RAW MATERIALS FROM THE SEA

E. FRANKLAND ARMSTRONG, D S C , F.R S.
AND L MACKENZIE MIALL, B.A.

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PREFACE

THE British Association Conference on Science and World Order has recommended a scientific review of the Mineral Resources of the World in connection with the fourth clause of the Atlantic Charter which promises to all States access on equal terms to the raw materials necessary for their economic prosperity.

Amongst these World Mineral Resources certainly not the least are the oceans, containing an unlimited amount of inorganic salts present in dilute solution, although so far little use has been made of them Widespread interest has been aroused by the winning in large quantities on an economic basis first of bromine and then of magnesium as hydroxide from the sea Any scarcity or monopoly of bromine has been ended for ever It is to be expected that other elements will be won directly from the sea in the future, as it is, several are today obtained on the land from deposits representing dried up ancient seas or those, like the Dead Sea, which are only partially evaporated

We seek in the following pages to give an account of the winning of such substances which come either directly or indirectly from the sea but preface it by a general reference to the chemical problems which the oceans represent and to the various elements present in them in minor quantities Such a study involves several sciences other than chemistry and a widely scattered literature

This book is a first effort to bring such information together, it makes no attempt to be exhaustive and is prepared under all the difficulties of war time conditions

E F A L M M

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INTRODUCTION

''THE air is all around us everywhere, the sea constitutes three quarters of the surface of the earth They are unlimited and inexhaustible Both are essential for life and they act as balancers to preserve conditions as we know them on earth They are storehouses of food for man, plants and animals whose life circle involves the abstraction of some compounds and the return of others,

Man through the ages is always making discoveries adding to his needs He wants, for example, all sorts of minerals which he has learned how to obtain from the stratified and igneous rocks The former were laid down from the oceans, the latter represent the original crust of the earth

The winning of minerals and indeed of any natural product is a question of economics , preference is given to the cheapest source A new process may make it economic to work deposits previously neglected As engineering technique progresses it has become able to deal with small quantities, i e , small percentages, and to win them at an economic and competitive cost from their surroundings Thus, for example gold can be recovered profitably from tailings , the rare gases can be extracted from the air, and particular salts from the sea, even when present in minute quantities The story of how this is done is full of interest, it forms one of the newest chapters of industrial progress, whilst the achievements point the way perhaps to further successes of like kind in the future

The study of the sea in particular brings in a great many sciences In reality they cannot be separated because it is the interplay of all the factors which results in the sea being as it is today

It can be shown that sea water contains many ingredients, some present in constant relatively large amounts which give it the characteristic properties, others present in traces, often infinitely small, notwithstanding which they play a part in the life history of marine animals and plants The former are tempting potential sources of the particular materials to the industrialist with his new knowledge of extracting them The latter are of extraordinary interest and hence we have been tempted to bring together here what is known about their occurrence and their meaning Whether or no the sea can serve as a source for their commercial exploitation remains to be seen As the technique of handling large volumes of wafer at a very small cost develops much may be possible if land sources of a mineral begin to fail many minerals are bound to become scarcer

The chemist knows of ninety-two elements, some common, some rare many play an important part in the world, others have as yet little or no meaning One must suppose that this is due to ignorance rather than fact and that there is a reason for every element, none being without use or purpose

As knowledge increases the importance of trace elements in the life history of plants and animals is constantly being brought to light The evidence from the sea is even more complete than that on land, where the distribution of trace elements is not so general The evidence is accumulating that marine life, the growth both of unicellular and multicellular organisms, is highly dependent on the presence of trace elements, so that these acquire a new significance

The sea represents a dilute solution in which a great variety of chemical reactions are going on all the time These are predictable and in sum total act to preserve constancy of composition There are local variations due to changes in temperature and the presence or absence of food elements which cause prolific growth and govern the teeming yet variable life of the oceans

The subject is a comparatively new one Its progress owes much to F W Clarke in Washington, who published the Data of Geochemistry , to V M Goldschmidt of Oslo who has contributed many papers (in German) to foreign journals , and to V I Vernadsky and his pupils whose work will be found in the Vernadsky Jubilee Volumes * written in Russian with an English summary More recently the Washington National Research Council 1932 has published a monograph entitled Physics of the Earth's Crust, Vol 5, Oceanography

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*** (Acad Sci U S S R 1936)**

CHAPTER i

SOMETHING ABOUT THE OCEANS

> " *There rolls the deep where grew the tree,*
> *O Earth, what changes hast thou seen*
> *There where the long street roars hath been*
> *The stillness of the Central Sea* "
> —TENNYSON
> *In Memonam*

'THE oceans, hydrosphere is the scientific name, cover about three quarters of the earth's surface—some 61 per cent of that of the Northern and 81 per cent, of that of the Southern hemisphere The ocean area is given as 132-140 millions of square miles It varies in depth but more than half the sea bottom lies below 2000 fathoms , the mean depth is approximately 2 2 miles At one place it is six miles deep The Atlantic ocean covers 25,000,000 square miles, the Antarctic, 30,000,000 , the Arctic, 8,400 , the Pacific, 50,000,000 , the Indian, 17,000,000 , the Mediterranean, 1,006,600 , the Caspian Sea, 160,000, the Black Sea, 950,000, the Baltic, 175,000 Including all inland bays and seas, the ocean comprises 147,800,000 square miles

The volume of the hydrosphere is estimated to amount in round figures to 300 million, it may be as much as 320 million, cubic miles The weight of the sea amounts to 278 kilograms per square centimetre of the earth's surface, whereas that of the dry atmosphere on the same area is 1 kilogram In metric units and more exactly

Goldschmidt gives the area of the oceans as 361 million square kilometres and their volume as 1369 million cubic kilometres The mean depth is 3792 metres

Since the beginning of the world the bulk of the materials which has resulted from the weathering of the primary rocks of the earth, or lithosphere, has passed by means of the streams and rivers into the sea, which may also from its very beginning have contained dissolved salts

Much of what is now dry land was once below the surface of the ocean, but it appears that the water covering it was never very deep The visible sedimentary rocks now many thousands of feet thick were deposited on the sinking floors of shallow seas Much of the floor of the ocean, however, has always been ocean bottom and during the millions of years that made up geological history the floors of the deeps as well as the shallows have been accumulating sediments which, lying layer upon layer upon the bottom, have been the repository of the historical record of the ocean

Such a record includes the contribution of the rivers which in the aggregate are calculated to bring into the oceans 248 short tons per square kilometre of the earth's surface of dissolved materials of which as much as half of the inorganic material is calcium carbonate A considerable proportion is organic material The fresh water of the world only amounts to 2 per cent of the sea water The two greatest drainage systems of the world, the Amazon and the Congo, which each drain large continental areas are practically unaffected by agriculture or industry , European and United States rivers contain sewage from industrial communities and the drainage from agricultural land to which fertilisers have been applied It is obvious that the sea must be the greatest source of some raw materials

The contributions of the rivers reflect the changing conditions on the continents as well as those of ice and wind and the myriad life in the water above The record of what happened in this water above is filed away in the mud and clay and ooze below Chemical compounds, the skeletons of marine organisms, constitute this record , its study forms the basis of the science of geology Besides these records of life there exists a chemical and physical record , oxidation and reduction reactions leading to precipitation have all left behind something for us to interpret

It is for the several sciences to make a physical, chemical and biological study of the sediments from well within the mouth of a river, out across the submerged delta, across the zone where the effect of salt water increases and into the deep ocean basin beyond

The floor of the oceans is thought to be the upper surface of the great basaltic cover of the earth and perhaps much of it is essentially what it was when the earth became cool enough to permit water to condense on its surface

The sedimentary deposits teach us something about the different periods of geological history, as for instance the Carboniferous, when a moist warm climate filled vast swamps with rank tropical vegetation or the more recent Pleistocene when great masses of ice spread over large areas of which Britain was one

The foregoing makes it clear that the study of the sea from the point of view of the substances dissolved in it must have reference to many factors—to the bottom of the sea floor, to the plant and animal life in the oceans and to the composition and changes in the atmosphere above it

The scientific interest in the sea has a long history, early volumes of the Philosophical Transactions of the Royal Society contain many records of work done on subjects connected with the sea Here there is no need to go further back than Robert Boyle and his treatise " Observations about the Saltness of the sea " Boyle estimated the total solids by evaporation of known quantities of sea water and ignition of the residues He found, as modern chemists know, that such a method was unsatisfactory and of no meaning and he came to the conclusion that " density" was the best measure of saltness He experimented with three methods of determining density.

The first actual analyses showing the salts in sea water are due to Lavoisier in 1772, Bergman in 1777, Vogel in 1813 and Marcet in 1819 As a result of these the idea originated that the salts are present in sea water in the form in which they are deposited when the water is evaporated Numerous analyses were later made by Forchhammer but most publicity has been given to the complete and accurate analysis of 77 samples by Dittmar at the University of Edinburgh They were collected by Buchanan, the chemist of the famous Challenger expedition, which sailed in 1872

The table gives the average of these —

Table 1

		Parts per 1000 parts water
Sodium chloride	NaCl	27213
Magnesium chloride	$MgCl_2$	3807
Magnesium sulphate	$MgSO_4$	1658
Calcium sulphate	$CaSO_4$	1 260
Potassium sulphate	K2SO4	0863
Calcium carbonate	$CaCO_3$	0 123
Magnesium bromide	MgBr2	0 076
		35 000

These analyses brought out the essential fact that though the saltness varies in different seas the variation in the proportion of individual salts to the total salts is very small This has been substantiated by the very large number of analyses made since and is fundamental

The proportions of the same salts in " salt lakes," such as the Dead Sea, which have formed in the areas of internal drainage in the hearts of the continents by evaporation of river water are entirely different from those -of the sea , single ingredients present in salt water may be absent altogether from these lakes

The groportions of salts in river and sea water are also quite different Very generally, whereas river water has 80 per cent carbonates, 13 per cent sulphates and 7 per cent chlorides, the proportions in the sea are o 2 per cent, carbonates, 10 per cent sulphates and 89 per cent chlorides There is therefore a regrouping and a precipitation of salts when the rivers reach the sea which, as viewed by the chemist, is a medium in which a great many chemical compounds are present continually reacting with each other

It is of interest to emphasise the difference between sea and river In the sea water the predominating cations (or metallic radicals) are, in order of abundance, sodium, magnesium and calcium , the anions (or acid radicals) are chloride, sulphate, bicarbonate and carbonate In fresh water the order is just reversed, calcium being the predominating cation and bicarbonate and carbonate the predominating anions

The sea through the centuries should have been gradually growing increasingly salt as more and more salts are being washed off the land and carried by the rivers to the sea, unless there have been processes at work at the same time which remove salts Experts differ as to whether the sea has always been salt from the beginning The evidence on both sides of the question is discussed by C H White in the American Journal of Science for 1942,[1] and the reader wishing to find more on this subject is referred to that paper

Another valuable paper is by E J Conway,[2] who discusses the variation of the composition of the ocean during geological time Apparently the ocean volume has remained essentially constant but there have been additions of chlorine either from volcanic sources or from the original atmosphere At some time removal of potassium by living organisms took place , the potassium became deposited as glauconite Another change in Cambrian time was an increase in calcium and magnesium

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[1] Vol 240, p 714

[2] Proc Roy Irish Acad 1943, *48,* B 9

and a decrease in sulphate concentration

It is now generally accepted, as suggested by Jeans and Jeffreys, that the earth was created from the parent sun about 2,000 million years ago The subsequent liquefaction and solidification of the detached mass of glowing gas formed the juvenile earth The earth's crust consists of a superficial layer of soil and sedimentary rocks forming a thin veneer underneath which there is mainly igneous rock, that is rock that has solidified from the molten magma or supposed fluid strata under the solid crust of the earth

The most obvious assumption is that the sea was originally formed of fresh water which was deposited when the earth first became cool enough to allow water to remain liquid On this assumption estimates have been made of the age of the ocean from the sodium content of sea and river water Joly, in 1889, obtained a figure of 97,600,000 years , Clarke, in 1924, estimated it to be 89,222,900 years Such estimates are very low compared with figures for the age of the earth obtained by other methods of which one of the most recent calculations obtained from radioactivity data is some 3 to 4 thousand million years and one obvious source of inaccuracy is that much of the sodium now being carried to the sea comes from sedimentary rocks , it has therefore been in the sea at least once before Salts are also supplied to the sea by marine volcanoes This introduces another error into the calculation

One of the arguments in favour of the oceans having always been salt is supplied by the fact that in the sea the chlorine ion or element is in excess of the sodium ion or element, whereas in rivers the opposite is the case If no other source of this excess chlorine can be found it must have been initially present in the ocean, and have been derived from a volcanic source That this is possible is borne out by the fact that the sodium content of volcanic rocks is some 50 times as great as in sedimentary rocks, but the chlorine content is some 2000 times greater in volcanic than in sedimentary rocks. It must, however, be remembered that the total of fresh water compared with that in the oceans is small It has been estimated that the rivers of the world bring in 6,500 cubic miles of fresh water annually to the sea Such a quantity of river water would contain 160,000,000 tons of sodium chloride

V M Goldschmidt considers that chlorine, boron, sulphur and iodine are found in such large quantities in sea water that a derivation from primary rocks by a weathering process seems impossible The percentages of boron and sulphur in fossils indicate that the concentration of these elements in the sea may have since been decreasing and not increasing Goldschmidt admits that these elements may have been supplied by volcanic springs

It is not to be supposed that a dilute solution like sea water contains all the ingredient ions arbitrarily combined There must be considerable dissociation or splitting up of molecules into ions and sea water is to be regarded as a mixture of dissociated solutions of particular salts, each one of which, after the lapse of sufficient time, fills the whole space as if the other constituents did not exist The uniformity of composition throughout the oceans is easily explained by this interdiffusion of ions It is only the total salinity which changes from point to point owing to evaporation or condensation of water

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TABLE 2

The principal ions occurring in sea water are given below for a water having a chlorinity of 19 374 per cent

	Grams per kilo	Moles per litre	Gram equivalents per litre
Cations			
Sodium Na +	10 722	0 4662	0 4662
Magnesium Mg + +	1297	0 0533	0 1067
Calcium Ca + +	0 417	0 0104	0 0209
Potassium K +	0 382	0 0098	0 0098
TOTAL	12 818	0 5397	0 6036
Anions			
Chloride Cl=	19 337	0 5453	0 5453
Sulphate SO_4 =	2705	**0 0281**	0 0564
Bicarbonate HCO_3—	0 097	**0 0016**	**0 0016**
Carbonate CO -	**0 007**	**0 0001**	**0 0002**
Bromide Br—	0 066	**0 0008**	**0 0008**
TOTAL	**22212**	05759	06043

When a quantity of sea water is evaporated the least soluble salt is the first to crystallise and others follow in order of decreasing solubility the problem is complicated by the formation of double salts and of hydrates As described later (page 139) Van't Hoff and his pupils have studied this sequence of separation of the salts experimentally and used their findings to explain the order of the deposition of the salts at the famous Stassfurt deposits

The original definition of salinity as the sum of all the dissolved solids has been abandoned largely as the result of the work of Sorensen and Knudsen in Copenhagen, in favour of a more precise definition, viz , as the total amount of solid material contained in 1 kilogram of sea water when all the carbonates have been converted into oxides, the bromine and iodine replaced by chlorine and all organic matter completely oxidised

The determination of salinity by evaporation, as Boyle found, is impossible but there is a constant relation between the salinity and the chlorinity which is expressed in the formula

$$\text{Salinity} = 0\ 03 + 1\ 805\ \text{CI}$$

The chlorinity is defined as the total amount of chlorine present in a kilogram of sea water when all the bromine and iodine have been replaced by chlorine

The advantage of this modern definition of salinity is that a simple determination of chlorine, which can easily be made by volumetric methods, suffices to measure salinity The determination is in fact that of the total halogens, i e all three expressed as chlorine The actual amount of chlorine may be obtained from the chlorinity by multiplying by the factor o 9985 All the chlorine exists as chloride, none as chlorate Besides the determination of salinity by titration against a standard solution, the method of measuring the specific gravity or density of sea water is often used, particularly since it is easy to carry out on board ship

The above definition of salinity was adopted by the International Council for the Study of the Sea in 1902

The chlorinity is determined by titration with a standard solution of silver nitrate using a couple of drops of a standard solution of potassium chromate, free from chlorides as an indicator The method is easy and quick to carry out and very accurate when properly performed, a fact of great importance

Knowing the temperature of the water in *situ* and the chlorinity, the density may readily be determined by reference to the Hydrographical Tables Such information is used for many purposes for example to calculate the rate of flow of an ocean current

The following tables give some idea of the distribution of chlorinity at different depths in the oceans and seas

TABLE 3

Depth metres	Pacific 6° 32' N 80° 26' W % Cl	Pacific 58° 55' N 147° 22' W % C1	Antarctic 62° 36' S 36° 02' W % Cl	Atlantic 42° 10 N 47° 19' W % Cl
0	1644	1787	18 86	19 51
25	1838	1784		
50	1924	1787	1904	1967
500	19 15	1877	19 17	1942
1000	19 12	1896		19 39
2000	19 17			19 35

TABLE 4

Depth metres	Barents sea 73° 30' N 30° E % cl	Green land sea 75° 47' N 12° 59' W % cl	Mediterranean sea' 36° 38'N 4° 22' E % cl	Puget Sound 48° 50' N 123° 20' W % cl	Gulf of St Lawrence 47° 52' N 60°04' W % cl
0	19 38	I748	20 16	16 88	17 56
25	19 38	1796	20 31	17 17	17 55
50	**19 37**	18 31	20 75	17 50	1778
100	19,39	1869		17 72	1808
200	1940	I909		17 81	1876
300	19 39	19 33		17 99	19 05

Lastly, the following table shows the changes in chlorinity at different depths during a complete tidal cycle in the San Juan Archipelago August 16-17, 1928 It and the two preceding tables are quoted from Oceanography[4]

TABLE 5

Depth metres	Average %cl	Maximum % CI	Minimum % cl	Difference between extremes % cl
Surface	16 24	1648	1584	036
10	1643	16 55	1616	039
25	16 61	1686	16 31	055
50	1689	17 14	16 60	054
100	1715	17 39	1680	059

On the assumption that the composition of sea water is constant, ratio constants with chlorine as unity have been determined for a number of ions with considerable care Three of these are —

SO_4 CI = 0 1396
Ca CI = 0 0215
Mg CI = 00669

No doubt a more careful study will detect variations in particular waters, for example, Robinson and Knapman, using a direct analytical method, have found a slightly higher ratio of sodium to chlorine in the coastal waters of Puget Sound than in the open Pacific Ocean

Most of the physical properties of sea water, besides the density, can be related to the chlorinity by straight line curves There is a definite relation between the osmotic pressure, freezing point, vapour tension, and boiling point by which when one of these constants is given the other can be calculated

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[4] Physics of the Earth V

Some of the properties of sea water and salt solutions of increasing concentration are collected in the following table —

TABLE 6

Physical Properties of Sea Water

Solubility parts per thousand	10	20	30	35	40
Freezing point (°C)	-0 53	-1 07	-1 63	-1 91	-2 20
Osmotic piessure (atmospheres)	64	13 10	19 7	231	26 6
Elevation of boiling point (°C)	016	0 31	0 47	0 56	0 64
Reduction of vapour pressure (mm)	42	85	130	152	176

Distribution of Salinity

The Challenger observations show that in each of the three oceans there are two maxima of salinity—one in the North, the other in the South tropical belt These are separated by a zone of minimum salinity in the equatorial region At the poles there are regions of still lower salinity The causes of this difference are mainly meteorological The tropical maxima coincide with regions of minimum rainfall, strong winds, high temperature and consequently of maximum evaporation

The maxima are —

TABLE 7

North Atlantic ocean		37 9	parts per thousand
South Atlantic ocean		376	
North Indian ocean		367	
South Indian ocean		364	it
South Pacific ocean		369	"
North Pacific ocean		35 9	"
Equatorial Belt	'Atlantic	35-34 5	"
	Indian	35-34	,,
	Western Pacific	34 5	"
	Eastern Pacific ..	33 5	"

Taking each of the oceans as a whole the Atlantic has the highest surface salinity 35 *37* per thousand

Salinities are increased by agencies which increase the rate of evaporation of water, such as those tending to warm the surface or move the air in contact with it The higher salinities are noted in the trade wind belts where warm winds are strong and there is bright sunshine In the doldrums, where there is much rain and general lack of wind, surface salinities are reduced

The average salinity of the whole surface of the oceans is taken as 34 5 or more roughly 35 parts per thousand

The variations in salinity and density are responsible for the oceanic circulation From the equator the water tends to flow north and south towards the poles in intermediate latitudes the denser water sinks below the surface and flows along the sea bottom back towards the equator In the polar areas the melting of ice lowers the density and sets up streaming movements towards the equator

The salinity of enclosed seas naturally varies in different areas of the same sea much more than in that of the open oceans, depending on the point of entry of large rivers and on other obvious factors

Some average figures are given in the following table —

TABLE 8[5]

	parts per thousand
Eastern Mediterranean	39 5
Red Sea (Gulf of Suez)	41-43
Red Sea	51-58
Persian Gulf	38
Malay Sea	30-34
Gulf of St Lawrence	30-31
Baltic (Skagerrak)	25-28
Baltic (East of Bornkolm)	7-8
Baltic (Gulf of Finland)	nearly fresh
Black Sea	18-22
White Sea	26-29
Norwegian Sea Central Polar Basin	25
Caspian Sea	120-285
Dead Sea	192-260

There are also differences in the vertical distribution of salinity at depth in the enclosed seas

The Science of Oceanography received an enormous stimulus from the voyage of the Challenger An 18 gun corvette of 2000 tons burden, she sailed from Portsmouth on the 21st of December, 1872, still carrying two of her guns to enable her to speak with effect to sea rovers The Challenger had the privilege of opening a new chapter in the natural history of the world The state of knowledge at the time of sailing is graphically summed up by Huxley in May 1873 in one of his essays—" The problems of the deep sea " The observations made on board the Challenger showed that the sea bottom is covered with a fine deposit of siliceous mud derived from the diatomaceous plants and radiolanan animals which throng the surface and from the spicula of sponges which live at the bottom

