickel. Small traces of impurities like calcium oxide or iron are detrimental. The preparation of the catalyst and regeneration of spent catalyst are very important processes in the Fischer-Tropsch synthesis, and are described in this publication. The operation and development of the Fischer-Tropsch process in Germany is also described by Hall[16]. In the cycle of catalyst preparation, use, and recovery there was an overall loss of only 4% of the cobalt. The processes of catalyst

manufacture and recovery required three factories in Germany, one with an annual output of 3,000 tons of catalyst. Catalyst maintenance represented 8 to 9% of the cost of production.

Although there is a trend at present in the Fischer-Tropsch process towards the use of iron and iron-nickel catalysts, cobalt may still be of importance for the production of synthetic chemicals and pharmaceuticals by this reaction.

Fluorinating Agent. Interest in the possibility of using the fluorocarbons for various purposes in the separation of uranium isotopes recently stimulated an enormous amount of work in the synthesis of fluorocarbons. The use of CoF_3 as a fluorinating agent depends on the fact that the lower fluoride, CoF_2, is changed to CoF_3 by passing fluorine over it at 200 to 250°, and the compound CoF_3 reacts with hydrocarbons to replace hydrogen with fluorine.

$$2CoF_2 + F_2 \rightarrow 2CoF_3$$
$$C_7H_{16} + 32CoF_3 \rightarrow C_7F_{16} + 32CoF_2 + 16HF$$

Temperature is an important variable in determining the products from the reaction of hydrocarbons and cobaltic fluoride. A reactor temperature of 250 to 350° is usually employed.

Although other metallic fluorides, such as Ag, Ce, Mn, Sb, have been used as fluorinating agents, cobalt fluoride remains the most satisfactory for general use.

A comprehensive series of papers on fluorination appears in the March, 1947, issue of *Industrial and Engineering Chemistry*, which is entirely devoted to fluorine chemistry[1, 2, 3, 4, 5, 13, 14, 19, 21, 22, 23, 24].

Hydrogenation Processes. Cobalt nitrate catalysts are used for certain hydrogenation processes, converting oils to edible products, but not nearly to the extent of nickel for this purpose.

While nickel, cobalt, and iron all have comparable activities toward the hydrogenation of C = C double bond in aliphatic compounds, nickel and cobalt are active for hydrogenating the benzene ring in aromatic compounds whereas iron is completely inactive.

Oxidation of Ammonia. Oxidation of ammonia may be catalyzed by cobalt oxide, with or without oxides of aluminum and bismuth.

Oxidation of Hydrogen Cyanide. Cobalt oxide catalyzes the oxidation of HCN in gas masks.

Decomposition of Alkaline Hypochlorites. The decomposition of alkaline hypochlorites is catalyzed by cobalt compounds, a continuous evolution of oxygen occurring from bleach solutions in the presence of these substances.

Decomposition of Acetylene. Finely-divided cobalt metal dissociates acetylene into carbon and hydrogen.

Oxidation of Carbon Monoxide. A mixture containing 50% MnO_2, 30% CuO, 15% Co_2O_3, 5% Ag_2O, oxidizes carbon monoxide into carbon dioxide and has been employed for this purpose in gas masks[25].

Dehydrogenation. It has been observed[27] that a change in the size of porous cobalt granules from 0.05 to 0.70 mm produced no change in the activity of a catalyst for dehydrogenation of cyclohexane.

Cobalt in Zinc Electrolysis. It might be mentioned here that cobalt exerts a peculiar action in depressing the deposition of lead on the cathode with zinc in the cell room of zinc electrolytic refineries. For instance at Broken Hill, Northern Rhodesia, the addition of cobalt sulfate at the rate of 4 mg Co per liter to the feed is used when the lead content of the melter zinc approaches or exceeds 0.03%. No satisfactory explanation can be given for this action.

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Chapter 12

Biological and Biochemical Relationships of Cobalt

Role of Cobalt in Plant Growth

Cobalt is not included among the ten essential elements of classical plant physiology, nor among the minor elements like Cu, Mn, Zn, B, etc. found in recent years to be indispensable. It is found in minute quantities in many plants[1,11,12,18,28] but its essential nature for plant growth has not yet been demonstrated. Its important role in correcting certain deficiency diseases of livestock in many parts of the world has led to the examination of numerous herbages and animal feeds for cobalt. A compilation of these is given in Table 25.

The effect of the addition of cobalt to soil, among a number of other elements, on growth of timothy was studied by Young[55]. The results are given in Table 26.

Of 35 minor elements applied, 33 gave an increased growth over the check at some concentration. With cobalt added the weight of plant material was slightly below the control even at a concentration of 0.1 ppm, and at higher concentrations the effect became more pronounced. It is pointed out that these results would undoubtedly vary with the plant and the soil. A clay soil, with its high content of colloidal matter and great adsorptive capacity, might conceivably fix a high concentration of these elements and render them innocuous to the plant. With a sandy soil, however, such as the Merrimac coarse sandy loam used in this work, the added elements would be rapidly and completely brought into solution and absorbed by the plant roots. This condition would be advantageous for a low concentration of rarer elements, provided that losses by leaching did not occur, but would prove deleterious if higher and toxic amounts of the elements were applied.

Algae were also used as test plants in these studies on the effect of a large number of elements on plant growth. A quantitative measure of the growth of these organisms was obtained by extracting the chlorophyll with hot ethyl alcohol and comparing the color in a colorimeter with a standard solution of potassium chromate. The results for cobalt are shown in Table 27 on page 139.

Table 25. Cobalt Content of Plant Products

	Reference	Cobalt (mg/kg)
Alfalfa hay	(3)	0.012
Apricot	(1)	0.032
Apricot, dried leaves	(1)	0.40
Beans, field; seed	(1)	0.011
Beans, wax	(4)	0.10
Beech, bark	(1)	1.10
Beech, dried leaves	(1)	0 35
Beech, wood	(1)	0.01
Beets, roots	(4)	0 05–0 09
Beets, tops	(4)	0.39–0 41
Buckwheat, grain	(1)	0.36
Cabbage, edible portion	(1), (4)	0.07–0 24
Carrots, leaves	(1)	0.31
Carrots, roots	(1)	0.02
Chard, Swiss	(4)	0.09
Cherries, edible portion	(1)	0 005
Clover, white, above-ground portion	(2)	0 28–4 6
Coffee, bean	(1)	0 002
Corn, grain	(1), (4)	0.01–0 02
Cowpeas	(4)	0.06–0.31
Cress, water	(1)	0.15
Figs	(1)	0.20
Lettuce, dried leaves	(1), (4)	0.05–0.23
Lime, dried leaves	(1)	0.20
Mangel-beet leaves	(4)	0.16–0.54
Oat, bran	(1)	0.011
Oat chop	(3)	0.02
Oat hay	(3)	0.02
Oats, grain	(1)	Tr.
Onions, bulb	(1)	0.13
Pear, pulp	(1)	0 18
Peas, green; edible portion	(1)	0.03
Potatoes, sweet	(4)	0 02–0.03
Potatoes, tubers	(1)	0 06
Rice, polished	(1)	0.006
Slough hay	(3)	0.015
Spinach, edible portion	(1), (4)	0 07–1.20
Spinach, New Zealand	(4)	0.09
Timothy hay	(3)	0.01
Tomato, fruit	(1)	0.096
Turnip greens	(4)	0.03–1 07
Walnuts, edible portion	(1)	0 05
Wheat, bran	(1)	0.011
Wheat, grain	(1)	0 012

(1) Bertrand, G., and Mokragnatz, M., *Bull. soc. chim.*, **47**, 326–331 (1930).
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It appeared probable that any element will stimulate the growth of algae at a definite concentration depending on the element and the organism. Some elements are not toxic in concentrations as high as 100 ppm or more; others are depressing at 0.2 ppm or less. Cobalt occupies an intermediate position, exerting a toxic effect on all three algal species at concentrations of 2 ppm or over. Smaller additions became harmless and

Table 26. Effect of Cobalt on Growth of Timothy

Concentration of Cobalt in Soil (ppm)	Dry weight of Plant, Tops Only (gm)
nil	0.5
0.1	0.4
10	0.2
100	nil
500	nil
2000	nil

Table 27. Growth of Algae Expressed as Concentration of Chlorophyll Measured Colorimetrically Against Standard K_2CrO_4 Solution

	Concentration of Cobalt in Growth Medium (ppm)	Growth of Algae expressed as Concentration of Chlorophyll	
		Chlorella	*Crucigina*
Series I	nil	10	23
	0.02	22	22
	0.2	20	26
	2	nil	4
	20	nil	nil
	200	nil	nil
		Algae No. 4	*Crucigina*
Series II	nil	7	19
	0.002	6	14
	0.02	5	19
	2	3	6
	10	nil	nil
	20	nil	nil
	100	nil	nil
	200	nil	nil
	400	nil	nil

eventually stimulating at concentrations of 0.2 to 0.002 ppm, depending on the species.