In the great oceans the siliceous deposit is obscured and overpowered by the immensely greater amount of calcareous sediment which arises from the aggregation of the skeletons of dead Foraminifera At very great depths

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[5] Figures quoted from Mellor's Chemistry

the sea bottom consists of an excessively fine red clay that is probably an organic formation and contains hardly any calcareous sediment

As the depth of the sea bottom increases there is a progressive diminution in the amount of calcium carbonate in the deposits, this is because the amount of dissolved carbon dioxide in the water increases as the pressure increases, and this in turn leads to an increase in the solubility of calcium carbonate There is thus a regular process of solution as the calcareous shells fall from the surface to the depths

The table shows how rapid this change is at depths below 2000 fathoms

TABLE 9

	Per cent of $CaCO_3$ in deposits
Less than 2000 fathoms	60 8 per cent
2000-2500	46 7 per cent
2500-3000	17 4 per cent
More than 3000	0 9 per cent

The red clay constituting the very deepest ocean deposits has less than 1 per cent of calcareous matter

The results of the Challenger expedition served as the basis for the classification and mapping of the deep sea deposits both according to their origin and their distribution in depth Classified according to their origin the deposits may be either terrigenous, volcanic, organic or chemical

The waste brought down by the rivers is deposited close to land in deep or shallow waters the fineness of the particles and their physical state determines the distance which they will travel, slimes, for example, will go very far The terrigenous deposits are found close to land, pelagic sediments are remote from the shore The terngenous deposits are often divided into red, blue and green muds according to their colour and certain

other characteristics they are a mixture of mud from the shore with a contribution from the remains of calcareous or siliceous planktonic[6] organisms At this stage also the various chemical changes leading to the'precipitation or absorption of various chemical elements brought in by the rivers are at a maximum The sediments therefore assume a complex character

The blue mud is most frequently found in the deeper waters—on an average of 1400 fathoms, surrounding the continents and in all enclosed seas The blue colouring is due to organic matter and to sulphide of iron in a fine state of division The sulphide is derived from the sulphates in the sea water owing to reduction by the decaying organic matter about 12½ per cent of blue mud is carbonate of lime

The green mud largely consists of glauconite grains containing iron and potassium , it is deposited along coasts, free from large rivers, where sedimentation is slow at depths from 100-900 fathoms It contains only 5 per cent of calcium carbonate

The volcanic deposits of which red clay is the most characteristic, occur at the greater depths of the ocean , they contain relatively little carbonate of lime and are largely composed of silicates, viz , hydrated silicates of alumina and iron (55 per cent), aluminium oxide (16 per cent), iron oxides (9 5 per cent) and small quantities of many other oxides The clay is chiefly derived from the decomposition of submarine volcanic rocks

The various oozes which derive from the skeletons of minute living organisms are regarded as distinct organic deposits they are best classified as calcareous and siliceous divided as follows —

r 1 Globigenna ooze
Calcareous 2 Pteropod ooze
3 Coral mud
Radiolanan ooze
Siliceous
\ 5 Diatom ooze

[6] Plankton—drifting or floating organic life

The globigerina ooze attains maximum development in the Atlantic The average percentage of calcium carbonate in it is between 60 and 70 per cent and may rise to over 90 per cent it generally decreases with increasing depth due to the solvent action of sea water already described The pteropods are pelargic molluscs especially characteristic of the warmer regions of the ocean , the ooze has a greater percentage of carbonate of lime sometimes up to 80 per cent , due to the presence of calcareous organisms other than Foraminifera The radiolarian ooze is a red clay largely composed of the skeletons of siliceous organisms it is confined to the greater depths of the ocean

The diatom ooze is a deposit of the dead valves or frustules of diatoms (algae) They occur in great abundance where there is an admixture of muddy water from the land and the salinity is low It is a characteristic deposit in high latitudes of the Indian ocean

The principal chemical products now being formed *in situ* on the floor of the ocean are —

1 Phosphatic concretions
2 Glauconite
3 Manganese nodules

Phosphate concretions are especially abundant on the East coast of the United States and on the Agulhas Bank where the amount of calcium phosphate in the nodules is as much as 50 per cent The phosphate originates from ammonium phosphate derived from the decomposition of bones of marine animals this reacts with calcium carbonate in the deposit to form calcium phosphate Sudden changes of temperature in the sea cause enormous destruction of life both to minute pelargic organisms as well as to larger animals There is a recorded instance in 1882 of a mass of dead bodies of fish amounting to 6 feet in thickness off the coast between Boston and New York The phosphatic concretions may well indicate past changes in the physical conditions of the sea causing the death of marine organisms as, for example, when warm gulf water containing vast shoals of fish displaces the cold current which usually extends to the American coast

Both nodules and vast slabs of manganese have been found in the ocean bottom Glauconite is another of the interesting minerals now being formed on the sea bottom, particularly because the grains have a complete analogy with those present in the long series of sedimentary rocks The mineral is a potassium iron silicate $KFeSi_2O_b$, H_2 containing thus 7-8 per cent of potassium oxide and serving to take large quantities of this element out of the sea

The Challenger expedition laid the foundation of modern ocean study It and subsequent explorations of the sea have largely established the fundamental data of what is happening in the ocean

Obviously the next step is to make a similar study of what did happen in the oceans in the past This information lies deep down in the bottom sediments and it is to obtain these that methods have to be devised to bring up to the surface not merely sediment but core samples of the ocean bottom

CHAPTER 2

CHEMICALS IN THE SFA

IT is probable that the sea contains at least traces of every element and their detection is therefore a question of sufficiently refined analysis

The modein methods of photo-spectroscopic analysis, such as are beginning to be widely used in soil analysis both for detection and for quantitative estimation, are also being applied to sea water and have indicated the presence of many elements

Certain elements have been so far only identified when concentrated as, for example, in the boiler scale of marine ships or in the ashes of marine plants and animals

It will be obvious that the accuracy of the determination of these small quantities of an element in the sea is uncertain and that no reviewer can decide which figure to accept or which to reject This accuracy is happily of little importance in most cases as the concentrations are so very small

In presenting a table representing the salts present in the sea, that given by Goldschmielt[7] which is quoted by H W Harvey in 1939, has been chosen

COMPOSIHON OF OCEAN WATER

Element	Per cent	Element	Per cent
Oxygen O	85 89	Silicon Si	0 0001
Hydrogen H	10 80	Fluorine F	0 0001
Chlorine CI	1 93	Rubidium Rb	0 000 02
Sodium Na	1 07	Lithium Li	0 000 007
Magnesium Mg	0 130	Zinc Zn	0 000 007
Sulphur S	0 088	Phosphorus P	0 000 006
Calcium Ca	0 042	Iodine I	0 000 005
Potassium K	0 037	Arsenic As	0 000 002
Bromine Br	0 0066	Copper Cu	0 000 001
Carbon C	0 002	Caesium Cs	0 000 000 2
Strontium Sr	0 001	Silver Ag	0 000 000 03
Boron B	0 001	Gold Au	0 000 000 001

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* This value appears to be ten times too great

[7] Fort der Mineral Kryst Petrog 1933, *17,* 112

It is of value also to have these figures expressed in quantities which have an economic meaning For this purpose the cubic mile has been chosen as the unit (there are 300 million cubic miles of sea) it weighs roughly 4,000 million tons and contains on the average 166 million tons of dissolved salts including —

TABLE II[8]

	Tons
Sodium Chloride	128,284,403
Magnesium Chloride	17,946,522
Magnesium Sulphate	7,816,053
Galcium Sulphate	5.939.747
Potassium Sulphate	4.068,255
Calcium Carbonate	579.832
Magnesium Bromide	358,270
Fluorine	1.374
Barium	916
Iodine	100 to 12,000
Arsenic	45 to 367
Rubidum	198
Silver	up to 45
Gold	23
Radium	5 grams

Separate chapters are devoted to those constituents of the sea which are of immediate industrial importance, e g salt, bromine, magnesium, iodine and potassium Those other constituents which are of chief interest are dealt with in this chapter, in alphabetical order, from a vanety of aspects in order that similar aspects should be treated together they are classified also in the sequence of the groups of the periodic table For completeness some brief notes are made on the scarcer constituents under this heading

An attempt has been made to indicate some of the methods for the analysis of the various elements in sea water in an appendix

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[8] **Quoted from Canadian Mining Journal, 1931, *52*, 852-855 The figures for many of the elements are only approximate**

Alkali Metals

An interesting question in regard to the alkali metals is why the sea contains so much sodium chloride and so little of the others It should be possible to draw up a balance sheet showing the relations between the amount of the elements present in the primary rocks and that present in the sea and in the sedimentary rocks which are derived from the weathering and breakdown of the primary rocks The proportions in the sea, however, of related elements such as those constituting the alkali metals group are not the same as those in the primary rocks because of the different extent to which these elements are absorbed and removed before they reach the ocean The disintegration of the primary rocks liberates soluble carbonates, chlorides, sulphates, etc , of the metals which the rivers eventually bring down to the sea In the rivers themselves, in the estuaries and in the waters near the shore absorption takes place on to the surface of the particles of clay which grow finer as they get further from the shore The ions of some of the alkali metals are preferentially absorbed by the clay particles to others thus potassium is retained by the clay in preference to sodium There is indeed a great difference in this respect and hence it comes about that though sodium and potassium are equal in amount in the primary rocks, so that presumably equal amounts of each are brought down by the rivers to the sea, some 66 per cent of the sodium from the rocks as compared with only 2 5 per cent of the potassium is to be found in the sea Potassium on the other hand will be in excess of sodium in the sedimentary deposits Hence the prevalence in relatively shallow waters of deposits of the mineral glauconite, which is a hydrated potassium iron silicate containing 7-8 per cent of potassium oxide (K_2O) This mineral is a characteristic ingredient of the sedimentary rocks, for example greensand The rarer alkali metals lithium, rubidium and caesium are even more strongly absorbed than potassium and accordingly are present in the sea only in the most minute traces and seem to have no significance in its biology

TABLE 129

Based on 1 kilo of sea water

	Originally introduced from the rocks	Present in the sea	Per cent
Sodium	16 8 grams	10 7 grams	66
Potassium	15 0 grams	0 37 grams	2 5
Lithium	0 03 grams	0 00007 grams	2
Rubidium	0 2 grams	0 0002 grams	0 1
Caesium	0 006 grams	0 000002 grams	0 03

Salt is won from the sea by solar evaporation in many lands It is also mined or pumped as brine from extensive deposits in Europe and America Some of this production is highly purified and sold at home and abroad for edible purposes but the bulk furnishes the raw material for the heavy chemical or alkali industries

It serves as the source of both sodium and chlorine ions, the former to make soda ash, caustic soda and sodium salts whilst chlorine is used as such, or in bleaching power or as hydrochloric acid

Quite recently the sodium ion has been extracted directly from the sea by the zeolite exchange method mentioned under copper and more fully described in Chapter 9 This is being done at the great nitrate factory of Heroya in Southern Norway for the purpose of converting nitrate of calcium into sodium nitrate No details of the process are available but it is suggestive as showing that it may be economic to extract the abundant sodium ion from the sea

The sea is a three per cent solution of sodium chloride

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9 W Noll, Nachr Ges d Wiss Gottingen, 1932, 122 W Jenny, Univ Missouri, Agri Exp Sta 1931 Research Bull 162 V M Goldschmidt, Fort Min 1933, *17*, 148 also Ges d Wiss Gottingen, 1933, 235

This accounts for most of its properties Marine animals, the cells of which are readily permeable, live with a body fluid of this high concentration We humans also require a salt solution in our body fluid or blood but it is less concentrated, namely 0 9 per cent of salt

Potassium salts are produced commercially from brines, salt lakes and deep deposits Although there are plenty of potash salts it is a fairly safe prophecy that the seas will one day be exploited more widely, for potassium The Italians have begun such exploitation

The percentage of lithium in the Sea is of the order of 0 1 parts per million For some unexplained reason lithium salts have become concentrated in the brines of Searles Lake, where the concentration is 0 021 per cent Lithium was first isolated from the brines in 1938 as crude lithium phosphate and Searles Lake now supplies the raw material for more than half the world's lithium production

Alkaline Earth Metals

Calcium is of such interest, particularly in connection with the formation of calcareous organisms and calcareous rocks, that it has been the subject of many investigations

Large amounts of calcium salts are carried down to the sea by every river , it is being withdrawn all the time from the sea to build shells or skeletons by animals which live on the sea bottom and in particular by the Protozoa to form the calcareous oozes Four times more calcium than chloride is carried into the sea by the rivers, whereas the oceans contain some forty-six times more chlonde than calcium In fresh water it is the most abundant of the three metals—calcium, magnesium and sodium , in sea water it is the least abundant Some idea of the magnitude of the deposition of calcareous matter is given by F W Clarke's statement that 1400 million tons are deposited annually The Ca/Cl ratio is 0 02174 , the average content of calcium in sea water is 0 042 per cent

Calcium carbonate, either precipitated or secreted, forms the building material of the innumerable shells which strew the sea bottom, it builds up coral reefs sometimes thousands of feet thick It forms the chalk hills and cliffs and the limestones and dolomites of our homelands In these many happenings through geological ages to a material originally dissolved in the sea it may have been redissolved, re-precipitated, altered by substitution of silicate and phosphate for part of the carbonate or sometimes magnesium has replaced calcium In the oyster a nacreous layer and sometimes a pearl is the result of the deposition of calcium salts

Calcium is removed from the sea on a vast scale by coral reefs Apparently the experts have not yet agreed on the exact mode of formation of these structures it is probable however that the problem is essentially a biochemical one

The water in shallow seas off the shores of the islands or in lagoons is saturated with calcium bicarbonate Calcium carbonate must therefore be precipitated if the amount of carbon dioxide in solution can be reduced This would happen with a rise in temperature of the sea or through violent agitation of the sea by storms or following an outburst of photosynthesis causing a withdrawal of carbon dioxide by manne plants A multiplication of denitrifying bacteria entailing an increase in alkalinity would have the same effect

It is therefore not certain that the coral reefs are merely the remains of the skeletons of reef-forming organisms as was at one time thought and far more likely that chemically precipitated carbonate of lime predominates in them Calcium carbonate is thrown out of solution in sea water as minute needle shaped crystals or little balls of aragonite

It is believed that precipitation of calcium carbonate is often caused by physical and chemical conditions indeed the geological evidence indicates that calcium and magnesium carbonates have been deposited when the carbon dioxide pressure fell gradually in past ages

The shell of the mollusca consists of an organic basis, often a polymerised ammo sugar[10] called conchiohn which is impregnated with carbonate of lime together with a small proportion, 1-2 per cent, of calcium phosphate. The zone of the external surface of the mantle secretes a layer formed of prisms of calcite , the rest of the epithelium or outer layer from this zone secretes the inner or nacreous layer of the shell composed of successive laminae

Sea shells apparently vary in composition, sometimes calcium phosphate partially replaces carbonate, in others it is suggested that some calcium fluoride is present Elsewhere part of the calcium is substituted by magnesium Whether these are primary or secondary changes in the shell is a matter of considerable interest. According to Clarke and Wheeler[11] the Brachipods fall into two distinct classes , the shells of one consist mainly of calcium carbonate with little organic matter, whilst the shells of the other group are formed mainly of calcium phosphate with much organic matter The two groups are physiologically quite dissimilar

The substitution of magnesium for calcium seems to be a question of temperatures it is favoured by warmer waters Colder waters on the other hand favour the introduction of strontium

It is known that different species of starfish[12] show a progressive enrichment in magnesia following an increase in the temperature The proportion of magnesium carbonate ranges from 7-10 per cent in colder waters, while those from tropical waters contain from 11-14 per cent Such differences may either be conditioned by different solubilities at different temperatures or they may be peculiar to the species

Strontium is present in the shells of some marine animals in much the same ratio to calcium as it is in sea

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[10] 1 e a sugar like glucose containing an ammo group of which several molecules are polymerised or joined together to form a complex substance

[11] Proc Nat Acad Sci 1915, *1*, 262

[12] Clarke and Kamin Proc Nat Acad Sci 1917, *3*, 401

water In very cold water strontium may replace calcium In the Antarctic strontium carbonate forms almost the entire skeleton of the radiolarian, *Podecanehus*[13] An explanation is perhaps afforded when it is remembered that strontium carbonate is more soluble in hot than in cold water whereas with calcium carbonate the reverse is true

It is stated by Dinger[14] that the celestine (strontium sulphate $SrS0_4$) in certain strata of the lower " Muschelkalk " is derived from sea water through the agency of radiolaria which extract it to form their shells

The relative abundance of the alkaline earths in the sea in the order calcium, strontium, barium is about 400 100 1 This compares with 17,350 100 400 in the lithosphere

Strontium is relatively more concentrated in the sea than in the lithosphere and inasmuch as sea water is not saturated in respect to any strontium salt in the way it is with calcium carbonate it is even possible that the strontium content is still increasing Sea water is capable of dissolving 3 or 4 times as much strontium as it already contains The present average is about 001 per cent Strontium is fifth in order among the metals found in sea water Small quantities of strontium are found as might be expected in the anhydrite region of the Stassfurt deposits

Barium has been found in the ashes of marine plants and in the boiler crusts of ocean vessels There are only traces in sea water as would be expected from the great insolubility of barium sulphate

Marine nodules containing 75 per cent of barium sulphate have been dredged from 675 fathoms off Colombo, Ceylon

Aluminium.

Aluminium is present in sea water to the extent of 0 6 to 2 4 parts per million Aluminium is one of the most common and widely distributed elements in the earth's

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[13] J R Bruce, J Marine Biol Assn 1928, 15, 553

[14] Chem Erde 1919, *4*, 167.

crust, coming third in the order of most abundance. Enormous quantities are carried down to the sea in the rivers but it is rapidly deposited or removed by chemical action The mud of the sea bottom contains alumina, chiefly as a hydrated silicate Aluminium has never been found as a constituent of living organisms nor has it been shown to be needed by them

Arsenic

Whereas the ratio of arsenic/phosphorus in sedimentary rocks is 1 2000, in the sea it is 1 3 The apparent enrichment is due entirely to the almost total withdrawal of the phosphate by living organisms The concentration of arsenic in the sea varies between 0 oi and 0 08 parts per million it is higher in estuaries with o 1 to 1 o parts per million It is considered by Atkins and Wilson[15] that it exists mainly in the form of arsenite. These authors have suggested that arsenates may partly replace phosphates in the metabolism of green plants as they have been found capable of doing in some fresh water algae

Arsenic enters into the life history of many marine animals and plants It is present in several shell fish of which lobsters with an average content of 40 parts per million contain the most

It is reported in many seaweeds, about 6 parts per million of arsenic having been found in Chrondus Cnspus and about 125 parts per million in Laminana Digitata Plankton may contain as much as 66 parts per million It is believed that the arsenic content of seaweeds is parallel to the iodine content and that both are in organic combination The arsenic content of the sea bottom is also high in comparison with that of the water above

In the Falmouth area for example material dredged from the sea bottom has been found to contain from 75 to 1200 parts per million whereas the sea water above had only 0 03 parts per million

Arsenic and the heavy metals, all elements highly

[15] **J Marine Biol Ass 1927,24,609**

poisonous to life, are removed in quantity from the sea largely at the point of entry by absorption on to alumina (clay) sediments and hence they collect in the mud at the sea bottom Were it not for this removal the sea would contain so much arsenic and perhaps other poisonous heavy metals that life in it would be impossible

Goldschmidt gives the following table in illustration that less than I per cent of the original amount of such elements remains in the sea

TABLE 13

	Brought in to 1 kg of sea	Present in 1 kg of sea	Percentage left in sea
Copper	58 mg	0 10 mg	or 0 02 per cent
Zinc	116 mg	0 07 mg	0 06 per cent
Lead	6 mg	?	
Arsenic	3 mg	0 02 mg	0 5 per cent
Gold	0 06 mg	0 0003 mg	0 5 per cent

Boron

Boron is one of those elements of which there is much more in the sea (10 parts per million) than can ever have come into it by the rivers from the weathering of primary rocks—50 times as much according to Goldschmidt's estimate Much larger quantities have been deposited from the sea in the course of geological time—10 to 20 times as much as it now contains Small quantities of hydroboracite ($CaMgB_6O_{11}$, $6H_20$) are found deposited in the anhydrite region at Stassfurt It is inferred that there has been another, probably volcanic, source of boron and that like chlorine it was present in the original gaseous envelope of the earth and was dissolved by the first ocean

Boric acid, a weak acid, undoubtedly plays a part in the equilibrium between carbon dioxide and carbonates The amount in marine organisms is much the same as in the sea Plants take up bone acid from the soil and the work of Miss Brenchley at Rothamsted has shown that it is essential for growth.

95 per cent of the world's boron comes from California At Kramer large deposits of sodium borate have been found

Carbon

The carbon dioxide content of the sea is a most important factor it is partly in solution but mainly in combination as bicarbonates and carbonates As on land it provides the raw material from which plants synthesize carbohydrates and other organic substances The amount of carbon dioxide also controls the alkalinity of the sea, which in turn influences biological life in it as well as affecting the solubility of calcium carbonate

In the atmosphere there is o 4 grams of carbon dioxide per square centimetre of the earth's surface In the sea there is some 27 times as much, equivalent to 10-13 grams per square centimetre (though Goldschmidt puts this as high as 20 grams per sq cm) of the world surface The quantity present as carbonates in sedimentary rocks —chalk, limestone, dolomite, is estimated as 6 56 kilograms with an additional 1 to 3 kilograms contained in coal, oil it into carbon dioxide, making a grand total of carbon dioxide, bound and free, in the world of 7 3 to 9 7 kilograms for every square centimetre of world surface This is the grand total in the world Expressed in another way the sea contains 45 c c of carbon dioxide in all forms per litre The sea acts as a balancer in controlling the amount of carbon dioxide in the air , for example, it is calculated that man's activity in burning coal and oil would double the percentage in the air within 300 years if the sea did not operate to keep it steady it is calculated that about 0 5 ce is absorbed per square centimetre per annum All the time the carbon dioxide in the sea is taking part in forming the calcium carbonate skeleton of organisms and it is claimed by Hogbom[16] that the amount so taken up in a year is of the same order of magnitude as the total present in the air.