Role of Cobalt in Human Nutrition

As indicated in the next section, cobalt has been remarkably effective in correcting widespread deficiency diseases of animals. The essential nature of this element in human nutrition, and its efficacy in overcoming

human disorders, however, are conflicting. In spite of a great deal of work done on this subject the results are inconclusive, but the majority of investigators incline to the belief that minute quantities of cobalt are necessary for humans.

Sherman[45] believes cobalt to be essential in human nutrition, while McCollum and coworkers[35] indicate that cobalt appears to be indispensable. Elvehjem and associates[2, 24, 51, 52] have tried many times to produce a cobalt deficiency in experimental animals, especially the rat, but have been unsuccessful. Shohl[46] concludes a brief review by stating that from recent reports cobalt must be considered a dietary essential. The same conclusion is reached by Calvery[18].

Mitchell[39] reports recently that in general the cobalt content of dry matter of plant material is 0.01 to 0.4 ppm and that herbage contents of above 0.09 ppm Co are necessary for animal health. The leafy foods usually contain the highest amount of cobalt.

Role of Cobalt in Animal Nutrition

For many years farmers and agricultural scientists were puzzled by the poor condition of cattle and sheep grazed on certain areas in various parts of the world. The condition resembled a mineral deficiency disease, but the composition of the herbage and feeds grown in the affected area did not differ appreciably in calcium, phosphorus, or any of the usual mineral elements from those obtained from neighbouring healthy regions. In the final task of tracing this disease to a deficiency of cobalt, investigators in Australia and New Zealand played a leading part. Afterwards many workers in other parts of the world found that cobalt corrected puzzling deficiency diseases. The field has been reviewed by several investigators [13, 34, 44].

The anaemic appearance of cattle and sheep suffering from "bush sickness" in New Zealand led Aston to try iron therapy[9]. The very large doses required and the irregularity of the results from different sources of iron led Filmer and Underwood in Australia to the belief that the curative agent was not iron itself but another element present as an impurity in crude iron compounds. Filmer and Underwood in Western Australia[26], Marston and coworkers in South Australia[31, 32, 33], and Askew, Dixon, and others in New Zealand[3, 4, 5, 6, 7, 8, 43] soon found that cobalt was the agent responsible for the correction of these deficiency diseases. It is not surprising that these findings were only established about 1935, in spite of the known occurrence of these disorders for many years. Nothing was known of the biochemical significance of cobalt, and reliable analytical procedures for determining very small quantities of this element in biological materials were not then developed.

It will be preferable to discuss briefly in turn the various deficiency diseases throughout the world which respond to cobalt.

Cobalt Deficiency Diseases

New Zealand

Bush Sickness. This disease occurs among cattle and sheep grazing on coarse pumice soils, granite soils, and loam in both North and South Island in New Zealand. The animals suffer progressive anaemia, emaciation, loss of energy, and finally death from exhaustion. In some areas the disease occurs at all times, in others it is seasonal.

It has been found by extensive investigations into the composition of the blood and organs of affected and healthy animals that the latter have a higher cobalt content. The onset of bush sickness can be prevented by administering a weekly drench of 1.4 mg of cobalt for ewes and 0.7 mg for lambs. It was found by Askew and Josland[7] that when sheep were drenched with 4 mg cobalt, only about 2% of the cobalt appeared in the urine, mostly during the first 24 hours, whereas the bulk of it was excreted in the faeces within 48 hours. This indicates the advisability of frequent small doses rather than occasional large ones. This principle has been confirmed by Filmer[25].

As a general rule bush-sick soils are lower in cobalt than neighbouring healthy soils. McNaught[37] found the cobalt soluble in $N/10$ HCl ranged from 0.05 to 0.23 ppm in bush-sick soils and from 0.33 to 0.94 ppm in healthy soils. Kidson and coworkers found in general that the cobalt soluble in concentrated HCl was less than 2 ppm for unhealthy soils, compared with a value of 6 to 20 ppm for normal soils[29, 47].

Askew and coworkers[3, 4, 5, 6, 7, 8] and McNaught and associates[37, 38] made a large number of determinations of cobalt in pastures. In general they find that unhealthy pastures contained less than 0.07 ppm cobalt on the dry basis. Seasonal variations occur; in cold and dry weather the cobalt content increases. Close grazing increases the cobalt in the pasture. Pastures vary slightly in their cobalt content depending on the species of plants. White clover contains more cobalt than perennial rye grass. While in general the cobalt content of a pasture follows the concentration in the soil, it may easily happen that the species of pasture plant can upset this correlation[47].

The cobalt content of a pasture can be increased by top dressing with cobalt salts. Annual applications of 2 lb of cobalt chloride per acre to unhealthy pasture have proved effective in controlling bush sickness, and recent experiments indicate that much smaller additions may be adequate.

Morton Mains Disease. This disease of grazing sheep found in certain

areas of loessic soil in Southland, New Zealand, is quite similar in many respects to bush sickness. Provision of a salt lick containing 4 oz of cobalt chloride per ton of salt for ewes and lambs was effective in preventing or curing this condition[22]. Cobalt in the blood and organs of affected animals was lower than in normal sheep from adjacent areas. Cobalt treatment restored both the reserve of this element in the body and bodily health. Top dressing pasture with cobalt salts, or limestone containing cobalt, increased the cobalt content of the livers of lambs grazing on the pasture and at the same time prevented or cured the disease.

Unlike bush-sick soils, there does not appear to be a definite relationship between the cobalt content of Morton Mains soils and the incidence of the disease. For example, Kidson[29] found that the cobalt extracted by concentrated HCl from three unhealthy soils was 3.3, 4.0, and 4.8 ppm, whereas the values for healthy soils were 2.8, 5.0, and 8.3 ppm.

The application of 10 lb of cobalt chloride per acre resulted in increasing the cobalt content of pasture from 0.44 ppm of dry matter in October to 6.7 ppm in November. It gradually decreased until in May it had reached its former level. Later work by Dixon and Kidson[23] showed that a dressing of 3 tons of limestone, containing about 0.25 lb of cobalt sulfate per acre, increased the cobalt content of Morton Mains pastures and of the livers of lambs grazing on these. This treatment was effective in preventing and curing the disease.

Mairoa Dopiness. This disease of sheep grazing in the Mairoa district of the North Island of New Zealand appears to resemble closely bush sickness.

Bonner, McNaught, and Paul[14] report the effect of fertilizing with cobaltized superphosphate containing 14 oz of cobalt sulfate per acre on the cobalt content of Mairoa pasture. The latter was increased from 0.06 to 0.08 ppm to 0.19 to 0.69 ppm of cobalt, depending on the season and length of time elapsing after application.

Australia

Enzootic Marasmus. This disease of cattle and sheep occurring near the south coast of West Australia and in the southeastern part of South Australia, is characterized by gradually decreasing appetite in the presence of good feed, depraved appetite for unusual objects, and general wasting[36].

A daily dose of 0.1 mg of cobalt was effective in maintaining good health in sheep on affected areas, while cows required 0.3 to 1.0 mg of cobalt daily[26]. The livers of affected sheep contained 0.07 ppm of cobalt or less, whereas the livers of healthy animals usually contained 0.20 ppm of cobalt or more.

In general, the cobalt content of affected soils was much lower than that

of healthy soils, the former ranging from 0.1 to 1.5 ppm of cobalt with a mean of 0.6, whereas adjacent healthy areas varied from 0.2 to 32, with an average of 5.6 ppm of cobalt.

All the affected pastures were considerably lower in cobalt than most of the healthy pastures. The cobalt content of an affected pasture consisting chiefly of *Trifolium subterraneum* ranged from 0.02 to 0.07 with a mean of 0.04 ppm dry matter, whereas healthy areas varied from 0.04 to 0.30 with a mean of 0.13[53].

Additions of 0.5 lb and 10 lb of cobalt acetate per acre, respectively, increased the cobalt content of unhealthy pasture from 0.08 to 0.22 and 0.96 ppm dry matter in approximately 4 months. About seven months after fertilizing, the value had increased to 0.30 and 1.60 ppm respectively[53].

Nutritional Anaemia. This disease of sheep has been reported in New South Wales and resembles the previous deficiency disorders[44]. Drenching with cobalt sulfate was stated to effect recovery from the condition, but since other variables were also introduced into the treatment, the presence of uncomplicated cobalt deficiency was not definitely proved.

Coast Disease. This disease, which closely resembles bush sickness and enzootic marasmus, is found to affect sheep and cattle in South Australia. Copper alone was not effective in overcoming this condition, cobalt was not much better, but a combination of cobalt and copper cured the animals. Investigators now agree that the condition is a dual deficiency of cobalt and copper[31,42]. Sheep can be maintained in perfect health in affected areas by topdressing the pasture with copper and cobalt sulfates.

Kenya

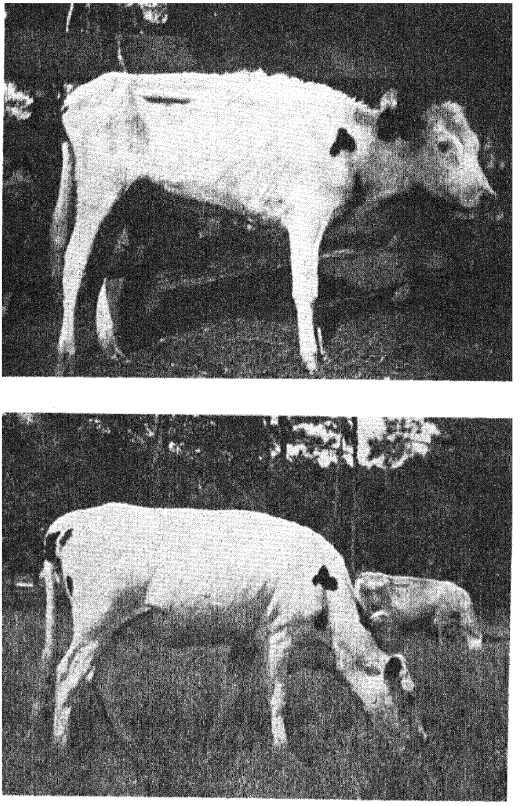
Nakuruitis. This disease occurs in cattle grazing in the Nakuru district of Kenya. Cobalt treatment was tried in 1936 and proved very successful[44]. A private communication from the Director of Veterinary Services of Kenya in 1943 to the writer indicates that experiments over a number of years have shown cattle can be maintained in good health indefinitely when a small amount of cobalt is given in a lick. For badly affected cattle it is recommended that 4 oz of cobalt nitrate be added to 150 lb of a mixture of bone meal and salt. As a preventative 1.5 to 2 oz of cobalt nitrate to the same amount of lick is given.

Britain

Pining. A wasting disease of sheep and cattle is found in many localities in Britain. For some years controversy arose among investigators regarding the primary cause of this disease, some maintaining it was due to mineral deficiency, others holding the view that parasitic infestation was

the principal factor in pining. It has now been definitely proved that pining can be cured by cobalt administration.

The average cobalt content of unhealthy moorland soils was found by



Courtesy Fla. Agr. Expt. Sta., Gainesville, Fla

FIGURE 41. *Above:* Salt sick produced in a 10-month old animal maintained on cobalt-deficient soils in Florida. Symptoms of deficiency are emaciated condition and declining appetite for feed. *Below:* The identical animal in a healthy state, after being fed cobalt supplements, and grazed on the same pasture. Second photograph taken prior to calving.

Patterson[41] to be 3.9 ppm compared with 16.7 ppm in lowland soils on which sheep recovered. He also reported that unhealthy soils in Devon had a cobalt content of 4 ppm, while healthy areas had a concentration of 19.6 ppm of Co.

In experimental plots of soil containing 2.9 ppm of cobalt, Stewart and associates[48,49] found that top dressing with cobaltized fertilizers increased the cobalt content up to a value of 9.6 ppm ten weeks after an application of 80 lb of cobalt chloride per acre.

Some workers reported that pasture on pining areas in Dartmoor had a mean cobalt content of 0.20 ppm compared with 0.45 ppm of cobalt in healthy regions[21]. Other investigators have failed to find any significant correlation between cobalt content of pasture and incidence of pining. It should be borne in mind, however, that since the cobalt content of New Zealand pasture has been found to fall during the growing season, individual results for cobalt content of pasture may frequently be misleading.

It has been suggested that pining in some cases may be due to a combined deficiency of cobalt and excess of molybdenum in the pasture.

United States

Grand Traverse Disease. For many years a wasting disease has been known in several regions of Michigan. In 1941 it was reported[10,30] that addition of cobalt to the feed of affected animals resulted in spectacular recoveries.

Hay from affected areas contained 0.03 to 0.06 ppm of cobalt compared with 0.12 ppm from a healthy area, and this appeared to confirm the results of the feeding trials that the disease was due to a cobalt deficiency.

Salt Sick. A wasting disease known as "salt sick" has long been known in cattle grazed in many areas of Florida. It has been found that usually both copper and cobalt additions are necessary to prevent or overcome this condition[9]. In some areas iron and copper alone were effective, but in others cobalt was also necessary for normal growth. These conflicting results might have been due to the presence of traces of cobalt in some of the iron and copper compounds used.

Other Cobalt Deficiencies. Cobalt deficiency has been reported by Geyer, Rupel, and Hart in the northeastern region of Wisconsin[27]. It was corrected by feeding of salt containing one ounce of $CoSO_4 \cdot 7H_2O$ per 100 pounds. When the salt was incorporated into the grain at the rate of 1 per cent, it will supply about 3 mg of elemental cobalt per day when 5 lb of grain are consumed.

Canada

Cobalt Deficiency. Sheep confined for long periods to a ration consisting of oat hay, timothy, brome grass, prairie hay, ground oats, iodized salt, and monocalcium phosphate in Alberta showed loss of appetite, listlessness, loss of weight, unthriftiness, and death. The addition of 4 mg of cobalt twice weekly prevented the occurrence of these symptoms and even cured the disease in sheep which had already developed it. Alfalfa

hay, which gave good results when fed as a supplement, contained much higher quantities of cobalt than nonleguminous hays grown on the same soil, alfalfa containing 0.16 ppm while other hays had only 0.01 to 0.02 ppm of cobalt[15, 16, 17].

Work is in progress on cobalt deficiencies in the Maritime Provinces, Quebec, and Ontario, and most animal nutritionists in Canada are of the opinion that further investigations will disclose the deficiency to be more widespread than is generally realized.

Dr. W. E. Swales of Macdonald College, Quebec, in a private communication to the writer, postulates a mechanism for the effect of cobalt in ruminants, from the standpoint of the parasitologist. He believes it is linked with vitamin B deficiency and that the bacterial flora in the rumen are unable to synthesize vitamin B without cobalt

Effect of Excess Cobalt

There does not appear to be any reported instance of an excess of cobalt leading to a livestock disease. While the chances of any pasture or normal stock feed containing exceptionally large quantities of cobalt are somewhat remote, the large amount of investigational work done with added quantities of this element would have revealed the effect of excesses if the latter had been critical in animal nutrition.

Future Developments

There are a number of aspects of the role of cobalt in animal nutrition about which further information would be desirable. Cobalt reserves of animals and cobalt content of pastures in Kenya and Britain, where deficiency diseases have been cured by cobalt, are recorded in only very few instances. The same holds true for work on coast disease in Australia and the salt-sick regions of Florida, where further clarification of the role of cobalt in the dual deficiency of copper and cobalt would be helpful. Then too, we do not know the role of cobalt in animal metabolism. It is to be hoped that studies similar to those of Comar and associates[19,20] on cobalt metabolism, using radioactive cobalt as a tracer, will throw light on the role of this element in the animal organism.

It was announced in April, 1948 by the United States Atomic Energy Commission that radioactive cobalt from the atomic pile was undergoing extensive tests as a substitute for radium in cancer aid. Although irradiated cobalt is not any more effective than radium, its cheapness and ease of handling compared with the latter give cobalt great possibilities in this field.

The relation of cobalt to plant and animal nutrition is well covered in the series of bibliographies of references to the literature on the minor elements compiled by Willis[51] and issued by the Chilean Nitrate Educational Bureau.

Thomas, Escritt, and Trinder[59] found that K_2O appears to reduce the absorption of cobalt in heather. Undoubtedly other elements may exert a similar effect on absorption of cobalt. This is a field worthy of extensive investigation.

Cobalt carbonate, chloride, and sulfate are sold by Harshaw Chemical Company and by other manufacturers for livestock feeding. The form of the anion is not critical.

An excellent recent summary of the effects of cobalt in pasture deficiencies in relation to animal health is given by Miss Russell of the Imperial Bureau of Animal Nutrition[41]. Mineral deficiencies in pasture are more important than vitamin deficiencies. The importance of pasture will tend to increase in the future since the consumption of dairy products and meat rises as the standard of living is raised. Grassland products form a large proportion of the total exports of some countries, over 90% for New Zealand and over 50% for Australia and Eire. Among the minor mineral elements apt to be deficient, cobalt holds a very important place, and the use of cobalt compounds as a constituent of livestock licks and pasture amendments is likely to increase considerably in the future.

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Chapter 13
Analysis of Cobalt

Cobalt is found associated in minerals and ores principally with copper, nickel, arsenic, silver, zinc, iron, and sulfur. It is an important constituent of many high-speed steels, magnets, and alloys. Cobalt is also used as a catalyst, for electroplating, in the glass, ceramic, and paint industries, as a fluorinating agent in chemical industries, and as a minor but essential element in livestock licks and feedstuffs, and pasture fertilizers.