[16] Svensk Kemisk Tidskr 1894, *6*, 169

According to Clarke[17] the annual deposition of calcium from the sea, mostly as carbonate, amounts to 1400 million tons—the greater part being due to the smallest Protozoa, of which one third dies every 24 hours and sink to the bottom

The free oxygen of the sea originates largely during the process of photosynthesis[18] when oxygen is liberated every atom of carbon sets free 2 atoms of oxygen The surface waters during active metabolism are saturated with oxygen

Carbon dioxide and the carbonates together with boric acid control the alkalinity of the sea and keep it approximately constant, for should it vary most of the present forms of life would be destroyed The bases are slightly greater in quantity than the equivalent of stable radicals hence sea water contains excess base combined with carbonic acid and is slightly alkaline The alkalinity, expressed as pH, varies slightly with time of year, temperature and geographical position but lies between 8 and 83 in the open ocean In the summer when the marine plant organisms are busy, enormous quantities of carbon dioxide are all the time being extracted, so that the carbon dioxide content falls and the pH rises In winter the reverse happens It may vary from pH 7 8 to 8 8 at the surface depending on conditions , the value at Port Erin is 8 1 in December and 84 in April

It is considered that the greater part of the carbon dioxide now in circulation has been gradually introduced during geological ages and calculations have been made of the annual quantity so added, largely as volcanic exhalations from the primary rocks

Copper

The average copper content of the ocean is small, being of the order only of o 01 parts per million but it is an element of very considerable interest There is much more copper in the rivers and in sewage Indeed the

[17] Data of Geochemistry 1924

[18] i e , making of organic compounds from carbon dioxide in sunlight

copper content of the fresh water in Long Island Sound fluctuates between 1 0 and 0 5 parts per million at high and low water Hence anyone desiring to extract copper would be well advised to go to the rivers rather than to the sea

Copper is one of those elements which the chemist has found out how to concentrate by means of the so-called base absorbing compounds or artificial zeolites Originally these were used for taking the hardness out of water—the calcium and magnesium ions which give rise to hardness to soap solutions were exchanged for sodium ions as the result of simple percolation through a bed of base exchanging material The base when saturated could be regenerated for further use by means of percolation with a strong solution of sodium chloride

Much success has attended the efforts of Beaton and Furnas[19] to use carbonaceous Zeolites to recover small quantities of copper which are afterwards recovered from the Zeolite by means of sulphuric acid Without going into details, it may be said that a solution containing 1 pound of copper in 6300 pounds of water can be turned into one of copper sulphate containing 1 pound in 6 87 pounds of water To do this 1 54 pounds of sulphuric acid (100 per cent strength) must be employed and simple arithmetic indicates that 1 pound of acid performs the same duty as the evaporation of 4,200 pounds of water for which a considerable amount of energy would be required The procedure is dealt with in greater detail in Chapter 9

It has been stated that the world's copper ores, which average 2 9 per cent of copper, will be used up in 70 years It is at present uneconomic to recover copper from ores with less than 1 per cent of copper and it has been estimated that the recovery of copper from the sea would cost much the same as to win it from these one per cent ores

What the chemist does with difficulty the oyster finds easy Apparently it gargles a barrel of water per day and

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[19] Ind Eng Chem 1941, *33,* 1500

around the British Isles and in certain parts of the Atlantic coast oysters become green due to the formation of a respiratory pigment, haemocyamn, containing copper.

The average amount of copper in a Long Island oyster is said to be 2 5 mg but it varies from i 24 to 5 12 mg , Cape Cod oysters have less Someone has calculated that

in Long Is

copper every year from the sea This quantity is small compared with the amount discharged as sewage, said to be 200 tons annually per million people

Copper salts apparently have a peculiar effect on oyster larvae inducing their attachment to the substratum and initiating their metamorphosis The result is that the best settling areas are found on bottoms affected by fresh water which brings down copper, whilst natural oyster beds occur mainly in the mouths of rivers[20]

It has been estimated in the United States that 200 tons of copper are lost in sewage each year per 1,000,000 people, together with 50 tons each of such metals as magnesium, lead, aluminium and titanium The 10,000,000 people of New York City provide ample copper for their oysters

Copper is known to be the metal in the respiratory pigment, haemocyamn, which is present in lobsters, shrimps, crawfish, and other shell-fish and plays there the same part as iron does in haemoglobin, the respiratory pigment of human red blood corpuscles It is found also in sardines, herrings, salmon, and other sea animals, and is obviously quite an essential element in marine life, notwithstanding its lowly proportion in the sea

Copper has been found in the ash of seaweeds *(Fucus)* and in corals

The marine organism reacts in a very distinct manner to slight fluctuations in the content of copper ranging from o 1 to 0 5 parts per million , greater concentrations are injurious, causing disintegration and death A number of other similar metallic elements have no effect

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[20] **Galtsoff J Wash Acad Sci 1932, *22.* 253**

whatever and different copper salts all have the same effect Yet copper is an element which is poisonous to life in quite low concentrations, as witness what happened when in May 1918 a vessel carrying copper sulphate was stranded and broken up off the coast of Cornwall Seaweeds and shellfish were killed over a wide area

Fortunately an excess of copper is prevented by the very effective means of removing most of it by absorption on clay particles before it reaches the ocean Goldschmidt has calculated that on an average 58 mg have been carried to the sea for every kilogram of water but that of this quantity only 0 01 mg remains, the rest having been precipitated thus only 0 02 per cent of the total copper remains in the sea

Gold and Silver

A matter in which the more credulous portion of the public is interested and on which much money has been expended is the possibility of obtaining gold from the sea There are many statements in the literature regarding the amount of gold in the sea, most of which are now known to be inaccurate It was originally thought that gold was present as chloride but it is much more probable that it occurs mainly as the metal and therefore does not stay in the sea but is removed by absorption on to the surface of clay particles or even of marine organisms and is taken down to the bottom In agreement with this the bottom sludges obtained by dredging in certain localities contain very much larger quantities of gold than there are in the sea

In very many seas gold has not been detected, it is certainly present only to the extent of less than 0 6 to 1 part in one thousand million, that is 1 milligram per cubic metre Haber's results are much lower than this

On the 1 milligram basis the amount of gold in a cubic mile of sea is only 4 tons—the figure 23 tons quoted in Table 11 must have reference to water containing much suspended matter and is of little significance

When estimating these extremely small quantities of a scarce element in sea water analytical errors are introduced by traces of the element in the reagents and reaction vessels In consequence most analyses give results which are too high this is particularly true of gold

Most of the published work on the extraction of gold from sea water describes methods by which it can be recognised in dilute solutions made up in the laboratory but when these methods were applied to the sea usually no detectable quantity of gold was present For example rags mordanted or fixed successively with tannin and then with stannous chloride absorb gold with great avidity from solutions of its salts even at extremely low concentrations , 1 gram of such rags absorbed 0 0005 mg of gold per hour from solutions containing from 5 to 100 mg. of gold per ton of water Yet tests carried out off the coast of Brittany by this method gave absolutely negative results

Another method is to add 5 cc of concentrated aqueous stannous chloride solution to a ton of sea water, and then by adding slaked lime to obtain a precipitate oi a tin salt with any gold that is present—and finally to extract the gold from this with dilute potassium cyanide as is done with the tailings on the Reef in Johannesburg Such methods discovered no gold in the English Channel or in the Mediterranean and only traces in the Atlantic

Liversidge used Muntz metal, an alloy of copper and zinc to remove the gold and claimed to recover from one half to 1 grain of gold per ton of sea

Several patents have been taken out for various methods of extracting gold from the sea B Stoces[21] suggested treating sea water with metallic sulphides, such as antimony sulphide, which retain gold B Cernik and B Stoces[22] suggested that sea water be pumped or otherwise passed through a screen containing materials such as pyrites or activated charcoal to absorb the gold

H C Parker[23] suggests extracting the gold by means of nickel granules

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[21] B P 273, 346, 23/12/25
[22] B P 289, 638 3/5/27
[23] U S P 2,042, 121, 26/6/36

George Duncan in Australia[24] is said to have designed a plant costing £10,000 to deal with 50 tons of sea water per 24 hours It recovered 1/10th grain, 1 e 6 5 mg per ton or 10 oz of gold per day

We owe the most complete study of gold in sea water to the celebrated German chemist Haber[25] After the last war Haber organised an expedition in an attempt to pay the German war debt with gold won from sea water, Haber started from the assumption that from 5 to 10 mg were present as gold chloride in a short ton of sea water It was proposed to precipitate this with sodium polysulphide and the cost of the proposed recovery operations was small His ship, the Meteor, equipped with a filtration plant and laboratory crossed the North and South Atlantic oceans but it found only a small fraction of the expected amount of gold Following on this systematic sampling of the oceans was begun in 1924 and continued until 1926 , from 1927-8 Haber returned to the attack studying the gold content of the oceans at greater depth*

Haber established that the average concentration of gold does not reach one tenth of a milligram per ton, indeed in general it does not exceed one thousandth of a milligram per ton The average gold content in the South Atlantic ocean is 0 008 mg per cubic metre and the highest value found there was o 044 mg per cubic metre In San Francisco Bay the figure was only very little higher in spite of the fact that it is fed by rivers from a gold producing region In a few places, particularly off Newfoundland, concentrations up to 8 46 mg per cubic metre have been found In the Arctic Ocean the average value is o 045 mg per cubic metre but samples of ice have given higher values of as much as 4 84 mg per cubic metre It is clear that samples of sea water give very variable results , that most observers have been misled and given figures which are too high, and that the concentration decreases with depth Gold as already stated

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[24] **Chemical Age, 1936, 232**

[25] **Z Angew, Chem 1927, *40*, 303**

is present as the metal and never reaches the sea proper, being absorbed and held by suspended matter and later settling in the mud Above all it is clear that it cannot be won economically from the sea when present in the concentrations stated[26]

Rumour has it that gold was actually extracted from **the** sea during **a** month's working of one of the American bromine plants but that the cost of doing so was several times more than the value of the gold recovered

There appears to be rather more silver in the sea, perhaps ten times as much as gold but this element has apparently no significance in marine affairs Like gold it is carried down with suspended matter

Halogens

The importance of the halogens in sea water is considerable and except for fluorine they are discussed in other chapters The halogens in the order chlorine, bromine, iodine occur in sea water in the proportions 1000 3 40 0023

It is interesting to note that whereas chlorine is an essential constituent of most living matter, and iodine is found in all marine plants, sometimes in relatively large amounts, bromine is less widely distributed in living organisms, but this may be due to failure to seek for it In that the halogens form few insoluble salts and are not readily precipitated it is to be expected that the concentration of these elements in the sea is slowly increasing

Fluorine is present in traces in marine boiler scale and

in the sea I

is **a** constituent of the mineral apatite It appears to be of very secondary importance The geochemical story of fluorine is not so clear This substance is almost as abundant in the original igneous rocks as its chemical companion chlorine Chlorine is a dominant constituent of sea water but this is not true of fluorine nor has this element yet been found in appropriate amount in the bottom sediments It is found in phosphate rock deposits

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[26] The methods of obtaining gold from the sea are reviewed by W E Caldwell (J Chem Educ , 193S, *15*, 507)

but although these are large they are hardly sufficient to balance the cycle

Fluorine in drinking water in an amount exceeding about 1 part per million is dangerous to children, causing fluorosis, the most obvious symptom of which is mottled enamel of the teeth T G Thompson and H J Taylor[27] find an average fluorine content of about 1 2 parts per million in the open sea, with higher values where there is fresh water contamination

Iron

Much more iron can be detected in the sea after oxidation by boiling with bromine water or evaporation with nitric acid than before such treatment This is an indication that most of the iron is present as organic iron compounds which may be supposed to act as catalysts in hasteni substances There are indications that the deeper ocean waters are slightly richer in iron than those at the surface, which latter show a seasonal variation in iron content decreasing as the number of diatoms increases Diatoms remove iron from solution Dried marine animal tissues have been found to contain from 0 01 grams to 1 985 grams per kilo of dry tissue[28] This gives additional evidence of the utilisation of iron biologically

The littoral sands which contain organic matter from land drainage also contain iron from the denudation of the rocks The putrefaction of the organic matter sets free hydrogen sulphide which acting on the iron compounds precipitates ferrous sulphide Hence the formation of an under layer of black sand round the coast on the zone between high and low water mark The ferrous sulphide becomes oxidised and bleached to ferric sulphate on the surface where the sand is bathed by the tides The iron present in blue and red mud and glauconite was deposited before it reached the oceans.

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[27] Ind Eng Chem Anal Ed 1933, *5*, 87

[28] Phillips, A M , Marine Biol Papers Carnegie Inst ,1917,9,91

Manganese

Manganese is present to the extent of 0 01 to 0 001 parts per million according to the analysis of Thompson and Wilson[29] made on water from the North East Pacific Ocean The dried mud from the sea bottom contained large quantities, 1 e from 0 05 to 0 3 per cent They also found 0 07 per cent in the ash of plankton and suggest that manganese may be removed by these organisms as waters which were rich in plankton contained less dissolved manganese

Manganese in small quantities is present in manne organisms for example the mussel, *Pinna Squamosa,* which has a brown respiratory pigment, prinaglobulm, in its blood which contains manganese in place of the copper normally found in haemocyanins

Manganese occurs in some quantity in fresh water particularly in certain Swedish ponds[30] and in fresh water molluscs It accelerates the nitrification of ammonia by bacteria

The discovery of deep sea nodules containing manganese by the Challenger expedition aroused considerable interest These vary from 4 per cent to as much as 64 per cent of manganese in the form of manganese dioxide Their origin is uncertain, Murray's theory was that they came from decomposed volcanic material, 1 e , manganese and iron bearing silicates An alternative is that they are derived from Subterranean springs from which manganese is precipitated on coming into contact with sea water The nodules occur as coatings on fragments such as sharks teeth or small grains and may reach considerable size They are most common in the Pacific

In some places there appear to be vast slabs of manganese covering many square miles on the ocean bottom Why this is so is not known a possible explanation is discussed under the heading of radioactivity

[29] J Amer Chem Soc 1935, *57*, 233

[30] Weibull Nahr Genuss 1907, 24, 403

Nitrogen

Nitrogen is present in sea water as dissolved gas and in various compounds—ammonia, nitrates, organic nitrogen—all in very small quantities

The concentration of nitrate is practically nothing at the surface but increases with increasing depth up to a figure of about 0,5 parts per million of nitrogen The nitrite concentration is very small and there are about o 1 parts per million of organically bound nitrogen Ammonia is formed by the decay of organic matter containing nitrogen and by the action of denitrifying bacteria on intrates and nitrites Very little ammonia is found except in closed or nearly closed basins like the Black Sea and in the vicinity of coral reefs It may vary from 0 001 to 0 3 parts per million One of the factors affecting the formation of calcium carbonate is the presence of ammonia, which causes calcium salts to react with carbon dioxide to give calcium carbonate, large deposits of which are formed by this purely chemical precipitation

The dissolved nitrogen compounds of the sea are in a continual state of change as to form and quantity They are subject to the action of both nitrifying and denitrifying bacteria and are an important limiting factor of growth

H W Harvey[31] who has studied their seasonal vanation and other factors, finds a regular seasonal change in the nitrate content of the waters of the English Channel It decreases during the spring in the upper layers, is nearly all gone by August throughout all depths and then is reformed in the bottom waters faster than the plants can use it Observations in Plymouth Sound show that the plant growth in the estuary uses up most of the nitrate before the water reaches the open sea in the summer months

There are two categories of nitrogen bacteria in the sea, namely those which make use of dissolved elementary nitrogen and build it up in combination with carbohydrates as protein and those that cause the breakdown of nitnte into nitrate, of nitrite into ammonia and of

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[31] **J Marine Biol Assoc 1926, *U,* 55**

ammonia into elementary nitrogen These processes, though antagonistic, proceed simultaneously, either of them being accelerated by an increase and retarded by **a** decrease in the temperature The denitrifying bacteria seem to be the more active and hence in tropical seas there is less nitrate and less phyto or vegetable plankton, whereas the Antarctic and Arctic ice-bound seas are enormously rich in diatom life and on the sea bottoms in the Antarctic over a zone of 10 million square miles the skeletons of diatoms predominate Hence also the abundance of nitrates and nitrites at the bottom of deep oceans where the temperature is about o° Centigrade As the dead bodies fall from above they are slowly converted into nitrates and the sea bottom would become very rich
in these bu
the occasional welling up of bottom water It is suggested that the total amount of nitrogen in the ocean remains constant and the same is true for oxygen and carbonic acid The various actions balance out the losses and gains

Inert Gases

The inert gases have also been found in the sea, as would have been expected seeing that there is free exchange at the surface between sea and air N W Rakestraw and V M Emmel[32] find that the total inert gas concentration is o 4 to o 2 ml/litre or parts per million Almost all of this is argon N W Rakestraw, C E Hernck and W D Urry[33] have shown that sea water is practically saturated with two of the inert gases, helium and neon, with an average of about $1\ 5 \times 10^{-4}$ ml/litre of the combined gases

Oxygen

Sea water at the surface is nearly saturated with respect to oxygen and nitrogen The actual amount of oxygen depends on the temperature, pressure and salinity, and will vary from about 5 to 10 ce per litre The distribution of oxygen varies considerably from super-

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[32] J Physical Chem , 1938, *42,* 1211
[33] J Amer Chem Soc . 1939, *61,* 2806

saturation at the surface to absolute deficiencies in the bottom waters of fjords and estuanes Waters near the equator show the lowest oxygen content, this gradually increases as the poles are approached The oxygen decreases in depth in the tropics to a minimum at 400-700 metres after which it gradually increases the same applies to temperate and polar regions where the minimum is deeper at 500-1500 metres There is a distinct diurnal variation in the concentration of dissolved oxygen during the spring or summer months, the maximum is obtained in the afternoon and the minimum before sunrise According to Harvey many marine animals do not survive unless the water is nearly saturated with oxygen and kept moving in a continual flow past the organism The oxygen originates by direct solubility from the air and various photosynthetic processes It is removed as the result of respiration of marine life and from various reactions of oxidation , fish, for example, extract it from water in their gills A direct relationship has been found between the amount of dissolved oxygen and diatom growth Diatoms and all marine plants behave like terrestial plants in that they respire by taking in carbon dioxide and putting out oxygen As sea water becomes warmer the amount of oxygen it dissolves falls and thus in tropical seas fish have to take in more water than their fellows in more temperate climates

Phosphorus

Phosphorus or rather phosphate, being the most important limiting factor for the growth of plankton, controls to a major extent the whole production of life in the sea

It is present in inorganic form as soluble phosphates and possibly also in organic form as complex albumenoids and phosphatides of which very little is known The quantity is always minute owing to the continual depletion, varying from zero to o 07 parts per million , the depletion occurs first in the upper layers early in the year when the amount of sunshine begins to exceed about 3 hours per day

After the death of the plankton the phosphate is carried down to the bottom where it may reach a considerable concentration and be lost for an almost indefinite time[34] Vertical mixing due to currents or upwelling of water from the depths is necessary to bring it to the surface again Large quantities of phosphate are also brought in by the rivers Another aspect of the phosphate story is the loss of the vital element from the land in sewage discharged from the sea It has been calculated that the sewage from 5,000,000 people is equivalent to 17,000 tons of rock phosphate in a year, and this happens to be the quantity present in the annual export of meat from New Zealand, which Dominion is the loser of the same amount The population of Great Britain discards as sewage the equivalent of 150,000 tons of rock phosphate, most of which reaches the sea An estimate of the annual losses of phosphate from all sources to the sea in the United States amounts to the equivalent of 60,000,000 tons of rock The world's consumption of rock phosphate is said to be 18,000,000 tons , there are of course some other sources of phosphatic fertilisers Many of the agricultural soils of the world are definitely short of phosphate and their crop-bearing qualities impaired in consequence

Selenium

This element, which accompanies sulphur in the primary rocks is only present in very small quantities in the sea V M Goldschmidt and L W Strock[35] found the selenium content of the North Sea water to be 3 8 *x* 10 7 gm/L (3 8 *x* 10 4 parts per million) Selenium reaching the ocean is not oxidised to selenate but is absorbed by iron and manganese hydroxides as these are precipitated

Silicon

This element is present in the form of soluble silicates

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[34] Harvey, Biological Chemistry and Physics of Sea Abater, Cambridge, 1928

[35] Nachr Ges Wiss Gottingen 1935, 11, *1*, 123

which are essential for the growth of diatoms, since from 60 to 75 per cent of these on a dry basis are composed of silica Enormous quantities are therefore being constantly taken out of the ocean, hence the variation in the published content of silicon from 0 1 to 3 0 parts per million The silicon content increases with depth as the pressure increases and more silicates go into solution

It was thought at one time that a lack of silica limited plant growth but the more recent work of Atkins indicates that the sea is not depleted of silicate to such an extent that it becomes a limiting factor[36]

On the other hand the demands of the diatoms are so great that the silicon found in solution in the sea is sometimes insufficient to supply them and it is highly probable that they obtain this element by splitting the clay particles suspended in water There is experimental evidence that this can happen

River waters contain at least 500 times as much silicon as the sea and they are discharging annually enormous quantities of suspended and dissolved silicates, which are largely precipitated when they come in contact with the sea There are often very heavy growths of diatoms near the mouths of rivers

Though the total amount of water in the rivers is small compared with the great bulk of the ocean it must be realised that all the time a great quantity of material in solution and suspension is being brought into the sea by them and deposited largely on the great continental shelf Thus silica is constantly being added to the sea, first as gravels, sands and muds near the shore, then as particles in suspens and, finally, in colloidal form, as very fine particles which are earned far out to sea and may be acted on both by marine bacteria and by diatoms themselves as a source of silica

There is not enough magnesium in the sea to cause precipitation of silicate as magnesium silicate but in basic solution both iron and aluminium silicates are almost

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36 J Marine Biol Assn , 1923, *13, 511,* 1926, *14,* 89

completely thrown out of solution In consequence glauconite, a hydrated potassium iron silicate, is very widely distributed near the mud line of the coastal shores in still, though relatively shallow, waters Bacteria are thought to play a part in its formation .According to Murray and Renard of the Challenger expedition the shell of an organism becomes filled with fine mud containing iron after death The sulphates of the sea water then react with the organic matter of the organism in presence of reducing bacteria to make iron sulphide Later this is acted on by dissolved oxygen to form ferric hydroxide which, with silica and potassium from the sea, forms glauconite This theory is quoted as an example of the complexity of the chemical reactions which are taking place slowly in the mud on the sea bottom The Radiolarian and Diatom ooze deposits contain some 55 and 41 per cent of siliceous organisms respectively

Sulphur

Sulphate Some 7 5 to 8 per cent of the total salts in the sea consist of the sulphate ion

The ratio between the amount of sulphate ions and the chlorinity is a constant, being 0 1396 In river waters the ratio is much greater—it varies from 1 to 9 In certain stagnant areas, for example the lower depths of the Black Sea, there are considerable quantities of sulphide due to reduction of sulphate by organic matter or by bacteria , such waters have no dissolved oxygen In the oceans proper there is only sulphate

Calcium sulphate (the mineral anhydrite) is the first salt to separate when the sea evaporates Consequently it forms the bottom bed of most salt deposits At Stassfurt, where there has been a certain amount of evaporation and deposition followed by fresh access of the sea and renewed evaporation, thin beds of anhydrite alternate with the salt There are deposits of it near Billingham on the north east coast of England

Calcium sulphate, apart from its wide use as plaster of Paris, is today used instead of sulphuric acid for the manufacture of ammonium sulphate from the air and also to some extent for the manufacture of sulphuric acid in rotary kilns like those used for cement

Vanadium

Vanadium which has been detected in sea water by spectroscopic methods has been found in the salt clays of the Stassfurt deposits Of much greater interest is its occurrence in the blood of an ascidian[37] and in a holothunan or sea slug[38] Where these animals live and die
in quanti
aggregated Vanadium acting as a catalyst is believed to have an influence in determining the nature and character of the mineral oil produced in geological ages from decomposing organic marine remains, a question further discussed in the following chapter

Zinc

Zinc salts are present in the sea in very small quantities Figures have been obtained varying from nothing to 0 007 parts per million of zinc Marine organisms have various amounts of zinc ranging from 3 5 parts per million in elasmobranchs to from 188 to 340 parts per million in oysters

Other Elements

As has been stated at the beginning of this chapter it is probable that minute quantities of salts of every element exist in sea water Of the eighty-nine definitely known elements all but the six inert gases (which form no compounds but are themselves soluble) form compounds which have at least a slight degree of solubility As all these elements exist in rocks in some part of the earth and these rocks are exposed to the leaching action of water, it is not stretching the imagination very far to conclude that if and when highly sensitive analytical methods for detecting these elements are worked out,

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[37] Henge, Zeit Physiol Chem 1913, *86*, 340
[38] Phillips, Amer J Sci 1918, *46*, 473

then they will be found to be present in the sea

T Ernst and H Hormann[39] by spectroscopic methods have found an average of o 5 x 10^{3} parts per million of vanadium, expressed as vanadium pentoxide, 0 1 x 10^{-3} parts per million of nickel as nickel oxide (N_1O) and 10^{-3} parts per million of molybdenum (as M0O3)

J Bardet, A Tchakinan and R Lagrange[40] have identified spectroscopically in sea water germanium, lead, tin, titanium, tungsten, bismuth, and gallium, in addition to elements previously mentioned Cobalt has been found in minute quantities in oysters and mussels

Radioactivity

Sea water has a very slight radioactivity This is rather variable E Foyn, B Karlik, H Petterson and E Rona,[41] show that there is about 2 x 10^{6} gms of uranium per litre, from o 03 to o 2 x 10^{12} gms of radium per litre, and under 0 5 x 10^{6} gms of thorium, if any, per litre Radium salts are apparently deposited from sea water Sanderman and Utterback[42] find that the deep sea sediments are richer in radium than are land deposits and that the radium is mostly to be found in a very thin film on the surface Plankton contains from a hundred to a thousand times as much radium as does the water surrounding it, but the radium in the deposits does not apparently come from plankton as there is as much radium in deposits from seas with little plankton as from those rich in plankton

It is remarkable that the concentration of radium in the uppermost sediments of the ocean bottom is much greater than in either the igneous or sedimentary rocks on land The concentration appears to be greatest in those portions of the ocean bottom more remote from land and lying at the greater depths where the material generally consists of so-called red clay.[43] The radium concentration

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39 Nachr Ges Wiss Gottmgen 1936, 11, *1*, 205

40 Compt Rend 1938, *206*, 450

41 Nature, 1939, *143*, 275

42 J Marine Research Sears Foundation *4*, No 2, 1941

43 Piggot, C S , Scientific Monthly, 1938, *46*, 201

falls off near shore where it approaches that in the sedimentary rocks It is thought that the uranium must have come originally from igneous rocks, that it exists in the sea water in solution and that some process is operating to remove it

The amount of uranium in sea water is not very different from that of other metallic constituents such as silver and gold It is suggested that this very deep water, which does not contain enough organic material to maintain a slightly reducing environment, has definite oxidizing properties Hence it is saturated with oxides of uranium and thorium and there is a tendency for them to separate out just as the iron and manganese do The three metals are similar in so far as their oxides are among their less soluble compounds, hence the presence of nodules of manganese and iron among the red clay in very deep waters

CHAPTER 3

THE BIO-CHEMISTRY OF THE OCEAN

> " *First life on my sources*
> *First drifted and swam*
> *Out of me are the forces* "
>
> SWINBURNE, *Hertha*

IN this chapter, even at the risk of some repetition, it is desired to deal with the relation of the living matter in the ocean to the chemical substances in it The ocean contains living matter throughout its whole extent from the tropics to the poles and from the surface to the bottoms even at great depths of as much as 6 miles

The study of marine life requires the co-operation of Chemist, Physiologist and Geologist Indeed Vinogradov has termed it " biogeochemical " research It demands precise investigations into the chemical composition of sea water, into changes in chemical equilibrium, into the effect of alterations in temperature and salinity and into the chemical consequences of the processes set up by marine bacteria

The sea is the chief habitat of organisms of simpler structure lacking ability to withstand extreme conditions These have to live in equilibrium with an ionic solution of uniform composition and within a comparatively narrow range of temperature

Marine animals are readily permeable to the water molecules and to the salts in solution The salts in their blood and body fluids are in some cases very nearly in the, same proportion as that in which they occur in the sea

The extreme limits of temperature in the oceans are from -1 9^0 to 30^0 C , the high specific heat of water keeps it from changing its temperature readily The larger number of organisms are able to endure but a very small alteration in temperature even in comparison with the small range in the sea itself No other characteristic of water is so important for the fisheries the meeting of a cold belt of water by a warm current involves death to the fish on the largest scale

Most sea organisms have limits of tolerance as the water becomes less salt and there is generally a distinction between salt water, brackish and fresh water forms There are exceptions such as the salmon and the eel, which tolerate both fresh and salt water at different periods of their life history The uniformity in the nature and relative proportions of the salts present in various parts of the oceans has given little opportunity for the development of forms requiring a very different ionic background

Since the energy for the synthesis of food substances by marine plants comes from the sun the matter of the degree of penetration of sunlight into water becomes of major importance

Light is biologically effective also in interfering with life processes or even in killing an organism Since the greater part of the ocean is practically dark there is opportunity for a host of forms to develop which would be adversely affected by the photo-chemical action Such animals depend on the shower of food falling from above coming from the plants living in the upper well lighted layers

For life in general the real significance of the ocean is that it contains vast reserves of those inorganic elements and substances which are necessary for life As everything drains into the ocean, sea water has all the needed elements of life to a greater degree than elsewhere It transpires that those elements which are present in small amounts compared with the needs of organic life will be found to be present to a greater extent in marine organisms rather than in solution in the sea water.

Once these substances are used by organisms they will be unavailable for new use till these organisms die and decompose They will fall to the bottom in quiet waters and lie there forming a reserve of fertilizer until they are circulated and raised to the surface again

The limiting factors of growth in the sea are thus the presence of certain nutrient substances particularly nitrates, phosphates and perhaps silicates, the presence of various essential trace constituents, and governing both these factors a means of recirculation of vast masses of water so that these materials are used over and over again

The periodic chemical changes which occur in the environment and in the organisms themselves affect in turn the plentitude of vegetable life, the abundance of animal life and ultimately the abundance of fish

Apart from the movement of ions, mixing is always going on in the sea as the result of the tides, which traverse the oceans twice each day, of waves and of currents at various depths There are also processes of vertical circulation which are of the utmost importance for sea life The sinking of the superficial layers rendered heavy by winter cooling provides rich water within reach of the sun's rays for the next season's growth Accordingly the temperate seas which undergo the greatest annual change in temperature provide the best fisheries, while the more uniform tropical and polar seas are comparatively barren Thus the Gulf Stream continually brings deep water to the surface making the full resources of a large mass of water available for plant growth On the Pacific coast of North America the phenomenon of upwelling of the deep water is quite pronounced

Wind action, particularly when extreme during storms, is a potent factor in bringing the deeper layers to the surface Hence the value of the waters off the Banks of Newfoundland and elsewhere where there are rich fisheries Where the sea is stagnant, as in Hudson Bay, it is usually largely barren

There is an immense number of botanical and zoological species in the sea It is recognised that this population is' subject to regular cyclic changes Certain forms appear, reach a maximum of abundance and then decline These changes have been demonstrated to be accompanied by changes in chemical composition with a decrease or increase in the amount of nitrates, phosphates and silicates Organisms, i e , diatoms, may grow very rapidly, withdraw salts until they are exhausted, accumulate these in their bodies and deposit them in a thick layer on the bottom One-third of the diatoms are said to die every 24 hours

Most elements are more concentrated in living matter than they are in the sea Vernadsky[44] speaks of potassium, boron and fluorine as concentrated 10 times, of sulphur, iron, copper, iodine as concentrated 100 times, phosphorus and silicon one thousand, and zinc as much as 10,000 times Other elements, e g aluminium, manganese, lead, titanium, and vanadium are also accumulated by organisms

Tin has been reported in the blood cells of the oyster to the extent of o 049 per cent The oyster, as is described on page 32, accumulates considerable quantities of copper, which element is widely distributed in the bodies of marine invertebrates It is there both in protein form and as a constituent of a respiratory pigment Lobsters have 2 parts of cobalt per million of dry weight and mussels o 14 parts per million Various molluscs contain 2 parts per million of nickel Lead to the extent of 2 5 parts per million has been detected in the dried liver from *Fasaolana gigantea*

Vanadium is essentially a trace element in sea water It has been found in the blood of an ascidian and in a holothunan, or sea slug in both these it is an essential part of the respiratory pigment In some places exceptional concentrations of vanadium are deposited on the sea bed by ascidians and they accumulate in the sea muds when the organisms pensh A study of the ashes

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[44] Rev Gen d Sc Paris 1924, *35*, 5-13

of **oils, bitumens and** asphalts of certain oil bearing regions, particularly those of the Volga-Ural provinces of Russia, indicates that they are extremely rich in vanadium The hypothesis has been formulated that the presence of vanadium on account of its marked catalytic behaviour has determined the later character of the oil onginating from the decomposition of marine animals or plants It would seem that vanadium selected and concentrated from the sea by the ascidian has been the tool to shape the kind of oil produced

Perhaps another rare element, germanium, which is found in considerable quantity in the ashes of some coals, may have a similar function in the production of coal The concentration of many rare elements in coal ashes is due to the washing out of the soluble inorganic constituents at the time of rotting of plant material There is evidence of an increase of the rare elements in humus soil, and coal is fossil humus

The accumulation of iodine by sea weeds and also by algae, corals and sponges is well characterised Small amounts of iodine have been recorded in various molluscs and fishes The physiological significance of iodine in these plants and animals is as yet unknown

During geochemical ages the supply of inorganic iodine on land was so scanty that iodine did not become a normal ingredient of common proteins Living things managed and evolved without iodine But early in the history of the multi-cellular organisms of the sea some of them learned to make it into di-iodotyrosme This same faculty has been preserved or at any rate repeated by the vertebrate animals where it is locahsed in the thyroid glands But they have accomplished one further chemical step in their evolution, which is indispensable to their being, namely the final conversion of di-iodotyrosme to thyroxine

Bromine, of which there is so much in the sea, does not appear to be so generally present in marine organisms as is iodine It is however present in seaweeds in amount equal to about 1/10th that of iodine In the winning of iodine from seaweeds the presence of bromine becomes obvious during distillation but it is not economic to recover it

The corals make an organic bromine compound dibromotyrosirie[45] The classical example of an organic bromine derivative is the purple snail of antiquity, from which the colouring matter of the Imperial Toga was produced, known as Tynan purple There are large underground deposits of bromine in the Middle East which underground hot springs are apparently bringing into the Dead Sea Dr E Bergmann has made the suggestion that these inorganic bromides are derived from the decay of countless such bromine containing snails of a past age

Although reference is continually made to traces, when consideration is given to the enormous amount of life in the sea and to the extent of the oceans it will be obvious that in total very large quantities of the elements are concerned

What is paramount is that, by various means of elimination of what is brought in by the rivers, the sea is able to keep the concentrations of these trace elements very low, so that they function as helpful elements in the life history of the marine forms which make use of them, and do not display their activities as poisons, such as would happen if they were able to accumulate

Sea organisms take part in a number of exceptionally many-sided geochemical problems During the past hundred years, the idea has developed that organisms consist of a limited number of certain chemical elements known as the biogenic elements Completely new data on the systematic presence in organisms, in addition to others in soils and alluvial deposits, of bromine, iodine, fluorine, rubidium, lithium, nickel, cobalt, vanadium, titanium, molybdenum, lead, copper, strontium, barium, boron, radium and other strongly radioactive elements, the discovery of the rare elements germanium, gallium, niobium, selenium, chromium, zirconium and many others, found by and published in the papers from

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[45] Morner 1913

Vernadsky's school in Russia, enable us to put the question differently nowadays, and no longer to speak of which elements go to make up a living organism but rather of which elements have not yet been discovered in organisms , among these are indium, hafnium, niobium, tantalum, tungsten, and tellurium, also elements of the platinum group, although they have not yet been systematically sought From a geochemical point of view, therefore, the organism and its environment are connected by the common history of all chemical elements. The question of the quantitative chemical composition of living matter and of various types of organism is therefore one of great interest

In general, the average chemical composition of organisms is reminiscent of the composition of soils forming the earth's crust Chemical elements of low atomic number predominate There is most of those chemical elements which under conditions on earth form easily moving compounds, gases, soluble salts, etc while there is little of those chemical elements which do not form such compounds, as, for example, scandium, tin, titanium, hafnium, zirconium, thorium, and many others In spite of the frequently high content of the latter elements in soils and rocks, their content in organisms is only one-thousandth to one ten-thousandth times as much So far as the former are concerned, the concentrators are known, organisms in certain districts are greatly influenced by the insufficiency or abundance of these chemical elements in their environment

The chemical composition of organisms is one of the distinguishing features of species

These observations on marine life are parallel to those on land regarding the significance of " trace elements " in relation to the diseases of plants and animals Some 20 or 30 endemic diseases are connected with insufficiency or superfluity of certain chemical elements in the environment A trace element is any element regularly occurring in minute amounts in living tissues whether it exercises any specific physiological function or not Metals such as aluminium are apparently inert and incidentally taken up by the action of plant roots copper and manganese are essential for both plants and animals, boron is necessary for the plant but not known to be so for animals, selenium and molybdenum are probably unessential for both plants and animals but are sometimes taken up by healthy plants in amounts which cause disease in the consuming animal[46]

The quantities of essential trace elements in plants are however no necessary indication of the quantities required by consuming animals and animals may waste away when grazing on luxuriant herbage or complete the cycle of their being on plants showing obvious symptoms of vegetative failure

Chile nitrate, the fertilizer, contains traces of a variety of minor elements, notably boron and iodine Its main value is to supply nitrogen to the crop but it is also a preventative of boron deficiency The iodine present cannot be shown to have any stimulating effect on plant growth but analyses show the crop to have a higher iodine content, so that it may be of greater value as food for animals.

The oldest accurate analyses of sea water are but 50 years old, a time which is so short relative to the age of the earth that any changes in its constitution would be imperceptible There is reason to believe, however, that some of the constituents may be increasing, namely, those which are not taken out of the sea by marine organisms or precipitated in one way or another Sodium, chlorine, bromine are perhaps among these, possibly also strontium

The salts remaining in sea water are those which have escaped both precipitation and absorption in past geological ages and the same process may still be going on. Goldschmidt has calculated that two-thirds of all the sodium derived from the weathering and disintegration of the primary rocks is in the oceans, the rest having been deposited in the sedimentary rocks. Very roughly, a distinction can be drawn between those elements forming

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[46] H H Green, Nature, 1943, *151*, 28

the sea solution and those trace elements which are all the time being made use of by marine life

It may well be asked how has the sea reached its present constant composition One picture provided to some extent by Goldschmidt is first, of solution during the weathering of rock , second, of precipitation of some elements as hydroxide, carbonate or sulphate , third, of absorption of other elements on these precipitates and upon the finely divided insoluble muds left after the weathering processes have finished

In brief, the sea forms an ideal medium in which every possible chemical interaction and physical process can take place according to the specific properties of every element and compound The final result is the completed reaction and the salts left in sea water are those which have escaped in past geological ages and will continue to escape in the future both precipitation and absorption

Physical conditions as would be expected largely govern what goes on in the sea, the maintenance, for example, of relatively constant slightly basic reaction conditions, temperature and solubility of carbon dioxide and oxygen are all important One example of the effect of temperature is seen in the composition of sea shells Increased temperature favours the replacement of calcium by magnesium, reduced temperature leads to the substitution of strontium for calcium

Marine organisms are generally divided into the bottom-living, rooted or sedentary forms, the actively swimming animals and the Plankton or drifting microscopic organisms

The plankton is again divided into zoo-plankton and phyto-plankton, the latter of which is composed of small cells from 2 to 50 in diameter including minute algae, diatoms, flagellate protozoa, etc

In general the phytoplankton is more abundant in the polar and temperate seas than in the subtropical and tropical zones It is practically restricted to the upper hundred fathoms of the sea and all forms of plankton are

in general

relatively low salinity

As on land all life in the sea depends on the power which the holophytic or vegetable organisms have of converting mineral substances into organised organic tissues This is in the main effected by the phytoplankton

The ultimate food substances required are water, carbon dioxide, the nitrates and nitrites of calcium and magnesium and other alkaline metals, phosphates, silicon compounds and traces of quite a large number of other elements Except the water all these are present in the sea in exceedingly small proportion, to be measured in parts per million , they are constantly being withdrawn by the growing phytoplankton and renewed either in the matter brought in from the land by the rivers or derived from the death and decomposition of animal and vegetable substances The sea solution is in fact so dilute in nutrients because organisms are using them all the time

The sea contains a readily available store of carbon dioxide, which can be drawn upon or added to, and such alteration makes very little change in the concentration of hydrogen ions

The distribution of nitrogen in the oceans is of profound interest and importance The water of the Antarctic contains about 0 5 parts per million, that of the North Atlantic about 0 15 parts per million and the equatorial seas still less, about o 1 parts per million There is more inorganic nitrogen at the sea bottom than near the surface, more near the land than in mid-ocean and more in the late winter than in any other season

In the temperate seas there is an outburst of vegetable life in the spring this produces food to bring about the vernal or summer phase of reproduction among animals

Nitrogenous and other salts have accumulated during the winter, the hours of sunlight increase and synthesis from carbon dioxide sets in vigorously The hydrogen ion concentration decreases and the water grows more alkaline as first the free carbon dioxide and then that derived by the dissociation of bicarbonates (usually magnesium) is used up When photosynthesis is very active the hydrogen ion concentration of sea water may change from pH 8 2 to 9.1 Experiments made at Port Erin in the Isle of Man show a change from pH 8 1 in December to pH 8 4 in April, which, if worked out only to a depth of 1 metre, is equivalent to a production of 6 tons of carbohydrate per square kilometre of sea from the carbon dioxide which has been used

A summer outburst of animal life follows because it lives on the great spring production of plant substances

Studies of the various fishes comprise the major activities of a department of all governments whose lands border on the sea because each is concerned with the maintenance and assurance of a future supply of fish as a source of food

An outline of the biology of the sea fisheries has been given recently by R S Wimpenny[47] on which the following summary is largely based

Fundamentally the sea fisheries depend on the ability of small floating algae to carry out photosynthesis in the presence of a sufficient supply of the inorganic salts necessary for their growth These may be termed producer plankton and consist mainly of diatoms These can only grow in the upper photic water layers and then only in the presence of adequate nutrient salts, they may be so abundant as to cause a perceptible clouding of the sea in certain places

When a nutrient salt such as nitrate or phosphate which occurs in very small quantities (30-200 mg per cubic metre) is exhausted the flowering or growth dies away This happens regularly in the off shore waters of the North Sea and the entrance to the English Channel and has been studied by Atkins[48] and by Harvey[49] Here thermal stratification isolates the upper water layers from about May to October, when they become cooler than those below them and vertical mixing takes place In these areas there is a spring and early summer outburst of diatoms, followed by another and generally

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[47] **Chemistry and Industry, 1943, *62,* 230**
[48] **J Marine Biol Assoc 1926, *14,* 447**
[49] ***Ibid,* 1926, *14,* 71**

smaller one at the time of the autumn turnover

Producer plankton does not show heavier crops in the the warmer waters of the world where production is more continuous and lighter than in higher latitudes This is probably because there is no big autumn and winter mixing of the photic layers of the sea with those deeper down, whilst the more intense light penetrates deeper so that photosynthesis is going on at all seasons, permitting no chance of the breakdown and accumulation of nutrient salts in the upper layers of water Towards the poles, however, an increasing period of winter rest is followed by increasingly vigorous outbursts of producer plankton So rich is the supply that even after the end of a big outburst of diatom growth in the Antarctic there is no exhaustion of phosphate

The zooplankton of sizes from roughly o 5 to 50 mm. feed on the producer plankton, they have a life of from 2-10 months and thus a much greater persistence than diatoms In these latitudes they build themselves up in the spring and early summer, production of diatoms rising to a maximum in the summer and remaining in strength until the autumn, when, after rising again with the second diatom flowering, production falls until the following spring