Cobalt may be determined by weighing as the oxide Co_3O_4, as the metal after electrolysis, volumetrically by titration with cyanide, potentiometrically, or colorimetrically. In certain cases it may be determined spectrographically or polarographically. The chief separations of cobalt are from members of previous groups by removal of the latter with hydrogen sulfide in acid solution, from iron by a zinc oxide or phosphate separation or ether extraction, and from nickel by precipitation of cobalt with α-nitroso-β-naphthol or separation of nickel with dimethylglyoxime.

In certain alloys or high-speed steels, chromium, vanadium, and tungsten are frequently associated with cobalt. These can be eliminated with a zinc oxide separation from an acid solution oxidized with nitric acid in the absence of copper and molybdenum. Other methods of separation may be employed, such as precipitation with sodium hydroxide in the presence of sodium peroxide to throw chromium and vanadium into the filtrate, and solution of the material in perchloric acid, fuming and filtering off the precipitated tungstic oxide.

Cobalt is very tenaciously retained by the hydroxides of iron and aluminum, and it is nearly impossible to separate cobalt completely from large quantities of iron and aluminum even by repeated ammonia precipitations. A large excess of ammonia and ammonium salts will minimize the retention of cobalt in an iron hydroxide precipitate[10]. This is undoubtedly the principal reason for the greater adsorption of cobalt by aluminum than by iron. Pouring the iron-cobalt solution into ammonia also appears to minimize the adsorption of cobalt by ferric hydroxide.

The following procedures are applicable to nearly all classes of material, and in the absence of interfering elements may be shortened accordingly.

(1) Gravimetric Determination as Co_3O_4 after Precipitation with α-Nitroso-β-naphthol

(A) Separation of Iron with Zinc Oxide. Weigh out 0.5 to 10 gm, depending on the cobalt content of the sample, and take into solution with HNO_3, HCl, H_2SO_4, and a few drops of HF if necessary. For high sulfide products initial treatment with a little bromine or potassium chlorate is advisable to avoid the inclusion of undissolved particles in a bead of sulfur. Evaporate to strong fumes of SO_3, cool, dilute with water, and boil. Adjust the acidity to 5 to 10% H_2SO_4, and gas out all Group 2 metals with H_2S. Filter off the precipitated sulfides and silica, and wash thoroughly with acidulated H_2S water.

Boil the filtrate for 15 minutes to remove all H_2S, oxidize the iron with H_2O_2, and boil to remove the latter. Nearly neutralize with Na_2CO_3 solution and boil to remove all CO_2. Add a suspension of zinc oxide until the precipitate assumes the color of coffee containing cream. Boil and filter, washing 3 to 4 times with hot water. Transfer the precipitate back to the original beaker, just dissolve with HCl, and reprecipitate with zinc oxide emulsion. Filter through the original filter paper and wash thoroughly 7 to 8 times with hot water. The filtrate will contain only Co, Ni, Mn, and a few other elements not affecting the α-nitroso-β-naphthol precipitation. A turbidity in the filtrate caused by colloidal zinc oxide may be disregarded, as subsequent acid treatment dissolves this. For very accurate work on small quantities of cobalt in the presence of large amounts of iron, aluminum, etc., a third precipitation may be necessary.

Add 20 ml of HCl in a volume of 500 ml to dissolve the colloidal zinc oxide, heat to boiling, and cautiously add sufficient α-nitroso-β-naphthol in 1:1 acetic acid to precipitate all the cobalt. Use 0.5 gm of α-nitroso-β-naphthol for each 0.01 gm of Co. Allow the brick-red precipitate of cobalt α-nitroso-β-naphthol to boil several minutes, remove from hot plate, and allow to stand in a warm place several hours.

Filter on a Whatman No. 42 paper, using pulp, wash several times with hot water, then 10 times with hot 5% HCl, and finally with hot water until free of chlorides. Place paper and precipitate in a weighed porcelain crucible, dry, ignite carefully in a muffle at a temperature not exceeding 850°. Cool in a desiccator and weigh as Co_3O_4.

$$Co_3O_4 \times 0.7344 = Co$$

For routine work the precipitate may be ignited in a fireclay crucible or annealing cup and brushed on to the balance pan.

It is sometimes recommended to add a suspension of ZnO to the sample in a flask, shake, allow to settle, and withdraw an aliquot portion of the

supernatant liquid for the cobalt determination. Our results have indicated that this practice is not satisfactory for accurate work[18].

The zinc oxide separation may be expressed thus:

$$ZnO + H_2O \rightarrow Zn(OH)_2$$
$$3Zn(OH)_2 + 2FeCl_3 \rightarrow 2Fe(OH)_3 + 3ZnCl_2$$
$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$
$$2HCl + ZnO \rightarrow ZnCl_2 + H_2O$$
$$Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4$$
$$H_2SO_4 + ZnO \rightarrow ZnSO_4 + H_2O$$

The α-nitroso-β-naphthol precipitation is represented thus:

$$3C_{10}H_6(NO)OH + CoCl_3 \rightarrow [C_{10}H_6(NO)O]_3Co + 3HCl$$

Hydrochloric acid must be present at this precipitation to keep in solution the nickel and uranium compounds formed with α-nitroso-β-naphthol. Uranium is precipitated with α-nitroso-β-naphthol in the presence of acetic acid, but if HCl is present uranium remains in solution.

If the precipitate of Co_3O_4 is contaminated with nickel, or if it is very bulky, it may be dissolved in HCl and reprecipitated with α-nitroso-β-naphthol. A better procedure, especially if iron contamination is suspected, is to transfer the cobalt oxide to a beaker, dissolve in acids, take to fumes of SO_3, and electrolyze as described below under (2).

(B) Separation of Iron with Sodium Phosphate. The zinc oxide separation of iron for cobalt determinations has several drawbacks. Two precipitations, and for very accurate work three precipitations, are necessary to liberate cobalt completely from the iron precipitate. It can only be used in conjunction with subsequent precipitation of cobalt with α-nitroso-β-naphthol, and this procedure is not suitable for large quantities of cobalt which are best determined electrolytically.

When iron is precipitated as ferric phosphate from a solution containing cobalt there is remarkably little occlusion of cobalt[18]. For all routine work, one precipitation, even in the presence of large quantities of iron, is sufficient. A filtrate is obtained upon which cobalt may be determined directly by electrolysis.

Decompose the sample with acids or by fusion, as described under (A), evaporate to fumes of SO_3, and remove copper and other Group 2 elements with H_2S in acid solution. Boil out H_2S, add sufficient H_2O_2 to oxidize the iron present, and again boil until H_2O_2 is removed.

Add sufficient trisodium phosphate solution to precipitate all the iron, plus 5 ml of excess solution. Ten ml of the phosphate solution given below will precipitate 0.05 gm of Fe. If aluminum and other elements precipitated by phosphate are present, additional phosphate solution must of course be added. To reduce the bulk of solution, for samples high in

Fe, Al, etc., use a more concentrated sodium phosphate solution. Then add NH_4OH carefully from a dispensing burette with vigorous stirring until purple cobaltous phosphate is formed. If the sample is low in cobalt it may be difficult to see the cobaltous phosphate, and a piece of red litmus should be used as indicator. When the litmus turns blue a pH of approximately 5.6 has been reached, and this is sufficient to ensure that cobaltous phosphate has been precipitated at pH 5.3.

The cobaltous phosphate is now dissolved by the addition of exactly 10 ml of glacial acetic acid, with vigorous stirring. This will be found to give a pH of 3 to 3.5. Oxidize the solution by adding 5 to 20 ml of H_2O_2 and stir thoroughly. The iron is now precipitated as a white creamy precipitate of ferric phosphate.

$$2Na_3PO_4 \cdot 12H_2O + Fe_2(SO_4)_3 \rightarrow 2FePO_4 + 3Na_2SO_4 + 24H_2O$$

Bring the sample to the boil on the hot plate, stirring occasionally to prevent bumping if a heavy iron precipitate is present. Filter through a Whatman No. 31 paper on a fluted funnel, using paper pulp. If a heavy precipitate of ferric phosphate is present, filter through a Buchner funnel. Wash the precipitate 8 to 10 times with hot acetic acid wash solution.

Proceed directly with the determination of cobalt by precipitation with α-nitroso-β-naphthol, or add 10 ml of 1:1 H_2SO_4, 40 ml of NH_4OH, and electrolyze immediately.

Reagents

Trisodium Phosphate Solution: Dissolve 34.05 gm of $Na_3PO_4 \cdot 12H_2O$ in 1 liter of water. Ten ml will precipitate 0 05 gm of Fe.

Acetic Acid Wash Solution: 25 ml of glacial acetic acid in 1 liter of water.

This method of first raising and then lowering the pH of the solution has been found to give the best separation of cobalt from iron. All the iron is precipitated and none of the cobalt is retained by one precipitation of the iron.

If a large excess of phosphate has been added and the cobalt is to be determined electrolytically, some of the cobalt will be precipitated as the phosphate on the addition of ammonia immediately before electrolysis. Keep the quantity of added phosphate to a minimum.