The zooplankton form an important link between fishes and producer plankton, their persistence may be thought of as a bank or store making food available over an extensive period Towards the poles life histories are longer and the zooplankton have a greater carry over of food value The more vigorous production at the poles in contrast to warm latitudes is confirmed by the fishery yields of the three areas

The young fish when hatched from their eggs feed at first upon phytoplankton and later upon the zooplankton later most fish are carnivorous The great commercial fishenes are not in or over deep water but on the shoaler banks and shallow waters down to a hundred fathoms or so Below this depth there is no reproduction aind growth of plankton, due to the lack of foods

The production of food fish is liable to considerable fluctuations Normal annual fluctuations due for the most part to events which occur in the early stages of the animal's life may be very great it is not uncommon to find that one year-class of fish is 50 times as abundant as another Such annual fluctuations however are strictly localised and may affect one species only There are other, approximately called long period fluctuations, which affect many species over a wide area

Two illustrations of this have been discussed by Kemp[50] in an address to the British Association There has been a steady deterioration in the numbers of fish in the Channel waters off Plymouth since 1931, due it seems to the lack of influx of phosphate rich waters from the Atlantic There have been incursions of Atlantic water, but these cannot be correlated with biological and phosphate data and the great influx of Atlantic water into the North Sea in 1921 was detrimental, quite contrary to expectation It would appear that only water rich in phosphate or potentially rich because it carries an abundant plankton will benefit the channel fauna

The second illustration concerns the great changes in the fauna and extension of the fishable area in northern waters owing to a rise of 1° or 2^0 C in the temperature of the water due to an increase in the strength of the Atlantic Drift By reason of this change many animals have been able to extend the limits of their distribution

Long period fluctuations are thus due to a widespread alteration in some hydrographic factor in the environment—it is in the open Atlantic that the reasons for it must be sought Until they are discovered they will at times render fishery prediction unreliable

Such questions as overfishing, size of fish caught, and in general our subject, but reference may be made to the suggestions that we should grow, collect, and eat plankton as a means of adding to our food resources The objections, definitely of a practical nature, to such a course are many , in

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[50] Nature 1938, *142*, 341 and 817

addition the yield of plankton is inconveniently spread in time and season The suggestion, therefore, fails but the result may be achieved in a different manner by cultivating fish The carp industry has been established for hundreds of years on the Continent, and both shell fish and such fish as trout have been grown on fish farms By the addition of suitable nutrient salts to water concentrations of both producer and consumer plankton very much greater than those found in nature may be cultivated

In this connection some work described by F Cross, J E G Raymont, S M Marshall and A P Orr* is of great interest A dam with a sluice was built across the narrow channel connecting Loch Craighlin with the tidal waters of Loch Sween in Argyll, Scotland Since April 1942 some 600 pounds of sodium nitrate and 400 pounds of superphosphate have been added to the waters of Loch Craighn These figures are equivalent to five and ten times the respective maximum winter nitrogen and phosphorus values

The addition of fertilizers had an immediate effect on the number of planktonic organisms The average number of -flagellates, which was 1,600 per cu mm the day after adding one batch of fertilizer, had risen to 8,000 per cu mm one month later The effect on the growth of fish was equally striking Some 2,700 small flounders and 600 plaice were transferred to the loch in 1942 and a further 22,000 flounders in 1943 In spite of the larger number of fish the plaice grew in a year by an amount that would under normal conditions have taken two or three years The flounders also grew nearly three times as fast as usual

The authors of the paper conclude that " the excessively low productivity of the sea as compared with the land, and as expressed in the low rate of both survival and growth of fish, is ultimately due to the scarcity of plant nutrients, that is, of nitrogen and phosphorus

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*** Nature 1944, *153*, 483**

That salt can be obtained by the evaporation of sea water has been known for centuries, long before the beginnings of chemistry and the realization that what we call common salt is sodium chloride The ancient Greeks, Romans and Egyptians all knew how to obtain salt by letting the heat of the sun dry off sea water and so must every nation or race of mankind that had no other source of salt, for sodium chloride is an essential constituent of the food supply of men and beasts and those countries which lack it will go to any end to attain it In New Guinea, for example, it was used by traders not so long ago as the best currency for the purchase of native goods In Britain and other parts of the world there are large deposits of pure salt resulting from the drying up of the inland seas in past geological ages Such rock salt is cheaper to work and easier to obtain than salt from the sea, but it is not universally available This salt also had its origin in the sea and was formed by nature in much the same way as man makes it from the sea

The salt trade is the most ancient commercial enterprise , after it followed the trade in salted fish The Phoenicians rose to power by their fish trade, just as Venice did The first trade routes of the world were established for the distribution of salt In the Middle Ages such a route as the Arlberg Pass, through the Tyrol over the Alps, which is now one of the highways of the summer traveller into Austria, was maintained to carry salt into Switzerland The cities of the Hanseatic traders were based on salt and herrings their eclipse followed the transference of the herrings to the warmer and more salty waters off the coast of Holland The very practice of banking originated with the salted fish sellers

Salt supplied no want of primitive man until he began to cook his food salt is present in meat but, in boiling, 70 per cent is lost Physiologists teach us today that man needs 16 to 17 Ib of salt per annum

To England is the credit of being the first country to repeal the salt duties, at the end of 1824 Salt was free from any tax up to the time of the Commonwealth, and the levy then imposed was taken off at the Restoration, only to be re-imposed by William III in 1694 The tax lasted, except for the period 1729-31, for 135 years, rising to 3s 4d a bushel before the Liberals took it off in 1729 Walpole put it on again as he needed this income to make up a deficiency in the Budget caused by his land tax concessions It grew steadily until it amounted to 15s on a bushel of salt worth 6d in 1805 Strenuous efforts were made to abolish it in 1822 and onwards, which were finally successful There is little wonder that a contemporary in Cheshire wrote, " This raw material is bestowed on us by Providence, like air and water, yet where it had existed in the greatest plenty the ingenuity of man had rendered it the greatest curse " Salt is still taxed in France, and each salt works has a resident customs officer

It is unlucky to spill salt and a mark of humble position to sit below it Salt is a symbol of sanctity, an emblem of fidelity and wisdom The phrases " worthy of his sal," " above the salt " recall other instances of its importance and mysticism

There is evidence in the dwellings of cavemen in Belgium that it was used in cooking wheat 5000 years ago. There is mention of salt from sea water in the Chinese language in the annals of Emperor Yu (2205 -2197 B C) At first the sea water was boiled in open kettles to evaporate the water , later it was let into a series of ponds and evaporated by the sun and wind

Salt was later found below the ground and mined as rock salt The great salt mines of Wiehczka in Poland have been worked since the 13th century Later still it was found more economical to flood the salt beds below the earth with fresh water, pump up the brine and evaporate it to crystallisation point Not only is the salt sold as such but great chemical industries are founded on it as a raw material

Salt has for a long time been one of the chief exports of this country it is the most important and most fundamental raw material of the heavy chemical industry and salt and the heavy chemicals made from it have combined to make the Merseyside area one of the most important centres of chemical industry in the world and Liverpool one of the world's greatest ports It is not proposed to discuss here the heavy chemical industry based on salt and the other uses of it This would require a book of its own and in that the bulk of the salt is not obtained directly from the sea it is outside the scope of this book It is worth while briefly to mention the chemicals obtained from sodium chloride to indicate what could be obtained from salt from the sea

From salt by the Solvay[51] process are obtained soda ash and washing soda Direct electrolysis of salt gives chlorine and caustic soda or metallic sodium From caustic soda is obtained soap Treatment of salt with sulphuric acid gives hydrochloric acid Sodium hypochlorite, the chlorates, and almost every compound containing chlorine are dependent on common salt for the chlorine atoms in their molecule There are other natural sources of the sodium atom in sodium carbonate, sodium sulphate, sodium nitrate and other compounds, but the majority of the sodium atoms in industry today must have first been obtained by man in the form of sodium chloride

In areas where the right conditions exist the recovery of salt from sea water by solar evaporation is not an expensive process, it demands a climate which is hot and dry with dry winds The largest producers today are in China and India, in Japan, along the Pacific coast of North America, and in the Philippine Islands There are numerous others, salt is produced anywhere in fact where the conditions are suitable The bulk of the world's salt production, however, is produced in England, France, Germany, and the United States from resources other than the seas in these countries most of it goes to the chemical industries Most of the smaller countries produce for their

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[51] The Solvay or ammonia soda process of making soda ash (sodium carbonate) from salt is now general in all countries

PLATE III. IN INDIA. COLLECTING THE SALT INTO RIDGES TO DRAIN.
(*From Imperial Institute Collections.*)

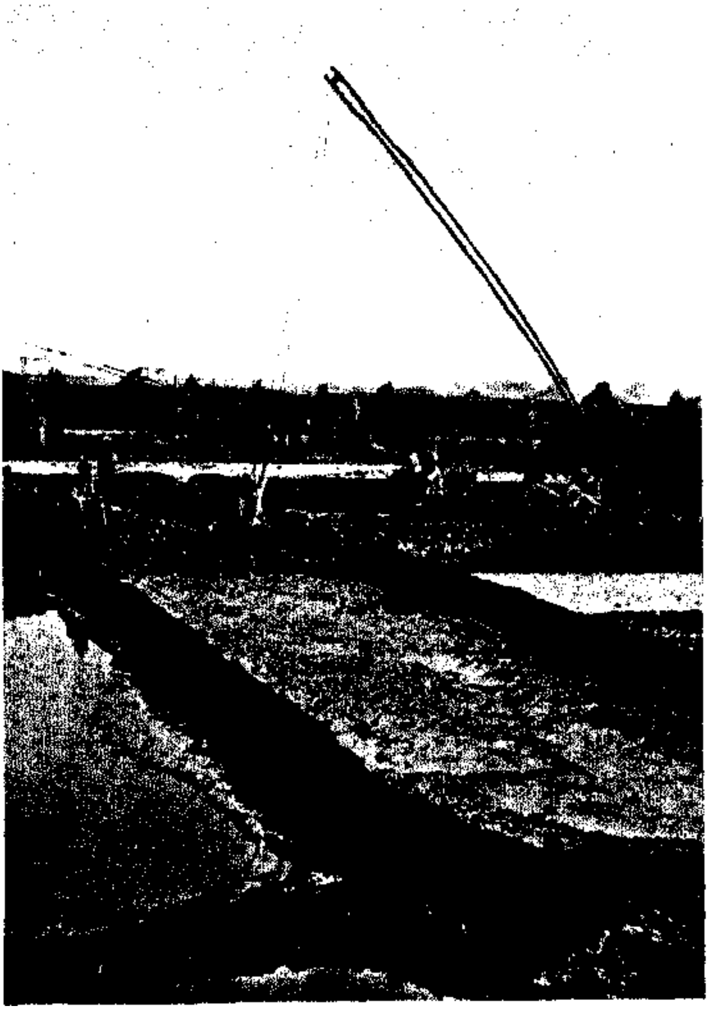

PLATE IV. EMPTY SALT PANS WITH " CHIANCHI" OR BRINE REMAINING.

(From Imperial Institute Collections.)

own consumption , since salt is a very low-priced commodity, freight rates are the most important factor limiting its distribution

The salt industry in India has been described in considerable detail in a monograph by S C Aggarwal [52]

India now produces about 1,500,000 tons of salt per annum compared with a total requirement of 2,000,000 tons Salt is made from the sea along the whole of the East Coast of Madras It is reddish in colour and contains about 93 3 per cent sodium chloride , it is sold by measure It is also made in the Bombay presidency, where there are some 400 works covering 17,000 acres it is of better quality than Madras salt Burma only produces a portion of the salt it requires and imported the rest, mainly from Germany, Port Said and Italian East Africa

Aden, in the Persian Gulf, is particularly suited for the manufacture of salt from the sea It has very little rainfall, the plants can work throughout the year, the temperature is high and strong winds aid evaporation , the intake from shallow lagoons is already concentrated whilst shipping facilities are good The efficiency of the works is good and the quality of the salt high

In the United States some 350,000 tons of solar salt are produced each year, mostly at the south end of San Francisco Bay where are combined the necessary factors for success, namely, sufficient evaporation during the making season, an almost impermeable soil, low rainfall and a suitable contour of ground, no dilution from fresh water streams and markets close at hand As much of the land as possible must be below the high tide level to keep pumping at a minimum There are two kinds of ponds *(a)* concentrating, *(b)* crystallising, the former being 10 times the area of the latter

The sea water is taken in at high tide at the times of least rainfall in April and moved forward from one pond to the next at a slow regular rate so that the calcium sulphate, which is continually crystallising out in a fine

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[52] Published by the Government of India Press, Simla, in 1937

state, will have sufficient time to drop to the bottom of the pond The pickle or saturated solution is pumped as required into the crystallising ponds Fresh pickle is added, sodium chloride drops out and the concentration increases until at a specific gravity of approximately I 28 the magnesium salts are ready to crystallise The solution, now known as bittern, is drawn off, fresh pickle run in and the cycle repeated

By August 1st there is enough salt to commence harvesting, which continues until the rains come in December The salt is from 4-6 in thick , it is picked up in various ways, scrubbed with salt water to remove mud, placed in storage piles to drain and taken as required to fill orders, or redissolved and recrystallised to give a purer product It is sold in 3 grades—crude, washed and dried, and refined of 99 9 per cent purity[53]

The bittern or residue left after deposition of the salt is used in California and in some other parts of the world for the production of magnesium compounds and bromine It can also" be used as a source of potassium salts Such processes are described in later chapters

W C Phalen[54] gives a full account of the various processes of making salt then in use and the localities where it was obtained

Production from the sea began in California in 1852 and still continues It was first obtained on the Atlantic coast in Massachusetts about 21 years after the Pilgrims landed in 1621 New Jersey also had its pre-revolution salt works None of the works on the Atlantic coast exist today The production of salt in the U S A has grown during the war, in 1941 it was 12,720,629 short tons, an increase of 23 per cent over 1940

In the West Indies the most important sources of supply are the Turks and Carcos Islands with an output of 25,000 tons since these have access to cheap sea freights they can find markets at a considerable distance The industry was started in 1678 to meet the needs of the fisheries of

63 J C Buchen, Mining and Metallurgy, July 1937, p 335

54 Technology of Salt Making in the United States, Bureau of Mines, Washington 1917

the New England States it is described in a Report of the Commissioner appointed by the Governor of Jamaica, 1937[55]

Considerable areas of land in the islands are level with or below the level of the sea The sea is run through wide canals into large common storage reservoirs where it is brought up to about 30° salinity and deposits lime mud (calcium sulphate) The brine is passed into raking ponds or pans each of ½-1 acre in extent where, after 10 days, salt begins to crystallise and after 20-30 days a cake of salt crystals is deposited at the bottom of the pan When the cake is about 3 in thick the surface water is drained off and the salt is raked and taken to heaps on the beach or shipping place The law specifies that the ponds should produce 5000 bushels per acre The quality is variable and not very good, the sodium chloride content is about 94 -95 per cent , there is an opinion locally that the sea salt has properties peculiarly adapted to the fish salting industry There are all sorts of local problems which have a bearing on the economic development of these small industries and jeopardize their future existence

The second world war has so upset transport throughout the world that temporary expedients have had to be devised everywhere The bulk of the table salt that has previously been used in South Africa has been the product of famous British firms Several brands of South African table salt are now being marketed and these are selling well in the absence of British supplies, but as they are not so highly refined as the British product, they are often only purchased because there is nothing else The salt produced commercially in South Africa is obtained from inland pans, shallow depressions with outlet in rocks which are somewhat older than most of the sedimentary salt beds mined in Europe and America Such beds of rock salt are not known to occur in South Africa The great bulk of the salt is obtained entirely by solar evaporation in shallow dams, though in the case of one or two producers artificial heat has been adopted for final con-

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[55] Published by the Crown Agents for the Colonies

centration of the liquor before precipitation The coarse salt obtained by solar evaporation is subject to contamination from dust and has to be graded in course of recovery according to its apparent quality A portion of the purest grades is subsequently ground fine for household and dairy purposes and put on the market in suitable contamers The quality of this is somewhat infenor to the European article If purchasers are satisfied with this kind of salt, the Union could be self-supporting in this regard The war is undoubtedly leading to a big increase in the output of the salt pans, as many new industries are demanding raw salt

Statistics relating to the world production of solar salt are only approximate and hard to come by, but the following relate to the year 1933 the amount may not all be solar salt —

TABLE 14

West Indies	28,000	tons
China	2,000,000	,
Japan	600,000	,
Philippine Islands	40,000	,
Siam	180,000	,
Indo China	70,000	,
India and Aden	1,500,000	,
Turkey	100,000	,
Algena	79,000	,
Tunisia	86,000	,
Eritrea	92,000	,
Somaliland	150,000	,
Libya	30,000	,

In countries enjoying a very cold climate, such as the U S S R and Sweden, salt can be obtained by freezing sea water The ice is nearly pure water and the unfrozen water contains the salts By removing the ice and freezing several times the water is concentrated until it is strong enough to evaporate with artificial heat Sodium chloride obtained by this means is not as pure as that obtained by solar evaporation but in Sweden it is said to be cheaper to obtain it by this method

CHAPTER 5

BROMINE FROM THE SEA

IT has been estimated that bromine with approximately o 001 per cent occupies about the 25th place, when the elements are arranged in the order of their abundance in the earth's crust Ninety-nine per cent of this occurs in the sea, the solid parts of the earth contain only about o 00001 per cent of bromine, and the vast majority of this comes from rocks which, like those of the Stassfurt deposits, have been originally deposited from the sea Bromine is to all intents and purposes therefore purely a marine element

Bromine was discovered by a Frenchman, A J Balard, who published this discovery in 1826, although his work was started a couple of years earlier Balard was engaged in studying the mother liquors obtained after salt had been crystallised out of the brines of the salt marshes at Montpelher and he noticed that when chlorine water was added to the mother liquor a deep yellow colour developed

It is interesting to note that the most modern methods for obtaining bromine follow in all essentials this method, though the later stages of the process are different Balard proceeded to extract the bromine from the mother liquor with ether He then treated the ether extract with caustic potash and thus obtained potassium bromide On heating this with manganese dioxide and sulphunc acid, bromine vapour was given off which condensed to an evil-smelling liquid which Balard first called *muride* and which was later rechnstened bromine

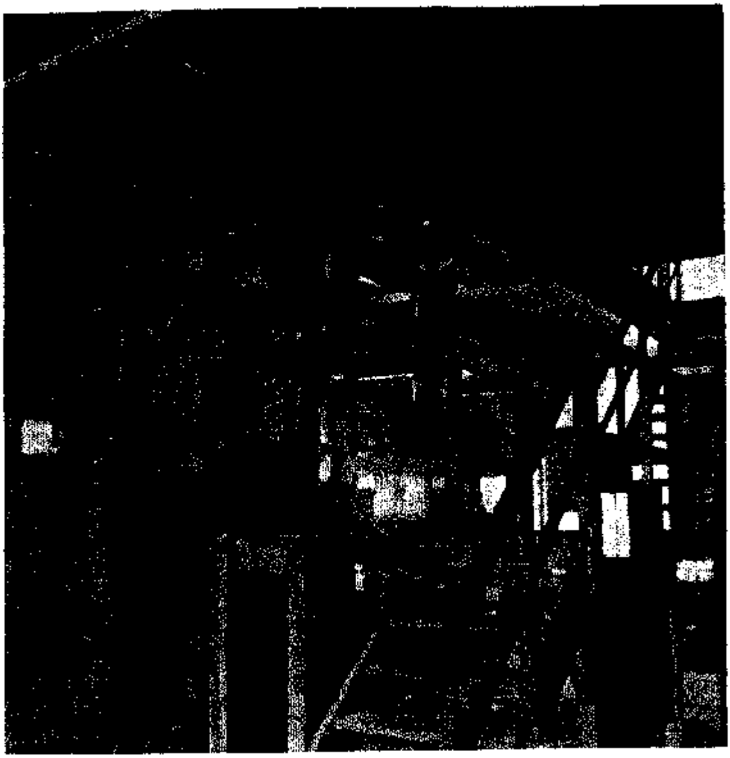

PLATE V. BROMINE FACTORY OF PALESTINE POTASH LTD.

For many years the production of bromine from the Stassfurt potash deposits was virtually a German monopoly although the Germans were not the first in the field Bromine was first worked up from carnallite from the Stassfurt deposits in 1865 but the production from natural brines in America began in 1848 and is still in operation, particularly in Michigan, Ohio and West Virginia Of the other present major sources of bromine, the production from bitterns obtained from sea water evaporation was begun in California in 1926 In 1931 the first bromine was produced from the Dead Sea and in 1934 the first large scale plant using ocean water as a raw material commenced operation at Wilmington on the Atlantic coast of the U S A

The carnallite at Stassfurt contains bromine, possibly through isomorphous replacement of part of the chloride by bromide The 10 million tons of carnallite mined per year correspond to 20,000 tons of bromine but only a small proportion of this is produced, there being but a dozen bromine plants amongst the fifty companies operating potash plants The mother liquor used here contains o 25 per cent of bromine, which is more than 35 times the percentage in the ocean The prewar cost of bromine unpacked in Germany was about 2d per Ib , whereas in 1927 it was sold for is 6d

German bromine was sold in 3 grades crude with 2-5 per cent of chlorine, refined with o 3 per cent chlorine, and chemically pure containing a trace of organic matter but no chlorine

In Russia, a factory on Sukashy Lake in the Crimea started up in 1926 on a scale expected ultimately to produce the Russian requirements

British Empire

With the exception of the mandated territory of Palestine, bromine has not been produced within the British Empire The sea is of course available to us In India there is a salt industry in the Rann of Cutch at Kharaghoda, where there are a number of brine wells.

The brines are treated by solar evaporation to produce common salt, they contain magnesium salts but no potassium salts The bitterns were found to contain nearly ½ per cent of bromine and the brine some o 06 per cent These deposits could be worked for bromine

No special search for bromine in the numerous Canadian sources of salt has been made, but in Australia a saline deposit with a bromine content of o 32 per cent is recorded at a point 100 miles west of Port Augusta A firm at Geelong, Victoria, which makes salt from sea water, produces mother liquors from which bromine could be made

The demand for bromine in Canada, Australia and India has been very small

There were few uses for bromine in quantity until the early 1920's when the demand was enormously increased, owing to the development of "Ethyl" petrol In addition to lead tetraethyl the finished anti-knock fluid is made up of ethylene dibromide, ethylene dichlonde and a dyes tuff The ethylene dibromide is present in order to eliminate the lead formed in the explosion It permits the formation of the relatively volatile lead bromide and the lead is thus removed without fouling the sparking plugs or the valves

The world production of bromine in 1938 was 17,800 tons mostly in America, the following figures for the total U S production of bromine (both free and combined as salts) show the big increase due to the use of ethylene dibromide

TABLE 15

1914	576,991 lbs
1917	895,499 lbs
1918	1,727.156 lbs
1921	711,953 lbs
1924	2,033,804 lbs
1928	2,164,000 lbs
1929	6,414,620 lbs
1930	8,462,800 lbs
1933	10,147,960 lbs
1935	16,428,533 lbs
1942	65,880,935 lbs

Amongst the producers of bromine compounds in the U S are the Dow Chemical Company, who first extracted it from natural brines at Midland, Michigan Their process at Midland consists essentially in treating the brine with chlorine to liberate the bromine, blowing the bromine out of solution with air and absorbing the bromine in alkali (much as in Balard's original process) Their brines contain approximately 1300 parts of bromine per million and they extract about 95 per cent of this Sea water contains about 65 -70 ppm bromine, about the same as the effluent from the plant at Midland Despite this fact the company developed and have operated successfully a process for extracting the bromine direct from sea water

The first process by which bromine was obtained directly from sea water without any concentration involved the precipitation of bromine as the insoluble tribromoaniline, by treatment with aniline and chlorine according to the reaction —

$$3\,NaBr + 3Cl_2 + C_6H_5NH2 = C_6H_2Br_3NH_2 + {}_3NaCl + 3\,HCl$$

This process was worked in 1924 by the Ethyl Gasoline Corporation at Ocean City, Maryland with a small-scale plant Sea water was pumped at a rate of approximately 25 gallons a minute It was necessary first to acidify the sea water to stop hydrolysis of the subsequently added chlorine In such very dilute solutions the chlorine tends to hydrolyse to form hypochlorous acid The sea water was acidified by running in 1 per cent sulphuric acid to give a minimum concentration of 200 parts per million of sulphuric acid Chlorine was added after acidification, this liberated the bromine which was then precipitated on the addition of aniline sulphate The overall yields were only about 50 per cent and much trouble was caused by the presence of suspended matter in the water, which contaminated the precipitated tribromoaniline

The process was then further developed on a larger scale by the Ethyl Gasoline Corporation in association with du Pont de Nemours A steel ship of 4200 tons, 253 ft 8 in long was bought and converted into a floating chemical factory, renamed the S S "Ethyl " The ship factory was constructed to treat 7,000 gallons of water per minute Working 25 days a month at an efficiency of 70 per cent from sea water containing 70 parts per million of bromine this would give 100,000 lbs of tribromoaniline per month or about 73,000 lbs of bromine The ship carried 500,000 lbs of 93 per cent sulphuric acid, 50,000 lbs of aniline and 66 tons of chlorine, stored between decks This was one month's supply For safety there were no bottom outlets on the acid tanks and the liquids were transferred when necessary by compressed air

The process was actually worked at a rate of 5,000 gallons per minute The sea water was violently mixed with the required amount of one per cent sulphuric acid, with chlorine, and with a dilute solution of aniline sulphate The aniline sulphate was prepared on the ship from aniline and sulphuric acid and was diluted down with sea water from which the bromine had already been removed, as was the sulphuric acid The formation of tnbromoanilme was instantaneous and the whole process only took five minutes from the mixers to the filter presses These were Schriver wooden presses, each with fifty plates, and with a cloth filtering surface The tnbromoaniline crystallized in needles, about o 001 inch long and a fifth of this in diameter The reader is referred to a paper by C M Stine [56]

The S S Ethyl made only one voyage in which she cruised off the coast of North Carolina There were many minor difficulties most of which were due to working on board ship, which was done to avoid contaminating the sea water from the effluent from the process, from which the bromine had largely been removed This process was subsequently superseded

One of the most important questions concerning any plant using sea water as a raw material is location In addition to the usual problems involved in any plant site, supply of labour, power, raw materials, etc , the question of the disposal of waste products is more important than with any other type of plant, the waste product being in this case spent sea water Despite the enormous volume of the sea the amount of sea water pumped is so vast that if the spent water mixed with the incoming water, the percentage of the substance to be extracted (in this case bromine) would soon drop It is therefore necessary to discharge the effluent where it will not mix with the incoming water It is also essential when bromine is the required substance that the sea water should not be appreciably mixed with fresh water and that there should not be large quantities of industrial wastes in the sea water, otherwise some of the chlorine needed in the process would be used up in oxidising the industrial wastes The water of all rivers entering the Atlantic Ocean on the U S coast flows southwards and for these reasons it was necessary that the plant should be situated on the north shore of a river close to its mouth and that there should be no other large river discharging fresh water for a number of miles north of the site The site finally chosen in 1931 was at Kure Beach on the long narrow promontory in North Carolina that separates the Cape

[56] **Ind Eng Chem 1929,21,434**

Fear River from the sea, the effluent being discharged into the river The Dow Company have since built another bromine plant on an adjoining site to their magnesium plant at Freeport, Texas, where the same conditions operate

A pilot plant was built in 1931 at Kure Beach to produce 500 lbs of bromine per day from sea water In July 1933 it was decided as a result of the successful operation of the pilot plant, to construct a plant to extract 18,000 lbs of bromine a day and the plant commenced production on January 10th, 1943

Details of the plant are given in an article by Leroy C Stewart of the Dow Chemical Company,[57] from which this information is mostly taken The sea water intake, which had to be very strongly built to stand the pounding of the waves, is about 200 ft long, extending about 30 ft into the ocean at low tide and 30 ft into the land at high tide The water flows by gravity through the intake into a settling basin, 122 by 76 feet in area and 12 ft deep From there it is pumped by two 30 in centrifugal pumps having a joint capacity of 58,000 gallons per minute through two 42 in steel pipe lines into one 72 in line which lifts the water over a concrete dam, the top of which is 23 ft over mean low tide level From here it flows by gravity along a canal about 2¼ miles long to the plant which is situated near the river bank In the summer the water is by-passed from part of the canal into a pond with a surface area of 900,000 sq ft The temperature of the water is raised by the heat of the sun and the efficiency of the process thereby increased

The chemistry of the process is comparatively simple Chlorine is added to the sea water and replaces the bromine in the bromides of sea water One ton of bromine requires the use of o 7 tons of chlorine, that is more than one and a half times the theoretical proportion The bromine is blown out of solution by a current of air and reabsorbed in a sodium carbonate solution to give a

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[57] Ind Eng Chem 1934. ***26,*** **361**

mixture of sodium bromide and sodium bromate thus —

$$3\ Na_2C0_3 + 3Br_2 = 5\ NaBr + NaBr0_3 + 3\ C0_2$$

The bromide-bromate liquor is then treated with sulphunc acid to liberate bromine which is blown out with steam and then condenses as liquid bromine

It is necessary carefully to adjust the acidity of the sea water before treatment with chlorine As stated earlier sea water has a pH of 8 2 At this pH chlorine would be wasted in neutralising the liquor and even in neutral solution the process is inefficient, as in such very dilute solution the bromine tends to hydrolyse according to the equation —

$$3\ Br_2 + 3H_20 = HBr0_3 + 5\ HBr$$

In order to stop this hydrolysis occurring and to obtain the best possible extraction of bromine it is necessary to adjust the pH to 3 5 This is done by adding approximately 0 27 lbs of 96 per cent sulphuric acid per ton of sea water The sulphuric acid is diluted in rubber lined tanks to a 10 per cent solution and added to the sea water as it is being pumped to the top of the blowing out tower The chlorine is added immediately after acidification The amounts of acid and chlorine added are most carefully controlled by a method depending on the oxidation potential of the solution This is the crux of the process

"The extraction of bromine from salt water," to quote Dr Willard H Dow, himself,[58] "was not a commercial economic process until comparatively few years ago, and that was only because in earlier days we did not have the equipment with which to make possible the careful and exacting acidity control of the ocean water For the first time in world experience we found how to handle enormous volumes of ocean water in continuous flow and at the same time control the acidity within narrow limits That was the real key that opened commercially,

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[58] Chem and Eng News, 1943, *21*, 849

in 1934, the first lock in the vast resources of the ocean "

In the Kure Beach plant the sea water having reached the plant as described above is treated in two identical bromine extraction units The water is carried to both units from the canal in a horizontal semicircular steel flume, 10 feet in diameter It passes through a travelling screen for final filtration and is pumped to the top of the blowing out tower in a rubber lined pipe, the sulphuric acid and the chlorine being added in that order while the water is rising to the top of the tower The tower is divided into numerous chambers filled with wood packing and the water is broken up into very small streams which percolate downwards A blast of air rises through the tower and absorbs the liberated bromide The spent sea water flows from the bottom of the towers direct to the Cape Fear river

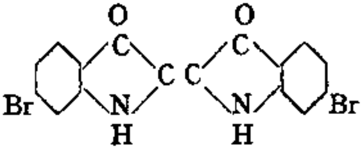
The air from each blowing out tower is drawn by fans into its adjacent absorption tower and the bromine is absorbed by a soda ash solution to give the bromide bromate mixture according to the equation already given Each absorption tower consists of nine chambers in series and the liquor from each chamber discharges into large tanks from which it is pumped to the top of the tower and broken up by sprays When the liquor in the first tank has reached the desired strength it is drawn off and replaced by the liquor from the next tank and so on according to the usual procedure of any counter current extraction. The remainder of the process is common to all methods of obtaining bromine from any raw materials The bromide-bromate liquor is acidified with sulphuric acid and next treated with steam which blows out the bromine It is then condensed to pure liquid bromine In the Kure Beach plant the bromine is then used for the production of ethylene dibromide Ethyl alcohol vapour is passed over a heated kaolin catalyst to form ethylene which is then brommated The overall efficiency of the process from sea water to ethylene dibromide is over 90 per cent

The plant has now been enlarged and the Ethyl Dow Company are now also extracting bromine from the sea at Freeport, Texas

The magnitude of the operation involved in the production of bromine from the sea is shown by some calculations made in one year's working of the plant at Kure Beach The bromine recovered was worth $3,820,000, the other minerals were all returned to the sea, had they been extracted they were worth $92,000,000 but it would have cost more than this amount to recover them In 1937 the Ethyl Dow Company pumped 100,000,000 tons of water or 1/40th of a cubic mile In subsequent years much larger quantities have been treated

Another marine source of bromine is the Dead Sea, which it has been calculated contains about 850,000,000 tons of bromine The concentration of bromine in the Dead Sea is about a hundred times that in the oceans and the mother liquors left after the crystallisation of salt and potassium chloride, which are those used as the raw material for the bromine plant, have a concentration as high as 1 4 per cent of bromine

The ratio of bromine to total salts in the Dead Sea is approximately 2 per cent whereas in the oceans it is approximately o 05 per cent The source of all the bromine is probably the hot springs of the Sea of Galilee, most of which discharge into the bottom of the lake This is carried down by the river Jordan to the Dead Sea The water running into the Sea of Galilee has no detectable bromine, whereas the outflow has 2 parts per-million Dr E Bergmann has remarked that bromine is particularly associated with the Middle East The famous dye of antiquity, Tynan purple, obtained from the shellfish *Murex brondarts* contains bromine and is the only organic bromine compound which has been found in the living cell It has the formula



As its name suggests it was manufactured amongst other places in what is now Syria and Dr Bergmann suggests that marine compounds containing bromine have decayed in the soil i and that the bromine they contained is now being given off in hot springs

A description of the Dead Sea plant for the production of potassium and other salts is given in a later chapter. The mother liquors are used for the production of bromine and the process is essentially the same as that used for many years to recover bromine from the mother liquors of the Stassfurt deposits The liquors pass down Kubierschky towers which are towers divided into compartments one above the other Each tower is about 20 feet high and is made of grey granite blocks packed with asbestos. The compartments are separated by earthenware plates in which are holes for the liquor to fall through Steam is blown in at the base of the tower and chlorine at the third compartment Various mechanical devices ensure intimate mixing between the falling mother liquor and the ascending gases The chlorine replaces the bromine in the liquors and the bromine (mixed with unused chlorine) is drawn off and condensed By careful control of the temperature contamination with too much chlorine is avoided The bromine is subsequently further refined

A similar process is used to extract the bromine from the Searles Lake brine in California This brine has a concentration of about o 085 per cent of bromine, about twelve times as much as in ocean water, but less than the concentration in the Dead Sea The brine has a pH of 9 5 "which is too alkaline to allow the process of removing the bromine with chlorine to be used direct on the liquor. The problem is solved by the fact that potassium bromide and potassium chloride are isomorphous and by suitable manipulation the bromide is made to crystallise out with the potassium chloride The mixture contains about 1 8 per cent bromine and, as it is neutral in reaction, it can be used directly as a raw material using chlorine to liberate the bromine The concentration of bromine is sufficiently high to make it unnecessary further to lower the acidity, as is done with sea water A saturated solution of the crystals is made up at 87^0 C and treated with steam and chlorine in Kubierschky towers made of Vermont granite. The liberated bromine passes through a Pyrex glass pipe to tantalum lined condensers and the crude bromine is then twice fractionated, giving a product 99 9 per cent pure Bromine was first produced at this plant in 1940 and the annual production from the Searles Lake brines was about 2,500,000 lbs of bromine This was about half the total U S A production for purposes other than anti-knock compounds before the present war demands arose

The production of bromine compounds from bitterns obtained by evaporating sea water was begun by the California Chemical Co in California in 1926 in association with the production of magnesium The bromine is recovered by a modified Kubierschky process with a 95 per cent recovery of bromine which is converted into ethylene bromide and inorganic bromides

In Chapter 2 was discussed the possible use of zeolites as base exchange mechanisms for extracting copper and other elements from the sea water Recent patents involve the use of an acid radical exchange on an active surface for recovering bromine and iodine from sea water. O. M Urbam and W R Stemen[59] pass the sea water through activated coconut carbon which has been treated first with ammonia and then with chlorine The chlorine is held by the active carbon and part, but not all, of it is replaced by bromine or iodine when solutions containing these elements are passed through the carbon The bromine and iodine are then recovered and the carbon regenerated The treatment with ammonia renders the process more efficient, and about one and a half parts of chlorine are used for each part of bromine, without the ammonia treatment, two parts of chlorine are needed for each part of bromine The absorption works most efficiently in an alkaline solution of pH 9 4 or over In

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[59] U S P 2, 246, 645-6, 24-6-41

an acid solution the bromine is not completely absorbed The presence of organic matter in the water does not interfere with the reaction

Of historical interest is the production of bromine by the French in Tunisa during the last war, when the German supplies were not obtainable France first applied to America for bromine, but prices were too high and supplies insufficient A source was then developed at the salt lake (Sebkha el Mela) south-east of Gabes, from which about 1050 metric tons of bromine were extracted The *sebkha* is a shallow basin of nearly 60 sq miles area with a surface 3 feet below that of the sea During the rains it receives waters charged with salts which evaporate later under the influence of hot winds The deposit is impregnated with a mother liquor which contains 2 24 per cent of magnesium bromide and 1 3 per cent of potassium chloride, it reaches the surface through natural wells The amount of bromine in the liquor is about 30 times that of ocean water Solar evaporation was used for the concentration of the mother liquor and the bromine was recovered in six Kubierschky towers by the use of steam and chlorine Nearly 2 tons a day was produced when working at full capacity

During 1918 a second bromine plant was built in Tunisia, but working at both plants was stopped at the end of the war as the result of the recovery of Alsace by the French, the Alsatian deposits being akin to those of Stassfurt The bromine recovery plant commenced working in Alsace in July 1926, producing at the rate of 60 tons per year, at a time when the French requirements were 200 tons per annum It was afterwards extended

Bromine is also obtained from the sea in Japan The process involves solar evaporation and the liberation of bromine from the bitterns with potassium chlorate and sulphuric acid[60]

As mentioned above by far the greatest user of bromine is the internal combustion engine in the form of ethylene

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[60] **S Imatomi.Sci Papers Inst Phys Chem Res Tokio, 1936, *30,* 138**

dibromide. Other applications include the use of methyl bromide in fire extinguishers It is used in the manufacture of certain dyestuffs, in particular dibromo- and tetrabromo-mdigo, and eosm, which is the potassium salt of tetrabromo-fluorescem Potassium bromide and other bromides are much used medicinally as sedatives Potassium bromide is also extensively used in the photographic industry ; when treated with silver nitrate, silver bromide is formed which is the essential compound acted on by light in films and plates Bromine and its compounds were used as chemical warfare agents in the last war, including bromoacetone (one of the most potent lachrymatory agents known), benzyl bromide (lachrymator) cyanogen bromide (a lung irritant), ethyl methyl dibromoarsines (lung irritants), xylyl bromide (lachrymator), and bromobenzyl cyanide, usually referred to as B B C , which, is a highly persistent lachrymator and was still considered a likely substance were "gas" to be used in the second World War

Some thousands of tons of bromine have been extracted from the sea each year by a war factory in Britain for fuel purposes, but it was impossible for security reasons to reveal this fact during the continuance of hostilities in Europe

CHAPTER 6

MAGNESIUM FROM THE SEA

MAGNESIUM metal was first obtained in 1808 by Sir Humphrey Davy Commercial production on a very small scale started in France in 1857 to supply the demands of flash light photography In 1864 the Magnesium Metal Company was formed with works at first at Salford and later at Patricroft, both in Lancashire It is of interest that at these works aluminium was first produced electrolytically about 1890 It was not until 1896 that the electrolytic method of production of magnesium was started on any real scale at Bitterfeld in Germany.

The subsequent development of the magnesium industry is closely connected with the two major wars of this century Whereas magnesium products have been known and used for centuries, the production of large quantities of metallic magnesium is a recent innovation, depending largely on the growth of the aircraft industry

Some information about the present position of the production of magnesium and magnesia in Britain may be gleaned from the report of the Select Committee on National Expenditure There are 4 firms producing magnesium, each of which uses a different process The costs are said to vary from over 4s to is 6d a pound The report also reviews five factories making magnesia, the general cost being between £12 and £13 per ton It is known that one of these was operating before the war and it is claimed that the first ingot of magnesium metal made from magnesia derived from the sea was produced in Britain before the Americans followed suit

In the U S A the production of the metal was begun in 1915, by the General Electric Company In 1917 there were five producers, including the Dow Chemical Company at Midland, Michigan, using natural brines as raw material. By 1920 only two of the companies were still in production and one of these shut down in 1927, leaving the Dow Chemical Company the only producers

The following figures for the production and price of magnesium metal in the U S A illustrate the rapid growth of the industry

TABLE 16

1915	39	
1918	127	
1921	21	130 cents/lb
1925	109	86 „
1929		56
1933	640	28
1936	1740	
1940	5580	

Production at the end of 1941 was at the rate of about 18,800 tons per annum , and at the end of 1942 at about 116,000 tons per annum. A programme to raise production to over 270,000 short tons was then undertaken.

An article in the Magazine Fortune for March 1945, page 157, describes the vicissitudes which have attended the various processes of making magnesium metal, 15 plants are listed, of which 3 use sea water, 2 brines, 1 magnesite.and the rest dolomite Most of them began production during 1942 Many technical difficulties have been encountered, particularly with the Hansgirg reduction process, which shows high costs, said to be 40 cents a pound The largest capacity plant located near Las Vegas, Nevada, which uses magnesite has high costs and the highest capital invested per pound of metal produced—it is kept alive largely for political reasons

It would appear that the electrolytic process based on sea water or brine has the best chance of existing after the war demand has ceased Opinions vary as to the magnitude of the post-war demand for magnesium The optimists envisage light weight planes, cars, vacuum cleaners, typewriters and many other uses As 90 per cent of the American plants are owned by the Governments Defense Plant Corporation, the Dow Company seems likely to maintain its position

Estimated figures for the total world production in recent years are

TABLE 17

24,500 tons in 1937
29,500 „ „ 1938
40,500 „ „ 1939
50,300 „ „ 1940

Of this total the German Production in 1940 has been estimated to be about 20,000-23,500 tons The largest individual plant was at Bitterfeld No figures are available for recent British production but just before the war it was estimated to be about 5,000 tons per annum Magnesium metal is made also in France and Italy

We have next to consider what are the raw materials 'from which this magnesium is produced, and how it is that the sea containing on an average o 14 per cent, magnesium or about 4 million tons per cubic mile, can compete as a raw material with rocks containing up to 300 times as much Magnesium occupies eighth place in the order of abundance of elements in the earth's lithosphere with 2 24 per cent magnesium The most important ores are dolomite, of which whole mountain chains are composed, magnesite ($MgCO_3$) with 28 per cent magnesium, the hydroxide brucite ($Mg(OH)_2$) with 41 per cent magnesium and carnallite ($MgCl_2KC16H_20$) with 8½ per cent, magnesium, which occurs in the Stassfurt deposits

PLATE VI. INTAKE OF SEA WATER. SETTLING TANK.
(Courtesy of British Periclase Co. Ltd.).