By the use of dilute acetic acid as wash solution there is no danger of precipitating cobalt phosphate in the pores of the ferric phosphate precipitate, and the latter may be washed entirely free of cobalt.

Aluminum phosphate will be precipitated at pH 3.5 and will be removed with the ferric phosphate. Manganese, calcium, nickel, and magnesium are not precipitated and will be found in the cobalt solution. The only one of these elements which may interfere in the subsequent determination

of cobalt is calcium in the electrolytic procedure if a large excess of phosphate is present. In this case, when ammonia is added calcium phosphate is precipitated and may occlude cobalt. If large quantities of calcium are present they may be precipitated as the oxalate in acetic acid after the phosphate separation.

Uranium, titanium, zirconium are removed by phosphate separation; chromium and vanadium divide. In their presence a preliminary sodium hydroxide separation may be made.

(C) Separation of Iron with Ether. Iron may be satisfactorily removed in cobalt determinations by means of an ether separation. This is particularly suitable for low cobalt steels or slags, since several 10-gm portions may be combined after the ether extraction.

After the sample has been completely decomposed by acid treatment and fumed to dryness with H_2SO_4, HCl is added and this is evaporated carefully to syrupy consistency. Transfer the contents of the beaker to a 250 or 500-ml separatory funnel, rinsing out the beaker thoroughly with HCl of sp. gr. 1.10 and finally several times with ether. Add more ether to bring the concentration up to 20 ml per gm of iron in 5 ml of HCl. Hydrochloric acid of sp. gr. 1.10 is made by mixing 526 ml of concentrated HCl with 474 ml of water.

Shake the funnel vigorously under the cold water tap, allow to settle and draw off the lower layer into a 400-ml beaker. This contains the cobalt together with Cu, Ni, Mn, etc., while the upper layer contains nearly all the iron. Extract the upper and lower layers again with ether and HCl of sp. gr. 1.10 to make a complete separation.

The upper layer in the separatory funnel, containing ferric chloride and ether, can be drawn off and placed in a Winchester. Add water and shake. The ferric chloride goes into the lower aqueous layer while ether remains on top. The lower layer can be removed by siphoning and is discarded, giving an excellent recovery of ether.

The partition coefficient of iron is approximately 50. With 1 gm of iron, the first ether extraction removes all but 0.02 gm. A second extraction removes all but 0.5 mg.

Place the beaker containing cobalt and other elements on the edge of the hot plate on asbestos until all ether has been driven off. Add 5 ml of HNO_3, 30 ml of 1:1 H_2SO_4, and take to fumes of SO_3. Cool, take up in water, adjust acidity to approximately 5 to 10% H_2SO_4, and gas out all preceding group elements with H_2S.

Remove H_2S by boiling, oxidize with H_2O_2, and if chromium and vanadium are absent, add 4 ml of HCl for each 100 ml of solution and proceed directly with the α-nitroso-β-naphthol precipitation. If chromium and vanadium are present, remove with NaOH-Na_2O_2 separation, or with zinc oxide.

(2) Electrolytic Determination of Cobalt

(A) Electrolysis in Ammoniacal Solution Following Treatment with H_2SO_4. For appreciable quantities of cobalt the electrolytic determination is the most satisfactory procedure. Depending on the nature of the sample, electrolysis may be preceded by separation of iron with zinc oxide or ether and precipitation of cobalt by α-nitroso-β-naphthol, or separation of iron with phosphate, or cobalt may even be electrolyzed in the presence of iron.

Dilute the sample, which has been fumed with H_2SO_4, with water, add 5 ml of 1:1 H_2SO_4, neutralize with NH_4OH and add 40 ml excess. If the sample was fumed to dryness add more 1:1 H_2SO_4 or ammonium sulfate to ensure the presence of the latter after making ammoniacal. Electrolyze overnight on a stationary cabinet at 1 ampere or on a rotating electrolytic apparatus at 2 amperes for 1 hour. Unlike the electrolytic copper determination, it is difficult to tell by dilution when deposition of cobalt is complete owing to the similarity in appearance between cobalt and platinum in the cloudy ammoniacal solution. The solution may be tested for complete deposition by withdrawing a few drops with a pipette onto a spot plate and testing with potassium thiocarbonate, phenylthiohydantoic acid, nitroso-R-salt, or ammonium sulfide, by the usual spot tests with these reagents.

Wash the cathode, taking particular care to wash any particles of ferric hydroxide which may be adhering to the meshes of the cathode if a little iron were present during the electrolysis. Rinse in alcohol, dry, and weigh the previously tared cathode.

If nickel was suspected in the original sample and the cobalt was not separated by α-nitroso-β-naphthol, place the cathode in a 300-ml Berzelius beaker, add 50 ml of HNO_3 and dissolve off the plating by placing on the edge of a hot plate for 10 minutes. Remove the cathode, washing thoroughly into the beaker, and test the solution for nickel in the usual manner with dimethylglyoxime. Subtract the nickel content, if any, from the weight of the cobalt deposit obtained on the cathode.

For routine work cobalt may be deposited electrolytically in the presence of iron. The following procedure is used by the laboratories of the Union Minière du Haut Katanga for high-cobalt iron products like alloys with 40% Co, 45% Fe. Remove copper with H_2S in dilute H_2SO_4, boil to remove all H_2S, add H_2O_2 and evaporate to a low volume. Alternatively, copper may be removed electrolytically. Cool, make ammoniacal, and add 30 ml of excess NH_4OH. Electrolyze the solution containing suspended ferric hydroxide in a tall 600-ml beaker for 45 minutes on a rotating apparatus at 2 amperes. Lower the beaker from the cathode, washing the latter, just dissolve the ferric hydroxide with H_2SO_4 and reprecipitate with

NH_4OH, adding 30 ml excess. Continue the electrolysis for 30 minutes longer, lower the beaker, dissolve the $Fe(OH)_3$ and reprecipitate as before to set free any occluded cobalt. Continue the electrolysis for an additional 30 minutes. This should result in complete deposition of cobalt, indicated by no test for this element when a small portion of the solution is withdrawn with a pipette, filtered, and tested on a spot plate with ammonium sulfide, phenylthiohydantoic acid, or nitroso-R-salt.

Since a little iron is occluded with the deposited cobalt on the cathode it is necessary in accurate work to dissolve the plating in HNO_3, take to fumes of H_2SO_4, make ammoniacal, and reelectrolyze. The second electrolysis at 2 amperes requires only about an hour or less with rotating anodes.

The procedure of dissolving the cobalt deposit in HNO_3 and eliminating the latter by evaporating to fumes of H_2SO_4 may be shortened by dissolving the plating in HCl, neutralizing with NH_4OH and reelectrolyzing. An excess of 60 ml of NH_4OH and 15 ml of a standard SO_2 solution are added, and electrolysis is carried out at 2 amperes and 10 volts. The deposited cobalt should be a light grey color.

(B) Electrolysis Following Removal of Iron with Phosphate. Large quantities of cobalt are readily determined electrolytically following removal of iron with phosphate[18]. In the presence of nickel the combined cobalt and nickel may be determined electrolytically and nickel or cobalt subsequently determined on the dissolved plating by dimethylglyoxime or α-nitroso-β-naphthol, respectively. Alternatively, cobalt may be separated with α-nitroso-β-naphthol after removal of iron with phosphate, and finally determined electrolytically.

Evaporate the filtrate from the phosphate separation of iron to a low volume, add 10 ml of 1:1 H_2SO_4, 5 gm of borax, and carefully add NH_4OH to neutralization, followed by 30 to 40 ml of excess. Electrolyze on a rotating cabinet with a current of 3 amperes and 6 volts. Do not prolong the electrolysis after all the cobalt is deposited, particularly in the presence of manganese, or a black cathode deposit will be obtained and results will be high. If a large excess of ammonia is present, and the electrolysis is not unduly prolonged after spot tests with potassium thiocarbonate, phenylthiohydantoic acid, or nitroso-R-salt indicate deposition is complete, excellent results will be obtained.

The addition of borax to the electrolyzing solution is optional, many chemists preferring an ammonium sulfate-ammonia medium only.

Spot Tests for Completion of Cobalt Electrolysis

Ammonium Sulfide. The addition of a few drops of ammonium sulfide precipitates black cobalt sulfide. A number of other Group 3 elements, of course, also give dark-colored sulfides under these conditions.

Potassium Thiocarbonate, K_2CS_3. This is prepared by saturating one half of a solution of 5% KOH with H_2S, adding the other half, and heating moderately with $\frac{1}{5}$ of its volume of carbon disulfide. The dark red liquid is decanted from the undissolved carbon disulfide and kept in a well-closed flask. Cobalt in ammoniacal solution gives a yellow color with little, and brown or black with much, cobalt.