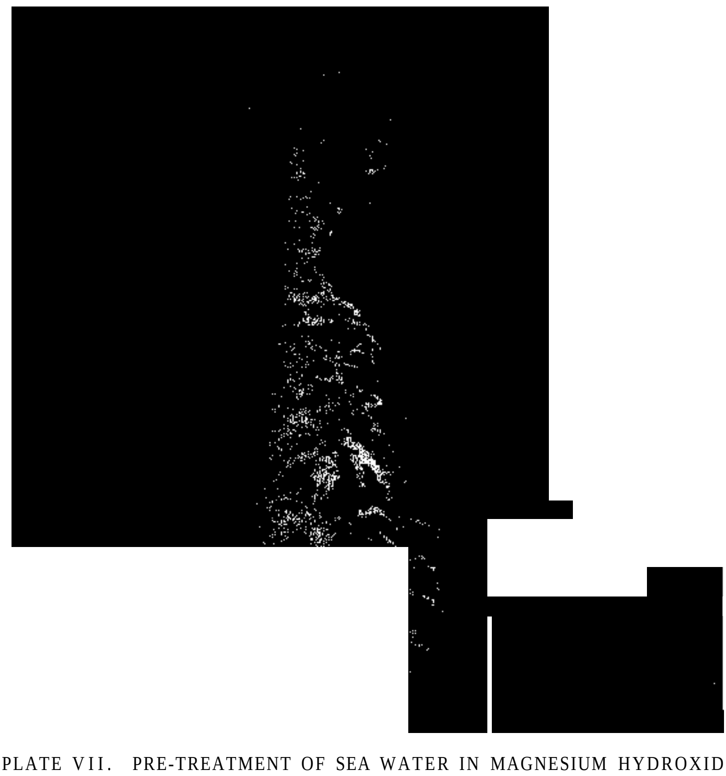

PLATE VII. PRE-TREATMENT OF SEA WATER IN MAGNESIUM HYDROXIDE RECOVERY PLANT. *(Courtesy of British Periclase Co. Ltd.),* True dolomite is $MgCO_3CaCO_2$ and contains about 12 per cent of magnesium, but the name is loosely used for many rocks containing magnesium carbonate and calcium carbonate in varying proportions Some dolomites are considered to have been originally formed under the sea, but others have been formed by the replacement of calcium by magnesium from fresh water

Magnesite is found in purest form in Austria, Greece and California There are large deposits of less pure material in Canada, USSR, Manchuria and the American States of Washington and Nevada

High grade magnesite is rare in America and impurities, particularly calcium, iron, aluminium and silicon, are difficult and costly to remove a high degree of purity is required if the metal is to be made from it. Natural brines have in most cases a higher magnesium content than sea water Some Michigan brines, for example, contain 10 per cent, but here the cost of drilling and the upkeep of the wells must be considered

The original Dow process was based on the recovery of 3 to 4 per cent magnesium chloride from brines nearly 1,500 feet below the surface at Midland, Michigan The brines found around Ludmgton in the same State contain as much as 10 per cent of magnesium chloride and are recovered at Marysville but as the recovery at Midland is tied in with other operations the costs here are probably the lower

Magnesia was first prepared from sea water at Argues Mortes on the Mediterranean coast at the end of the last century Magnesia was precipitated with milk of lime, collected on a sand filter, and dried by the heat of the sun in summer and by other means in winter

The first large scale production of magnesium compounds from the sea was in association with the production of sodium chloride by solar evaporation in California described in Chapter 4 Descriptions of the process worked by the California Chemical Company at Newark are given by M Y. Seaton[61] and P D V Man-

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[61] **Chem and Met Eng 1931,** ***38,*** **638**

ning[62]. The solar evaporation of sea water is a seasonal process and the spent bittern is stored in vast vats with a total storage capacity of about a hundred million gallons The bittern is usually first used for bromine production as described in Chapter 5, but this stage may be omitted and the raw material for the magnesia plant may still contain bromine The bittern is then treated with a solution of calcium chloride, when a double decomposition occurs to give magnesium chloride and calcium sulphate The mixture passes to two Don-thickeners in series and the calcium sulphate slurry is filtered, washed and dried Much of the gypsum produced is used in a neighbouring cement plant, providing an example of the utilization of another raw material from sea water, sulphates The magnesium chloride liquor is then treated with lime to give magnesium hydroxide and calcium chloride, the latter being re-used for the first stage in the process The magnesium hydroxide is first thickened in a Don thickener and washed by the usual countercurrent technique in four more thickeners before being filtered and calcined to magnesium oxide This plant in 1938 was producing about 60 tons per day of various magnesium products, principally dead burnt magnesite for use as a refractory, but was not producing metallic magnesium

The lime used in this process is also a product of the sea, being obtained from the enormous deposits of oyster shells in San Francisco Bay. The shells are dredged into barges and on their voyage to the plant are thoroughly washed with sea water in a rotating screen The shells are then calcined to give lime, some of which is used in the magnesia process while more is marketed

Also in California in South San Francisco is the plant of the Marine Chemicals Company which produces magnesium compounds direct from sea water without any preliminary concentration. The process, described by

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[62] Chem and Met Eng 1938,45,478.

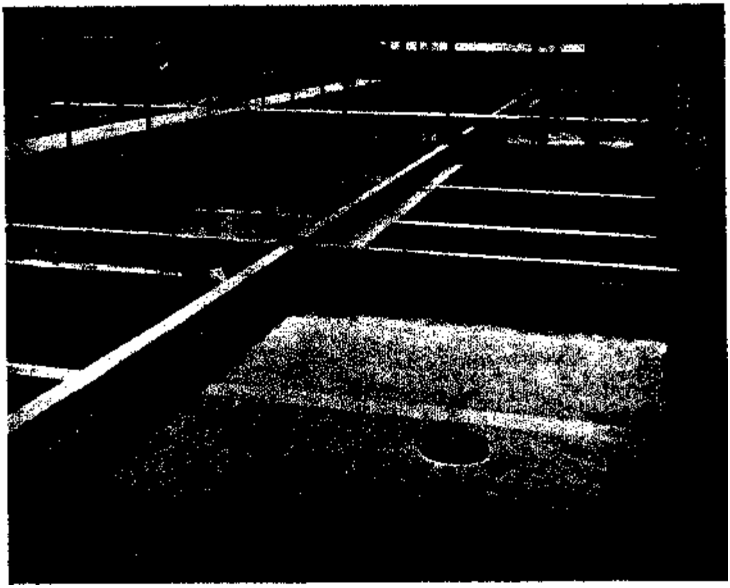

PLATE VIII. SAND FILTERS FOR SETTLING PROCESS, MAGNESIUM HYDROXIDE RECOVERY. *(Courtesy of British Periclase Co. Ltd).*

peninsular in Freeport Harbour, surrounded by sea on three sides, but so placed that the spent water can be diverted into the Brazos river, which discharges into the sea where it cannot contaminate the incoming water

Freeport Harbour had been built by the United States Engineers Corps, when the former channel of the Brazos river was dammed five miles above its mouth The river now flows into the sea five miles south of its former mouth The site is near the source of important raw materials and of natural gas and petroleum, and has also been used for a duplication of the Kure Beach bromine plant

The heavier salt water lies underneath the fresher water in Freeport Harbour and the plant intake has therefore been placed thirty feet below the surface Four centrifugal pumps (three working and one spare), each driven by a 500 horse-power motor and with a capacity of 71,000 gallons per minute, pump some three hundred million gallons of water daily into the plant

This water is first filtered through link-belt screens and then through a finer filter of specially designed 6-mesh rotary screens It then passes into a 10 foot flume and the greater part of it goes to the bromine plant The magnesium plant takes its water from the flume by centrifugal pumps delivering five to ten thousand gallons per minute

For magnesium production the sea water is treated in a rectangular tank, 80 feet long by 28 feet wide and 14 feet deep, called the flocculator, with a slurry of milk of lime, prepared, as on the Pacific coast, from calcined oyster shells These shells are dredged from the neighbouring Galveston Bay and well washed with sea water, after which they are then calcined in a 300 feet long natural gas lime kiln, and then slaked and the milk of lime suspension pumped to a very large **Dorr** thickener, 150 feet in diameter and 18 feet high After thickening the milk of lime meets the incoming sea water in the flocculator The sea water enters at one end of the flocculator and passes through to the other, while the milk of lime enters at the top Very careful control of the hydrogen ion concentration is necessary and this is effected by the use of a glass electrode

From the flocculator the precipitated magnesia passes to four Dorr thickeners, each 200 feet in diameter The overflow from these, which is slightly alkaline, mixes with the slightly acid liquor from the bromine plant The underflow goes to storage tanks The magnesium hydroxide is filtered in very large presses of the plate and frame type, 90 feet long and with about 100 leaves The presses are transported by an overhead travelling crane which lowers them into the tank containing the thickened slurry A cake, about an inch to an inch and a half thick, is drawn into the plates by vacuum and then the whole press is raised again and transported elsewhere The cake is then blown off by compressed air The magnesium hydroxide is next treated with 10 per cent hydrochloric acid solution in rubber-lined tanks to produce magnesium chloride The magnesium chloride solution is concentrated to crystallize out the solid magnesium chloride, which is then dried Both the concentrating and drying plants have remarkable features and differ widely from more usual plants, but descriptions of them are only indirectly related to the production from sea water, and the reader desirous of learning more on this subject is referred to an excellent paper by S D Kirkpatnck[65] **from** which this description has largely been obtained

The process sounds simple and straightforward, but in practice many difficulties would arise unless it were very carefully and accurately controlled The precipitated magnesia, for example, must be of a certain grain size

in order to

down as an unfilterable sludge Furthermore it must be removed before other impurities, such as calcium sulphate, have time to crystallize All this requires accurate control of such things as temperature and hydrogen ion concentration

Another difficulty arises because of the presence of

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[65] Chem Met Eng 1941, *48*, 76

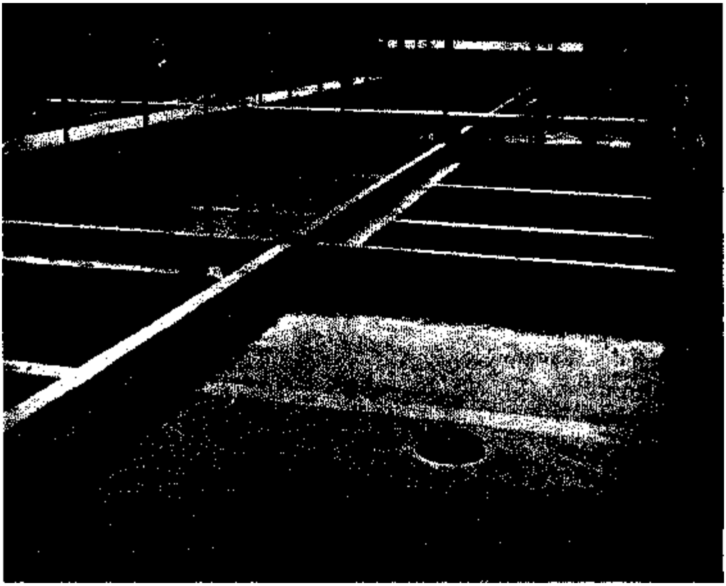

PLATE XI. EXTRUSION PROCESS IN MAGNESIUM HYDROXIDE RECOVERY FROM SEA WATER. *(Courtesy of British Penclase Co. Ltd.).*

of interest on magnesium and is not only the most up to date, but also one of the most inclusive, publications on this metal

British Penclase, Ltd obtain their sea water from a derelict harbour, the entrance of which is now closed by a caisson This harbour serves to act as a reservoir of water between successive high tides About ten million gallons of water are pumped daily into two tanks in which enough lime is added to convert the calcium bicarbonate present into insoluble calcium carbonate This is settled and filtered off The water is then treated with a milk of calcined dolomite In that dolomite contains one molecule of magnesium carbonate to one molecule of calcium carbonate, the magnesia obtained is about double that which is obtained when lime is used as the precipitating agent, but only half the magnesium produced, of course, has its origin—or its immediate origin—in the sea An additional advantage is that the magnesia particles in the calcined dolomite act as nuclei on which the magnesia from the sea water is deposited, thus giving better gram size

The milk of calcined dolomite is sprayed on to the sea water and the mixture then flows into a Dorr thickener The slurry is heated by steam in order to increase the rate of filtration Filtration is through cotton filters and the magnesia is then burned in a kiln, the degree of burning depending on the purpose for which the magnesia is required This company produces metallic magnesium by electrolysing magnesia, not magnesium chloride as in the Dow process For electrolysis the magnesia needs only to be partially calcined

Messrs Ocean Salts, Ltd , who also extract magnesium from sea water in Britain, use an essentially similar process, but as dolomite is not immediately available to them, use lime as the precipitating agent

The firm has taken out a patent[68] in which the sea water, instead of being pretreated by adding just enough lime to remove the calcium as carbonate, is treated with

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[68] B P 553731,3-6-42

lime more than enough for this purpose. This results in the precipitation of some magnesia with the calcium carbonate The mixed precipitate is filtered off, calcined, and used again, this time for precipitating magnesia from the already treated sea water The advantages claimed for this process are that the pretreatment is rapid and easy, the rate of settling is increased, the lime used for pretreatment is recovered and the rate of filtration of the magnesia is increased Messrs Ocean Salts Ltd , have also taken out patents[69] for the precipitation of magnesium from sea water as magnesium silicate by treatment with sodium silicate

Magnesium compounds have also been obtained from sea water in Japan A process is described by S Imatomi[70] by which the solar evaporation of sea water gives magnesium chloride

The uses of magnesium metal are well illustrated by the U S consumption 1940 —

TABLE 18

		Per cent,
Structural products (80 per cent of which were in the aircraft industry)	3290 tons (long)	64
In Aluminium alloys	1580 tons	
In Zinc alloys	31 tons	31
In other alloys	8 tons	
As a scavenger and deoxidizer	160 tons	
Fireworks, etc	20 tons	
In chemical industry	31 tons	
Other uses	22 tons	

[69] B P 535852-4, 20-9-99

[70] Sci Papers Inst Phys Chem Res Tokio, 1936, *30*, 138

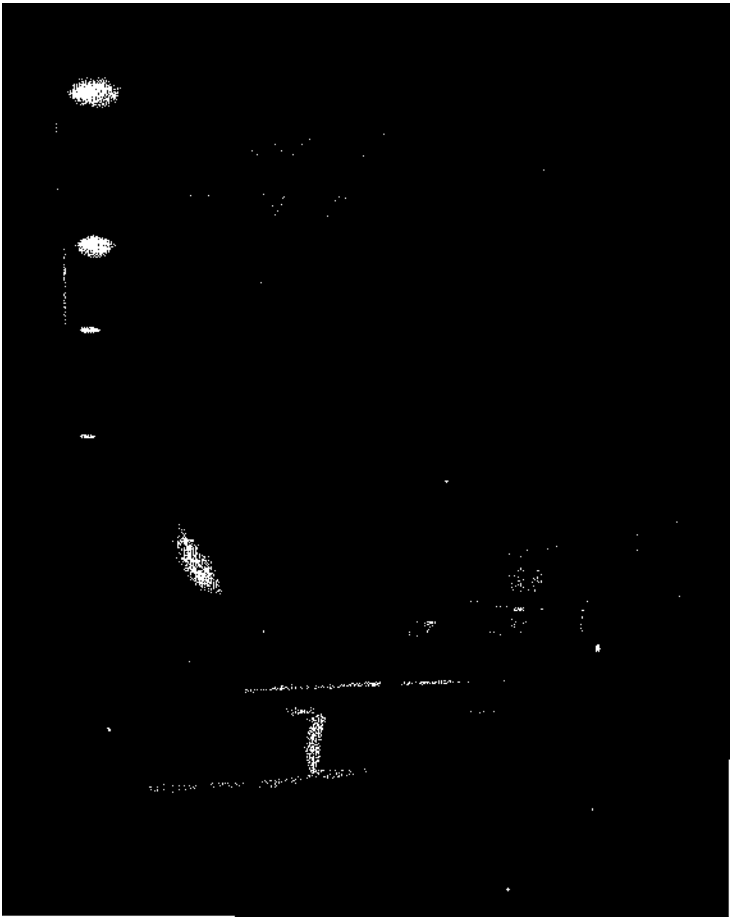

PLATE XII. MAGNESIUM FROM SEA WATER. ROTARY KILN.
(Courtesy of British Periclase Co. Ltd.).

It is not within the compass of this book to deal at any length with the metallurgy of magnesium and the variety and use of its alloys The production of the metal on the largest scale and the development of its applications is essentially associated with the war and we have been concerned mainly with the methods of obtaining the element from the sea and its conversion into metal

The chief use for metallic magnesium itself is as a scavenger for some non-ferrous metals, but this, it will be seen from the above table is only a very small proportion of the total amount of magnesium used Other uses are almost entirely in the form of alloys, which have a greatly increased mechanical strength

The aircraft industry is obviously by far the greatest user of magnesium It has been estimated that every American aircraft now being built contains an average of half a ton of magnesium and this probably applies to aircraft of every nationality Magnesium alloys are used in many parts of aero engines, including crankcases and their covers, camshafts, accessory drives and various unstressed castings In addition such items as landing wheels, brake shoes, seats and instruments are made partly or wholly of magnesium alloys

Magnesium alloys were first made known as Electron Alloys and developed by what later became a branch of the I G Farbenindustrie During the war the remarkably swift and thorough development of the metal and its alloys was due largely to the work of such producers as Magnesium Elektron Ltd. of Manchester, England, and the Dow Chemical Co of Midland, Michigan, U.S.A High Duty Alloys of Slough, England, have also played a notable part in the developments. Apart from Dr C H Desch's lecture to the Royal Society of Arts *

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* 1943, 91, 273

there is much in**formation** on the **subject to be found in** a book Magnesium, its Production and Us e, by E. V Pannell †

Magnesium alloys have a great number of uses where light weight and strength are important considerations Magnesium is lighter than aluminium, having a density **of 1** 74 and aluminium **of** 2 70, but magnesium alloys are more susceptible to corrosion and in general have less tensile strength than aluminium alloys Magnesium alloys are, however, much more resistant to alkaline corrosion than aluminium alloys , the reverse is true with acid corrosion Magnesium alloys are very easily machined

Magnesium alloys usually contain over 85 per cent **of** magnesium They are much the same in Britain. Germany and the United States except that the tendency in America is to use relatively high percentages of aluminium whereas the Germans use low percentages In addition to aluminium the standard alloys contain manganese, zinc, and in Germany o 1 to o 2 per cent of silicon

Magnesium added to aluminium alloys improves their resistance to alkaline corrosion Magnalium is a straight aluminium-magnesium alloy with 10-30 per cent magnesium Most of the duralumin type alloys contain about o 5 per cent of magnesium

As magnesium is very reactive towards both oxygen and nitrogen it is used as a deoxidiser and scavenger in non-ferrous metallurgy It is used to remove bismuth from lead and to purify aluminium, solder, copper and its alloys, and nickel and nickel alloys

The use of magnesium as a pyrotechnic is another instance of its great importance in war time Its use in incendiary bombs comes under this heading and it is also used for flares, star shells and tracer ammunition It is

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† **Pitmans. 1943**

still, of course, widely used in its first industrial use—for flashlight photography

Makers of magnesium metal are greatly concerned with its post-war future Obviously the less economic processes based on costly raw materials will have to shut down, One of the most promising fields is in transportation other than aircraft where it is of advantage to reduce the dead weight of the equipment The same applies to the appliances used by the housewife and the office worker—vacuum cleaners, typewriters, business machines, radios, etc It will have a use in portable tools Other possibilities will be found outlined in an article by L B. Grant * *

Turning to compounds of magnesium, the most important applications are probably for refractories and ceramics Magnesium oxide has a melting point of 28oo^{g}C It thus has a very high temperature resistance, it is also very resistant to reduction It is very largely used in steel manufacture It has been estimated for instance, that two to four pounds of "dead burned" magnesite are consumed per ton of steel produced For work at exceptionally high temperature artificial periclase, containing 93-94 per cent magnesia is used

Magnesia and also the basic carbonate are used as heat insulating materials Another use for the basic carbonate is to prevent caking in table salt The addition of only 1 per cent of magnesium basic carbonate separates the sodium chloride crystals and absorbs water Magnesium oxide and carbonate are used as fillers in the rubber industry, chiefly for mechanical rubber goods, and in the printing ink trade for carrying the pigment and giving a dull finish

Magnesium hydroxide has been used as a reagent in the treatment of petroleum In the so called "sweetening process" it acts by removing mercaptans It has been so used for neutralizing corrosive crude oils and in towers for removing impurities from vapours

* * Chemistry and Industry, Sept 2, 1944, p 314

Magnesium salts have many uses in the medical an cosmetic lines, for stomach powders, toothpastes, om ments, face powders and the like The use of magnesiu sulphate (Epsom salts) as a purgative is well known, an milk of magnesia is consumed in America at the rate c 15,000 gallons a day (containing 7-8½ per cent, of magnesium hydroxide)

Much information about the properties, uses and production of magnesium and its compounds is given u a monograph by V Lumsden[71]

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[71] "Magnesium, Magnesite and Dolomite/' published by the Imperial Institute, London, in 1939

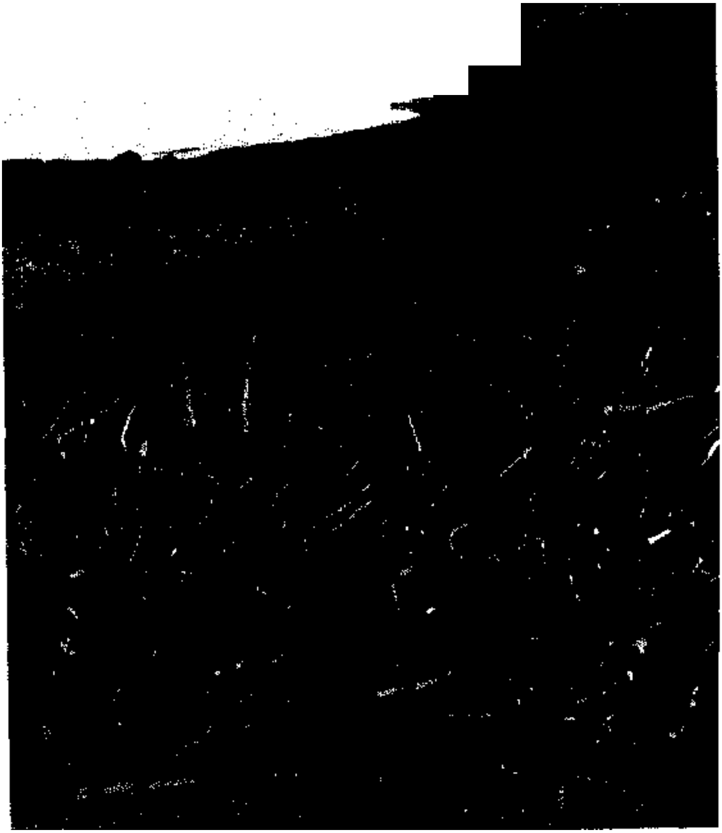

PLATE XIII. TYPICAL SEA TANGLE THROWN UP ON THE COAST OF THE OUTER HEBRIDES. *(Courtesy of Albright and Wilson Ltd.).*