Phenylthiohydantoic Acid, $C_9H_{10}O_2NS$. A few drops of a solution of 1 gm of phenylthiohydantoic acid in 100 ml of ethyl alcohol added to an ammoniacal cobalt solution gives a pink color.

Nitroso-R-Salt, $C_{10}H_4OH \cdot NO(SO_3Na)_2$. To a few drops of the cobalt solution add several drops of 50% sodium acetate, acidify with HNO_3, and add several drops of a 0.5% solution of nitroso-R-salt in water. A permanent red color indicates the presence of cobalt.

(C) Electrolytic Deposition as Cobaltic Oxide. A method has been published in which nickel and cobalt are separated by electrolysis by depositing cobalt on the anode as Co_2O_3[17]. A diaphragm revolving electrode was used as cathode. About 0.04 gm of Co could be deposited on this anode successfully, together with 1 gm of nickel on the cathode. The deposited cobaltic oxide contains a little nickel and must be dissolved and redeposited. The solution must be well buffered at pH 5, and a high temperature is desirable for best deposits. This procedure is not suitable for routine work.

(3) Volumetric Determination with Potassium Cyanide

In the absence of nickel, cobalt may be determined by cyanide titration in a manner similar to this familiar procedure for nickel.

Potassium cyanide reacts with cobaltic sulfate to give a complex cobalt cyanide. The end point of the reaction is determined by an indirect indicator, silver iodide, which gives a turbidity to the solution until a slight excess of potassium cyanide is present. Silver iodide is formed *in situ* by the action of $AgNO_3$ on KI.

$$AgNO_3 + KI \rightarrow AgI + KNO_3$$
$$AgI + 2KCN \rightarrow KAg(CN)_2 + KI$$
$$10KCN + Co_2(SO_4)_3 \rightarrow 2[2KCN\ Co(CN)_3] + 3K_2SO_4$$

The end point of the reaction is indicated by the disappearance of the cloudy precipitate of silver iodide. Since it is generally easier to detect the appearance of a turbidity than its disappearance, a slight excess of KCN is added and a back-titration with $AgNO_3$ carried out until a faint opalescence is again formed.

Decompose the sample with HNO_3, HCl, HF if necessary, in the usual manner, add 10 ml of 1:1 H_2SO_4 and fume strongly to dehydrate silica. Dissolve up in water, gas out copper and other Group 2 elements with H_2S, and filter off the precipitated sulfides, silica, etc. Boil out all H_2S,

and oxidize thoroughly by adding 10 ml of HNO_3, 1 to 2 gm of potassium chlorate, and boiling gently for 15 to 20 minutes.

Cool in a water bath, add NH_4OH just to the neutral point, and add 10 to 20 ml of ammonium citrate-sulfate buffer solution for each 0.1 gm of iron present. Place a piece of litmus paper against the side of the beaker and carefully add NH_4OH until the litmus turns blue. Add exactly 2 ml more NH_4OH and boil gently for 2 to 5 minutes.

Cool in a water bath, add 5 ml of 10% KI and 2 to 3 ml of standard $AgNO_3$ solution from a burette. Add standard KCN solution from a burette with constant stirring until the cloudiness produced by silver iodide disappears. Finally add standard $AgNO_3$ solution drop by drop with constant stirring, over a black background, until a persistent cloudiness is again produced. The total number of ml of standard $AgNO_3$ solution used is then subtracted from the number of ml of standard KCN to give the percentage of cobalt.

$$10KCN + Co_2(SO_4)_3 \rightarrow 2[2KCN \cdot Co(CN)_3] + 3K_2SO_4$$

1 gm Co = 5.5234 gm KCN

$$AgNO_3 + KI \rightarrow AgI + KNO_3$$

$$AgI + 2KCN \rightarrow KAg(CN)_2 + KI$$

130.22 gm KCN = 169.89 gm $AgNO_3$

1 gm Co = 7 2060 gm $AgNO_3$

Standardize the cyanide solution against the silver nitrate, and in addition titrate the cyanide solution against a solution containing a known amount of cobalt. One gram of $CoSO_4 \cdot 7H_2O$ contains 0.2097 gm of cobalt, and a 25-ml aliquot from a liter of solution containing one gram of this salt gives a convenient quantity for titration against dilute KCN. Check the solution of $CoSO_4 \cdot 7H_2O$ electrolytically. It is useful to have two standard KCN solutions, one for low cobalts, with a value approximating 1 ml = 0.001 gm Co, and another for high cobalts possessing a titre of 1 ml = 0.005 gm Co.

These solutions are made up to contain 5.6 gm of KCN plus 1 gm of KOH per liter, and 28 gm of KCN and 5 gm of KOH per liter, respectively. They are standardized against silver nitrate solutions containing 7.2060 gm of $AgNO_3$ and 36.0300 gm of $AgNO_3$ per liter, respectively. Standardization should be carried out at least once a week.

After the addition of silver nitrate to the samples, keep them out of direct sunlight, as the latter has a tendency to reduce AgI to metallic silver and give erratic results.

The ammonium citrate-sulfate solution has the following composition:

Citric acid	200 gm
Ammonium sulfate	270 gm
Ammonia	200 ml
Water to make	1000 ml

With the exception of copper which is removed with H_2S, and of course nickel, very few elements interfere with the cyanide titration of cobalt[4].

(4) Colorimetric Determination of Cobalt

(A) Ammonium Thiocyanate. Cobalt forms a complex with ammonium thiocyanate which can be extracted with amyl alcohol and ether, and the blue cobaltothiocyanate color measured in a colorimeter[19].

$$CoCl_2 + 4NH_4CNS \rightarrow (NH_4)_2\,(Co(CNS)_4) + 2NH_4Cl$$

Decompose the sample with HNO_3 and HCl, adding a few drops of bromine or HF is necessary. For high iron material use HNO_3 and $KClO_3$. Evaporate the samples to dryness, but do not bake. Traces of HNO_3 have no effect on the formation of the thiocyanate complex.

Dissolve the samples in approximately 25 ml of water, and add exactly 1 ml of HCl for every 50 ml of subsequent dilution of the sample. Boil, cool, and wash out into appropriate measuring cylinders or calibrated

Table 28. Weights and Dilutions of Samples According to Percentage Cobalt Present

Co in Sample	Weight of Sample Taken for Analysis (gm)	Dilution (ml)	Aliquot Taken for Analysis (ml)	Factor for % Co
(%)				
0.01–0.20	2.0	50	5	0.5
0.16–0.80	0.5	50	5	2
0.80–3.20	0.5	200	5	8

flasks. The amount of dilution of the samples depends on the amount of cobalt present and can be read off from Table 28.

(*a*) *Cobalt Samples with Less Than 36 Mg Iron.* Measure out 5 ml of sodium thiosulfate solution, 3 ml of sodium phosphate solution, and 10 ml of ammonium thiocyanate solution. Add with vigorous agitation 5 ml of the solution of the sample. The pH is now 3.5 to 4.0 and the concentration of NH_4CNS is 26%.

Add 10 ml of the amyl alcohol-ether mixture and shake the whole thoroughly again. Transfer to a separatory funnel, run off the lower aqueous layer, and discard. Transfer the solution of the cobalt complex to a test tube or a 1-cm absorptiometer cell. For visual comparison, match the intensity of color of the test solution with the standard copper sulfate solutions. The comparison may be carried out in a La Motte comparator for hydrogen-ion determinations with a source of artificial light, or the tubes may simply be held against a white background out of direct sunlight. It will be found possible to take a reading half way between any two of the standards if the color of the test solution lies between them.

In the photoelectric comparison, absorption of the test solution is compared with an amyl alcohol-ether blank. The amount of cobalt present in the test solution is then read off from the calibration curve.

By either means of comparison the amount in milligrams of cobalt present in the extract is obtained and the percentage of cobalt in the sample is given by multiplying by the appropriate factor shown in the last column of Table 28.

(*b*) *Cobalt Samples with More Than 36 Mg Iron.* Carry out the analysis of these samples in exactly the same way as for those under (a), but in this case add 2 ml of ammonium acetate solution. The pH is still 3.5 to 4.0 and the concentration of NH_4CNS is 21%. Unless iron is known to be absent it is preferable in all cases to add 2 ml of ammonium acetate as a routine procedure. Copper does not interfere with the production of the blue color of the cobalt complex even when present to the extent of 60%. Iron, if present in amount greater than about 36 mg, will interfere unless ammonium acetate is used. Vanadium forms a blue complex which is extracted with the amyl alcohol-ether solution. If, however, ammonium acetate and a few drops of tartaric acid are added to the reagents this blue complex is not formed, and vanadium will not interfere. The following do not give colored complexes which are soluble in amyl alcohol-ether: Cr, Mn, Ni, Zn, Ti, Mo, U. Other common elements such as Al, Si, Cr, Mg, P, Bi, As, Pb, and the alkalies are without effect.

This rapid procedure is very satisfactory for a range of 0.02 to 0.50 mg of cobalt or 0.01 to 4% Co.

Reagents

Ammonium Thiocyanate: Dissolve 600 gm of NH_4CNS in 1 liter of water.
Sodium Phosphate: Dissolve 83.3 gm of $Na_2PO_4 \cdot 12H_2O$ in 1 liter of water.
Sodium Thiosulfate: Dissolve 200 gm of $Na_2S_2O_3 \cdot 5H_2O$ in 1 liter of water
Ammonium Acetate: Dissolve 700 gm of $NH_4C_2H_3O_2$ in 1 liter of water
Tartaric Acid: Dissolve 50 gm of $C_4H_6O_6$ in 1 liter of water
Amyl Alcohol-Ether: Mix 3 parts by volume of amyl alcohol with 1 part of ethyl ether.

For visual comparison, solutions of copper sulfate may be used as permanent standards since the blue color of the copper sulfate solutions matches almost identically the blue of the cobalt complex. A solution of copper sulfate in water containing 8 gm of $CuSO_4 \cdot 5H_2O$ per liter will match an extract containing 0.02 mg of Co per 10 ml. For photoelectric comparison, of course, a calibration curve for the absorptiometer, giving drum reading against mg of cobalt, is drawn up once, using extracts of standard solutions, and values of future unknowns are read off directly from this curve. Photoelectric comparison is more satisfactory for this and similar color matching.

(B) Nitroso-R-Salt, $C_{10}H_4OH \cdot NO(SO_3Na)_2$. This determination is based on the fact that the colored complexes formed by most of the com-

mon elements with nitroso-R-salt, except cobalt, are destroyed by nitric acid. The full development of the color with cobalt is attained in the presence of sodium acetate, and such variables as quantity of nitric acid and of nitroso-R-salt, time of boiling, etc. have an influence on the development of color[21].

The color comparisons are conveniently done in a photoelectric instrument such as a Spekker photoelectric absorptiometer. A calibration curve is drawn, plotting drum readings against concentrations of cobalt. To 0, 1, 2, etc. up to 11 ml of standard cobalt sulfate solutions are added 2 ml of Spekker acid, 10 ml of nitroso-R-salt solution, and 10 ml of sodium acetate solution. A blank is made by adding 2 ml of Spekker acid and 10 ml of sodium acetate solution, but omitting the nitroso-R-salt. The blank and standard solutions are brought to a boil on the hot plate. Five ml of HNO_3 are added and the solutions are boiled for at least 1 minute and not more than 2 minutes. The standards and blank are then cooled and diluted to 100 ml with water.

The absorption of the standards is measured on the Spekker photoelectric absorptiometer using 1-cm cells and Hilger No. 6 blue filters. The blank is set at 1.0 and the differences obtained are plotted against the weights of cobalt taken.

Procedure. For samples containing 0.01 to 0.20% cobalt, use a 0.25-gm sample. With higher grade materials take a 0.5-gm sample and after decomposition dilute to volume and take a suitable aliquot containing 0.01 to 0.5 mg of cobalt for analysis. For very low concentrations of cobalt, as in refined metals, larger aliquots representing 1 to 20 gm may be taken. The maximum quantity of cobalt permissible in a sample is 0.5 mg, as above this concentration the solution no longer appears to follow Beer's Law exactly.

Decompose with HNO_3, HCl, and bromine, add 5 to 7.5 ml of 1:1 H_2SO_4 and take to strong fumes. Some products will require the use of HF for complete decomposition. Care should be taken in the addition of reagents, as an excessive concentration of salts in the final solution will increase the absorption.

Cool, dilute to about 30 ml, add 2 ml of HCl, and boil to solution of soluble salts. Pass a brisk current of hydrogen sulfide through the solution for 10 minutes and filter through a Whatman No. 40 paper, washing well with acidulated H_2S water. Boil off H_2S, add 5 ml of HNO_3 and take to fumes of SO_3. For products like blister or refined copper, determine cobalt on the solution obtained after the electrolysis of copper. Evaporate this solution to fumes of SO_3 and continue heating until only a small amount of H_2SO_4 remains.

Cool, dilute to about 25 ml with water, and boil to solution of salts.

Cool and carefully neutralize with 20% NaOH to a point where the solution becomes a deep wine red. Should there be little or no iron present, add 2 drops phenolphthalein and take to the first faint pink. Immediately add 2 ml of Spekker acid, followed by 10 ml of nitroso-R-salt solution and 10 ml of sodium acetate solution. Bring to a vigorous boil, add 5 ml of HNO_3, and then boil for at least 1 minute and not more than 2 minutes. Cool and dilute with water to 100 ml.

At the same time carry out a blank exactly as was done in calibrating the graph. The absorption of the sample is measured in the same manner as were the standards, with the blank setting at 1.0. The drum reading obtained for the sample is subtracted from 1.0 and this difference is measured off on the calibration graph to obtain the weight of cobalt present.

Copper must be removed, and with it, if H_2S is used, all Group 2 elements will be eliminated. Manganese over 10%, nickel over 3%, and chromium above 5%, must be removed prior to the color comparison. The following were without effect on the determination, even in quantities over 100 times that of the cobalt: Fe, Al, Zn, Ti, Th, U, Zr, W, Ba, Sr, Ca, Mg.

Reagents

Cobalt Sulfate: Dissolve 0.2385 gm of $CoSO_4 \cdot 7H_2O$ in water and make up to 1 liter. 1 ml = 0.05 mg Co.

Nitroso-R-Salt: Dissolve 1 gm in water and make up to 500 ml.

Spekker Acid: Mix 150 ml of H_3PO_4 and 150 ml of H_2SO_4, and make up to 1 liter.

Sodium Acetate: Dissolve 500 gm of $NaC_2H_3O_2 \cdot 3H_2O$ in water and make up to 1 liter

(5) Potentiometric Determination of Cobalt

A very satisfactory procedure for cobalt in many products is a potentiometric one, based on the oxidation of cobalt in ammoniacal solution by potassium ferricyanide[4]. In the cold and the presence of ammonium citrate practically the only common element which interferes is manganese, and this can be removed by a nitrochlorate separation. The potentiometric procedure is applicable in the presence of large quantities of copper, nickel, and iron, the three commonest interfering elements in other methods for cobalt.

The details given below apply to most nonferrous mining and metallurgical products, and can be modified slightly for irons and steels or other samples.

Reagents

Ammonium Citrate Solution: Dissolve 200 gm of citric acid in water and add slowly 270 ml of ammonia. Cool and make up to 1 liter. Tartaric acid may be used in place of citric acid if desired.

Cobalt Nitrate Solution: Weigh out 5 gm of AnalaR cobalt nitrate, dissolve in water, and make up to 1 liter. Standardize the solution by determining the cobalt electrolytically. One ml of this solution should contain 1 mg of Co.

Potassium Ferricyanide Solution: Weigh out 11 gm of potassium ferricyanide, dissolve in water, and make up to 1 liter. This solution must be kept in a brown bottle since it decomposes if exposed to light.

Standardization of the Potassium Ferricyanide Solution. Measure carefully 10 ml of potassium ferricyanide solution from a standard burette or pipette into a 600-ml beaker. Add 20 ml of ammonium citrate, 80 ml of ammonia, and make up to 400 or 500 ml with water. Place the beaker in position on the Cambridge potentiometric titration apparatus or a similar instrument and switch on the current and stirrer. Unclamp the galvanometer and turn the center switch to normal. By altering the coarse and fine adjustments, the light beam is brought either to the middle of the scale or to the left hand side.

Run in standard cobalt nitrate solution from a burette until a large and permanent deflection is given on the galvanometer scale. The end point is very sensitive and will be given on the addition of a drop of cobalt nitrate. The setting of the galvanometer for the titration of the standard must be retained for the titration of the samples. Ten ml of potassium ferricyanide should be equivalent to 20 ml of cobalt nitrate, or 1 ml of potassium ferricyanide equals 2 mg of Co.

Procedure. Decompose the sample with HNO_3, HCl, and Br or HF if necessary. When all the sample is in solution boil thoroughly to drive off nitrous fumes, but it is not necessary to evaporate to low bulk. If the samples cannot be decomposed without the addition of H_2SO_4, add 10 to 25 ml of 1:1 H_2SO_4 and evaporate to fumes.

If manganese is present evaporate the mixed acid solution nearly to dryness. Add 40 to 50 ml of HNO_3 and carefully add several successive small portions of sodium chlorate, boiling gently after each addition. Dilute slightly and filter off the MnO_2 through Whatman No. 42 paper.

The insoluble matter other than MnO_2 need not be filtered off, but if large quantities are present it is a good practice to do so. Cool the samples and titrate carefully with ammonia until the iron just begins to precipitate. Redissolve the iron by the addition of a drop or two of 1:1 HNO_3. Cool the samples again thoroughly.

Measure out carefully from a standard burette or pipette into a 600-ml beaker sufficient excess potassium ferricyanide solution to give a back titration of 10 to 15 ml of cobalt nitrate solution. Add 10 to 20 ml of ammonium citrate for every 0.1 gm of iron present in the sample, followed by 80 ml of ammonia. Pour the sample very slowly with constant stirring into the beaker containing potassium ferricyanide, etc. There must

be no heating effect produced at this point and if the sample has been almost neutralized and cooled beforehand no heat will be developed.

Place the beaker containing the sample on the potentiometer and switch on the current and the stirrer. Set the instrument in the same way as directed under standardization of the potassium ferricyanide. Back-titrate the excess potassium ferricyanide with standard cobalt nitrate solution until the end point is shown by a large and permanent deflection of the galvanometer beam.

If chromium and vanadium are present the samples should be decomposed with HNO_3 and HCl, and then taken to strong fumes of a low volume of perchloric acid. The sample is then poured directly into the beaker containing excess ferricyanide, ammonium citrate, and 80 ml of ammonia, without preliminary neutralization. Vanadium is in the vanadate state and does not interfere with the titration.

Quantities of cobalt up to 100 or 150 mg in complex materials can be accurately and rapidly determined in this manner. The following are without interference: Hg (ic), Pb, Fe, Ni, Cu, Bi, Cd, As (ic), Sb, Sn (ic), Se, Te, Mo, Cr (ate), Be, Al, Zn, Ti, W, U, V (ate), Zr.

Table 29. Interfering Elements in Spectrographic Determination of Cobalt

Cobalt Line (Å)	Concentration of Elements Which may Interfere with Traces of Cobalt Sought (Concentration expressed in % in zinc matrix)										
	Bi	Cb	Ce	In	Ir	Li	Mo	Ti	V	W	Zr
3405.120	10	—	10	—	—	—	1	10	10	—	0.1
2521.363	—	1	—	1	—	—	—	—	—	0.1	—
2424.930	—	—	—	—	1	10	—	—	—	—	—

(6) Spectrographic and Polarographic Determination of Cobalt

Spectrographic procedures for cobalt have been reported by Gallaher[3], and Standen[13], and polarographic determinations by Maasen[9], Thanheiser and Maasen[15, 16], Kolthoff and Langer[6], Kolthoff and Lingane[7], Lingane and Kerlinger[8], Jones[5], and Stromberg and Zelyanskaya[14].

Gallaher[3] has described a method for the spectrographic determination of beryllium and cobalt in copper alloys. Up to 2% Be and 0.5% Co can be obtained from the lines Cu 1 3247.5 Å, Be 1 3321.3 Å, and Co 1 3453.5 Å.

Standen[13] has reported the most sensitive cobalt lines for qualitative work are 2424.930 and 2521.363 Å, the limit of detection being approximately 0.001% in a zinc matrix. A useful table is presented showing the concentration of other elements which may interfere with identification of traces of elements sought. Table 29 above is extracted from this source.

Determination of Oxide Cobalt

It is often necessary in the mining and metallurgical industries to differentiate oxidized cobalt from sulfide cobalt. The following procedure is applicable to ores and concentrator products[20]. It is based on the selective solvent action of dilute H_2SO_4 or HCl, in the presence of HF and the reducing agent sulfurous acid, on oxidized cobalt minerals.

Depending upon the quantity of oxide cobalt present in the material and on the analytical method used for cobalt, select a weight of minus 200-mesh sample that will enable an accurate determination of cobalt to be made on the leached portion. For instance, in a mill feed or tail running 0.02% oxide cobalt, at least 25 gm must be taken for the initial sample if cobalt is to be precipitated by α-nitroso-β-naphthol and weighed as oxide or determined electrolytically. If the colorimetric nitroso-R-salt procedure is employed on the same sample, a weight of 0.25 gm will suffice.

The ratio of leach solution to sample may vary quite widely, depending on the quantity of oxide cobalt present and on the other constituents of the ore. In general, add 15 to 25 ml of 10% HCl saturated with SO_2, or of 5% H_2SO_4 saturated with SO_2, to each gram of material in a stoppered Erlenmeyer flask or covered beaker. When the initial effervescence and attack has subsided, add 0.1 to 0.3 ml of HF per gram of sample. For large samples these quantities of HF can be reduced proportionally.

Shake the flask or beaker for 10 to 15 seconds every 10 minutes for an hour, allow to stand an hour, and again agitate briefly at intervals of 10 minutes for the third hour. Filter the sample through a Whatman No. 40 paper, using pulp, and wash thoroughly with hot water. Add 10 to 20 ml of 1:1 H_2SO_4 if necessary, boil out SO_2 from the filtrate, and evaporate to fumes of SO_3. Cool, dilute, boil to solution of salts, and remove copper and other Group 2 metals with H_2S.

Filter off copper and other sulfides and wash well with acidulated H_2S water. Boil out H_2S from the filtrate, and proceed with the determination of cobalt by any standard method. For gravimetric or electrolytic procedures iron may be separated by zinc oxide, ether, or sodium phosphate, and the cobalt precipitated with α-nitroso-β-naphthol and weighed as oxide or deposited electrolytically. If the nitroso-R-salt method is employed the filtrate after oxidation of the iron with HNO_3 is taken to fumes of SO_3 before proceeding with the development of the color in the usual manner.

Determination of Metallic Cobalt

The following procedure, based on the report of Smirnov and Mishin[12], has given good results on Rhokana products when taken in conjunction with microscopic studies of metallic cobalt in mattes, slags, etc.

To 2 gm of minus 200-mesh slag add 50 ml of 7% mercuric chloride

solution. Boil 1 minute, filter through Whatman No. 42 paper and wash thoroughly with hot water. The following reaction occurs:

$$HgCl_2 + Co \rightarrow CoCl_2 + Hg$$

Metallic cobalt passes into the filtrate and can be determined by any suitable procedure.

The following, if present in metallic form, will be extracted along with the cobalt: Mn, Cr, Fe, Ni, Bi, Cu. Cobaltosic oxide, Co_3O_4, is insoluble in the mercuric chloride solution, and cobaltic oxide, Co_2O_3, is only soluble to the extent of 0.1 to 0.3%. Cobaltous oxide, however, appears to be slightly soluble. The extent of its solubility is difficult to determine as it is invariably mixed with Co_3O_4 and Co_2O_3. Cobalt sulfide and cobalt silicate are apparently insoluble in the mercuric chloride solution.

When determining cobalt on the filtrate it is necessary to keep in mind the following facts: The α-nitroso-β-naphthol and ammonium thiocyanate procedures can be applied directly, electrolytic or nitroso-R-salt methods must be preceded by elimination of mercury with H_2S. By using an excess of NH_4Cl the potentiometric procedure is directly applicable.

Other Analytical Procedures for Cobalt

A number of other procedures for the determination of cobalt have been proposed and doubtless give good results in certain cases. They will be briefly cited here, but the author has not had sufficient experience with some of them to justify recommending. The other procedures described in detail in this chapter have been used successfully for many years by the writer or his associates.

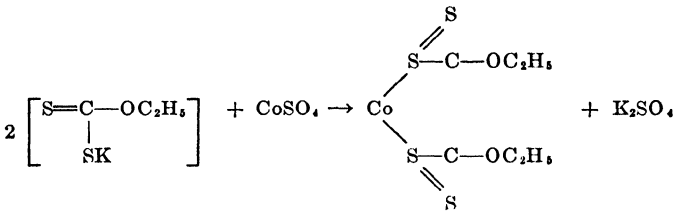
Schoeller determines substantial quantities of cobalt by weighing as pyrophosphate obtained by ignition of cobalt ammonium phosphate. Since the solubility of the latter increases with ammonia concentration, complete precipitation requires a delicate adjustment. Schoeller[11] adds a slight excess of ammonia and recovers the remaining trace of cobalt from the filtrate as sulfide. The major cobalt fraction is weighed as $Co_2P_2O_7$ and the minor fraction as Co_3O_4. The procedure has obvious drawbacks for large numbers of routine determinations.

Cobalt may be precipitated as potassium cobaltinitrite, $2K_3Co(NO_2)_6 \cdot 3H_2O$, by adding a hot solution of potassium nitrite to an acetic acid solution of cobalt and allowing to stand overnight. So many substances interfere, however, such as oxidizing agents, free mineral acids, Group 2 elements, appreciable quantities of Fe, Al, Cr, alkaline earths and ammonium salts, that for most materials cobalt and nickel must be isolated by electrolysis before carrying on with the potassium cobaltinitrite procedure. The details are outlined in Scott and Furman's "Standard Methods of Chemical Analysis".

Fairchild[2] prefers to weigh cobalt as sulfate at 550 to 600°.

Ellis and Thompson[1] determine cobalt in biological materials with nitro socresol.

Cobalt may be separated, together with copper and silver, from a num ber of other elements by potassium or sodium ethyl xanthate in ammoniaca solution, keeping the iron in solution by tartrate.



Results with this separation at Nkana have not been promising fo accurate analyses.

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