CHAPTER 7

IODINE AND THE SEA WEED INDUSTRY

" Breaking the silence of the seas
Among the farthest Hebndes "
WORDSWORTH

Considerable interest attaches to the presence of iodine in the sea, where it is one of the very scarcest of the non-metallic elements It is hard to detect and to analyse the results of different investigators range from o oi to o 07 parts per million with an average of 0 05 assumed by Goldschmidt and half as much, namely 0 025 parts per million given in " Iodine Facts "—on this last basis there will be 100 tons of iodine in every cubic mile of sea[72] Yet iodine is almost universally present in marine animals and diatoms and plants, particularly in sponges, corals and some seaweeds, so that in the aggregate the amount of iodine is considerable In the seas the amount of iodine seems to bear some relation to the salinity, thus it is high in the Red Sea (0 66 parts per million) and low in the Baltic (0 oi parts per million)

Iodine was first discovered by Bernard Courtois under circumstances which are of historical interest During the Napoleonic Wars France was blockaded by the British fleet and unable to import saltpetre for gunpowder It was made artificially in various parts of the country from decomposing nitrogenous organic matter mixed with calcium carbonate in the form of powdered limestone or old mortar The calcium nitrate in a subsequent operation was boiled with potassium carbonate from wood ashes Courtors was a saltpetre maker and had resource to a cheaper source of the alkali, namely, the ash produced on incinerating dried seaweed

On one occasion he used strong sulphuric acid and heat to clean out his plant when beautiful violet-coloured

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[72] There is a review of the iodine content of sea water in a took by J F Clendon, viz , Iodine and the incidence of Goitre (Minnesota Press 1939)

CHAPTER 7

IODINE AND THE SEA WEED INDUSTRY

**" Breaking the silence of the seas
Among the farthest Hebrides "**
WORDSWORTH

Considerable interest attaches to the presence of iodine in the sea, where it is one of the very scarcest of the non-metallic elements It is hard to detect and to analyse the results of different investigators range from o 01 to o 07 parts per million with an average of 0 05 assumed by Goldschmidt and half as much, namely 0 025 parts per million given in " Iodine Facts "—on this last basis there will be 100 tons of lodme in every cubic mile of sea[72] Yet iodine is almost universally present in marine animals and diatoms and plants, particularly in sponges, corals and some seaweeds, so that in the aggregate the amount of iodine is considerable In the seas the amount of iodine seems to bear some relation to the salinity, thus it is high in the Red Sea (0 66 parts per million) and low in the Baltic (0 oi parts per million)

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vapours were seen to arise and condensed on the cooler parts of the vessel in dark metal-like crystals

The discovery was made about 1811 but not communicated to a scientific body till November, 1813 There was controversy between Gay-Lussac and Humphrey Davy as to which of them first decided the new substance was an element[78]; it was undoubtedly named by the Frenchman

All fishes and all animal products from the sea appear to contain iodine in minute quantity Some species of sea weed, notably *Lammaria*, contain up to o 5 per cent on the dry matter basis It is established that the seaweed from deep water areas, 1 e , from low water mark down to about 20 fathoms, contains more iodine than weed from near the shore, which is exposed to tidal ebb and flow, and driftweed has less iodine than fresh material

The amount of iodine in land plants is not large, it is much higher in fresh water algae but still more so in marine algae Iodine is present in mineral waters and in the waters or brine pumped up from petroleum wells to the extent of 50 to 90 parts per million

Apparently the iodine of the world is in a state of continual exchange between sea, air and land The air at sea level contains a noticeable quantity, o 00005 parts per million, though at the height of Mt Blanc the quantity is very much less

It has been suggested that iodine is present in the sea in a form such that it can pass into the air as free iodine It is far more probable that it is there as iodide earned up into the air as spray It is stated that near the surface where the water is exposed to air and sunlight the lodate ion predominates, at a greater depth the proportion of iodide increases The question is still indefinite and awaits better analytical methods What is clear is that iodine in the sea is in a continual state of change, undergoing oxidation and reduction and entering into organic combination

Ram washes this iodine out of the air and has been found to contain 0 001—0 003 parts per million , river

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73 See F D Chattaway, Chemical News 1909, p 193

water has about half this amount Most of the iodine in rain is taken up by the top layers of the soil, which is cited as containing from 0 6 up to 8 0 parts per million, with a mean of 2 0 parts per million Soils near the sea have the higher content The older agricultural soils appear to be fully saturated with iodine, but newer deposits continue to increase in the amount of iodine they contain This iodine may have some relation to fertility though this has not been proved Some of the iodine goes into the crop and, to this extent, makes it of better quality as an animal food

There are scarcely any minerals containing iodine as an essential constituent, and the few that have been found are mineralogical curiosities

According to Irvine Masson[74] it would seem that during the two thousand million years which span geochemistry, iodine played a part that was practically nothing, and that had the element never been created, the inorganic earth would not be appreciably different from what is But with the origination of organic life (800 million years ago, or earlier) iodine began to matter First it became not wholly dispersed, but partly to be segregated from solution in the sea into the colloids of living organisms floating there Then, as the forms of living things developed, the iodine was not only taken up into them, but also became a chemical part of some of them They developed still further and more variously , and now, the vertebrates, and we ourselves, could not continue without iodine, either as individuals from month to month or as species from generation to generation

As already stated, three living organisms stand out far beyond the rest as being rich in iodine one is vegetable, two are animal The chemical form of iodine is undecided in seaweeds, though it is believed to be organic, but in the sponges and corals it is, surprisingly, present as an aromatic amino-acid, namely 3 5—di-iodotyrosine Probably the protein ingredient, tyrosine, is supplied ready made in their food to the animal cells, but the

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[74] **Nature 1938, *141,* 227**

Iodination would seem to go on in the cell, for which purpose the co-operation of an oxidising enzyme is necessary It has elsewhere been mentioned that organic halogen compounds of any kind are extraordinarily rare among natural products The only others known at present are dibromotyrosine, obtained by Morner (1913) from horny corals, and dibromoindigo, the classical Tyrian purple dye Certain aromatic chloro compounds have been isolated from lichens

In the sponges and corals the iodine is accumulated not in the fleshy cell tissue but in the horny skeleton, and it may be either a discarded product or a reserve store

In man iodine is localised in the thyroid gland, which contains thyroxine and di-iodotyrosine, this being undoubtedly the precursor of the all important thyroxine When the traces of iodine in the food are inadequate the thyroid gland functions irregularly, basal metabolism is disturbed and such diseases as goitre, imperfect growth, myxoedema or cretinism may happen

Iodine has many uses, as an antiseptic, as a curative and in veterinary practice It is added to animal feeding stuffs and to salt, particularly in the Middle West of the United States , it finds use in dyestuffs, disinfectants and photography Efforts are being made to find still further applications

Iodine is won indirectly from the sea The oldest source is the ashes of seaweeds which was superseded by the discovery of iodine as iodate in the *caliche* or crude nitrate of soda deposits in the desert regions of Northern Chile These are on the Pacific coast some 3,000 feet above sea level the nitrate fields are concentrated in a narrow strip about 300 miles long and 15 to 20 miles wide

The raw material, *caliche,* is of variable composition, containing nitrates, chlorides, sulphates, borates, perchlorates, iodates, sodium, potassium, calcium and magnesium Their origin and that of the iodine is still a matter of controversy One theory is that a sea containing great masses of seaweed evaporated , during the process it underwent decomposition by nitrifying bacteria

Another suggests the same bacteria acting on land vegetation, the deposits representing the final drainage water from a wide region Iodine as iodide may well have been brought in continuously as spray from the Pacific Ocean for a long period and oxidised in presence of the intrate to insoluble lodate In this manner it would escape being washed out by subsequent rainstorms

Still another explanation of this natural occurrence of iodine suggests the existence of a vast prehistoric forest of seaweed and other marine vegetation which, through the pressure of some terrestrial upheaval, underwent decomposition, yielding petroleum as an organic residue and iodine as an aqueous extract It has been proved that the concentration of iodine by seaweeds and still more by plankton diatoms creates the necessary conditions for an accumulation of iodine in sea muds During the process of the metamorphosis of muds the iodine enters into solution with the water forming strata of mineral lodme-bromme waters, which have considerable regional distribution and are a source of commercial iodine

The mtrate of soda of commerce contains 0.022 per cent, of iodine, equivalent to 8 ounces in every ton

The iodine industry in Chile is a by-product manufacture and has never been particularly efficient The amount *oi* iodine varies considerably in the different deposits, usually it does not exceed 0 02 per cent, though it may be as high as 0 17 per cent, equivalent to 3 8 lbs per ton of nitrate " Iodine Facts " gives an average of 0 15 per cent, for caliche The amount of iodine corresponding to the normal output of nitrate would be 15,000 tons per annum but less than 10 per cent of this is won normally.

The Chile iodine industry started about 1874 The solutions used to extract sodium nitrate which are returned again and again to the leaching plant become in time saturated with sodium lodate, a normal concentration being from 5 to 8 grams per litre A portion of these mother liquors is set aside for iodine recovery, which is effected by precipitation with sodium bisulphite The iodine is collected after washing and purified by volatifcsation

The old method of recovery, which is still largely used, is to precipitate the iodine with a solution of sodium bisulphite Variations sometimes used are *(a)* passing sulphur dioxide gas direct into the mother liquor , *(b)* using sodium thiosulphate and sulphuric acid Method *(a)* gives the cheapest iodine, under the best conditions there is a recovery of 80 per cent

The next step is sublimation , the iodine " cheeses " are broken up and heated in cement-lined retorts for several days The iodine and the moisture are caught in earthenware pipes, of which several are luted together except for a few inches at the bottom of each joint The condensed water escapes here, the sublimed iodine forms crystals in the receivers[76]

This iodine is sent to Europe or the United States for further purification and conversion into other products

There is iodine in the final mother liquors both at Stassfurt and Searles Lake Petroleum and naphtha wells are usually associated with salt deposits—large quantities of impure brine are therefore brought to the surface It has been found possible to extract iodine from this in California

Subterranean waters in the great oil bearing strata of Java contain iodine in amounts varying from 003 to .015 per cent These waters are pumped, filtered and the iodine liberated in the free state by meeting a counter current of sulphur dioxide The treated waters pass through troughs in which bundles of copper wire are suspended on which the iodine is precipitated as cuprous iodide The precipitate is removed by washing with slightly acid copper sulphate The wires are then ready for use over again The copper iodide is filtered, dried and ground, it has an iodine content of 52-55 per cent , it is shipped to Europe for conversion into potassium iodide The industry began in 1920 and of recent years between 30 and 40 tons have been annually exported

The American iodine industry, described by P V D

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[75] See J B Faust, Ind Eng Chem. 1926, *18*, 808, also M B Donald. Ann Sci 1936, I, 29-47, 193-216

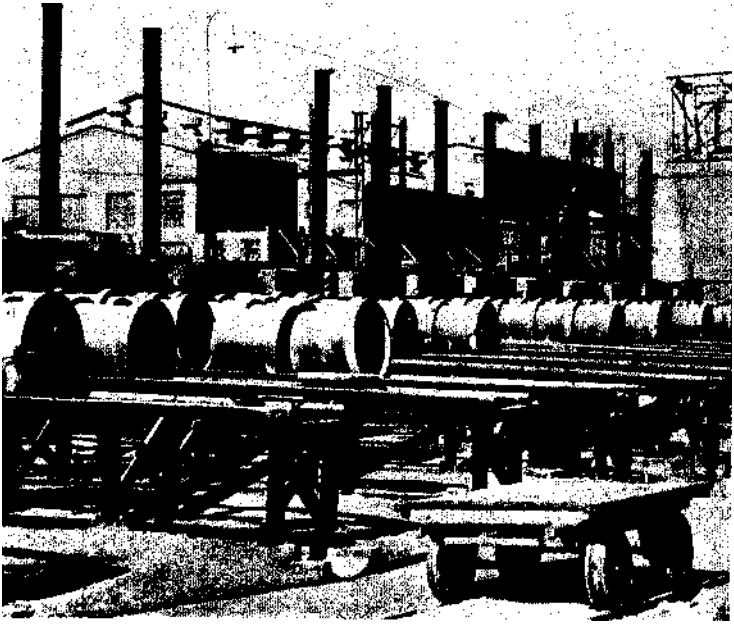

PLATE XIV. IODINE PLANT AND DISTILLATION RETORTS.
(Courtesy of Nitrate Industry of Chile).

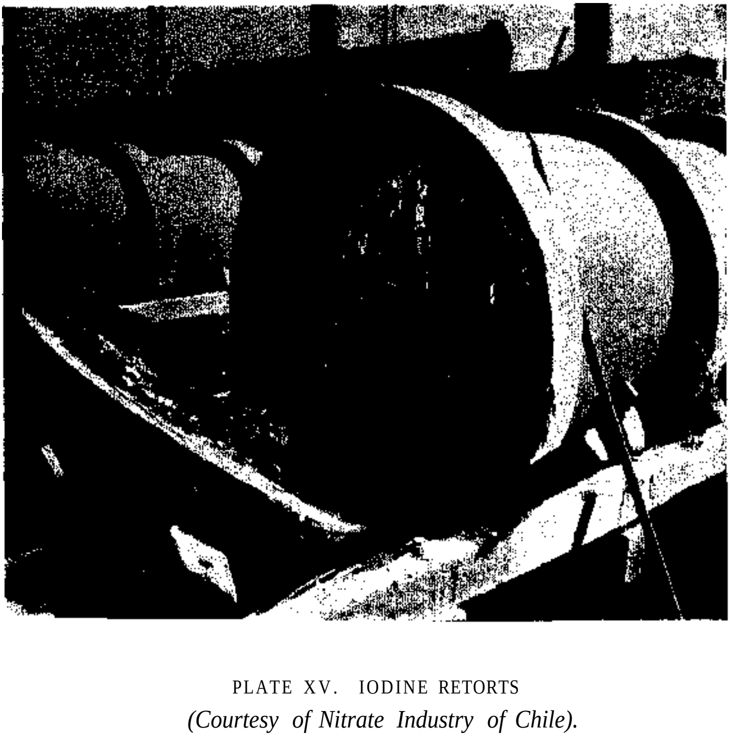

PLATE XV. IODINE RETORTS

(Courtesy of Nitrate Industry of Chile).

Manning[76] starts from the ' 'community'' processing plant forced on the refiners near Long Beach, California," to prevent oily waste liquors being ejected into the sea. This brine is cleansed to a stage at which it can be acidified with sulphuric acid and sodium nitrate, when it is extracted

in successi

reached maximum saturation with iodine The charcoal is filtered off, drained and iodine leached out by a hot solution The charcoal returns to the process whilst the iodine is liberated from the purified liquor with chlorine and steam The original brine contained only 50 parts of iodine per million, much the same as the Java waters

An alternative process is precipitation with silver nitrate, to which a small quantity of ferric chloride is added to hasten the subsidence of the precipitate The mixed precipitate of silver iodide and ferric hydroxide undergoes further treatment Other processes which have been experimented with on an industrial scale are precipitation by mercurous or by cuprous salts, blowing out liberated iodine with absorption in a solvent, or extraction by a solvent such as kerosene, which is immiscible with water

Iodine is sometimes recovered as cuprous iodide by means of copper The reverse process is also possible, namely, the recovery of copper in small quantities by means of iodine This is the basis of the Gonzalez process , 1 ton of copper requires 2 tons of iodine of which all but 1 lb is recovered to be used again[77]

There are Iodiferous mineral springs in various districts in the North of Italy The production from these today is said to be 50 tons annually To extract the iodine the water is treated with sodium nitrite and sulphuric acid, the free iodine thus liberated is then taken up with petroleum, which is separated in centrifugal machines The iodine is recovered from the solvent by treatment with sodium sulphite and finally elementary Iodine is made from the sodium iodide, obtained by means of

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[76] Chem and Met Eng 1934, *41*, 568

[77] Mining Journal, 1942, June, 13

an acid solution of sodium dicromate Crude iodine is brought up to 998 per cent purity by melting under concentrated sulphuric acid and drawing off the liquid iodine phase, which only needs to be washed free of acid and dried over calcium chloride An alternative method of purification is by steam sublimation

The world consumption of iodine is around 1,000 tons per year, of which the Chile monopoly produces 75 per cent The *possible* production outside Chile is estimated as —

TABLE 19[78]

			Source
Europe	140	tons	Seaweed
Japan	150	„	Seaweed
Java	80	,,	Artesian
U S	500	,,	Oil well
Russia	240 ?	,,	Seaweed and oil well
	1,110	**tons**	

These figures were published at a time when it was sought to break the Chile monopoly—the plant capacity was not then in being to make such quantities

The following table in metric tons relating to the world production of iodine is taken from "Iodine Facts" —

TABLE 20

Year	*Caliche*	*Seaweed*	*Waters*	*Total*
1904	370	150	–	520
1914	570	230	–	800
1917	1030	210	—	1240
1920	582	176	9	767
1924	635	185	54	874
1934	351	255	211	817
1939	874	109	226	1209
1940	1192	112	444	1548
1941	1068	94	249	1411

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[78] P F Holstem, Chem Met Eng 1932,39,422

The heading, "Seaweed", in the table, comprises Scotland, France, Japan and Ireland as sources "Waters" refers to Java, Italy and the United States

The modern theory of the origin of petroleum is that it is derived from a vast prehistoric forest of seaweed and other marine flora and fauna which, through various agencies, underwent decomposition,yielding hydrocarbons. This is confirmed by the association of petroleum deposits with salt deposits of similar composition to sea water. The iodine may well originate from that in the seaweeds.

The price of iodine is a vexed question and the industry is an example of those in which a by-product to a large industry can be sold at almost any price to eliminate competition and maintain a monopoly The Chile production costs are 1/- a pound or less The old pegged price level was 4 65 dollars which fell by stages to 3, 2 and 1 dollar in 1934, when American competition appeared in the shape of three companies in California, who extract it from oil well brine their peak production reached about half the then American requirements

The iodine industry in Chile has been accused of being inefficient, and of neglecting research, particularly that devoted to finding new uses for the element This is no longer true The Chile producers maintain non-commercial educational bureaux in both hemispheres They publish[79] a series of booklets called " Iodine Facts " which are conveniently numbered for reference The first of these is dated October 1940 and the latest May 1943 We are much indebted to these booklets for information

in this chap

information about the applications of iodine, particularly to medicine

Iodine from seaweed.

The seaweed industry has a most interesting history It dates from 1720 when the weed was burned for the recovery of soda and potash from the ashes It was particularly flourishing in the West Highlands of Scotland and in the early part of the last century the kelp from

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[79] **From Stone House, Bishopsgate, London, E C 2**

the Hebrides alone gave 20,000 tons of soda a year, with a value of up to £400,000 This is interesting as another example of the sea as a source of sodium salts The soda was largely used in the soap and glass industries , there was a firm at Dumbarton which used this soda and was famed for the quality of its glass

Kelp was then the only source of soda in the British Isles, otherwise such an expensive process would never have flourished as it only yielded at the most 4 per cent of alkali The rise of the Le Blanc process for the production of soda from common salt led to the extinction of the seaweed industry for the first time and by 1840 kelp had ceased to be a source of soda

But Courtois' discovery of iodine in 1811 and the subsequent discovery of its medical importance revived the seaweed industry In 1846 there were twenty manufacturers of iodine from kelp in Glasgow, which was the most important centre of the industry in Britain Potassium salts were also extracted The seaweed used was not the same as that previously burnt for soda as the weeds which contained most soda contained least potash and iodine The quantity of iodine is very variable The gelatinous algae like *Chrondus crispus* contain no iodine, whereas *Laminaria digitata* (tangle) contains up to o 45 per cent, iodine on a dry weight basis Only certain species of seaweed are worth burning for kelp When they are properly burnt the kelp should contain 1 4 to 1 8 per cent iodine or 33-40 lbs per ton In general the ash from mixed drift seaweeds would contain less than 15 lbs of iodine per ton and in the older processes only some 8 lbs per ton were recovered The iodine is present in the form of iodides which are extracted from the kelp with water The extract is then concentrated and potassium sulphate, potassium chloride and sodium chloride crystallize out The final mother liquor is rich in sodium and potassium iodides which are extracted from the kelp with water and considerable quantities of sulphides, sulphites and thiosulphates Sulphuric acid and manganese dioxide are added and iodine is liberated according to the equation

$$2\,NaI + 3H_2SO_4 + MnO_2 = I_2 + NaHSO_4 + MnSO_4 + H_2O.$$

The iodine is then distilled off and purified by sublimation

E C Stanford, in 1863, introduced two other processes In one, the *char* process, the dried seaweed was distilled in iron retorts, leaving a residue which was extracted for iodine In the second, or *extraction* process, the weed was boiled with sodium carbonate, the pulp filtered and the alginic acid in this precipitated with hydrochloric acid The second filtrate is evaporated to dryness and carbonized, leaving the iodine and potassium salts behind

A good deal of the manufacturing work on seaweeds has been done by Stanford One method introduced by him in 1863 was to carbonise the stems of *Lammaria* in closed retorts, thus making charcoal and collecting the products of destructive distillation A very porous charcoal was produced, containing magnesium carbonate, which proved to be an excellent decolonser and deodoriser this contained all the iodine in the weed, which was extracted by lixiviation, i e, percolation with water This process was in use for a number of years but broke down largely on the question of supplies

The rival processes have been compared by J G King[80] and by W Singleton[81], there is a note also by G M. Dyson[82]

In France, the *Varec,* as it is called along the coast of Brittany, is usually air-dried and burnt in long ditches dug in the sand The ashes are leached and the insoluble portion used by farmers as a fertiliser The liquor is neutralised with sulphuric acid to remove sulphur, and iodine precipitated from the filtrate as cuprous iodide by means of copper sulphate By the De Villers process 80 per cent of the iodine is removed by washing the dry weed with water and precipitated with cuprous iodide

[80] Fuel Research Board Technical Paper, 1924

[81] Industrial Chemist, June 1927, p 267

[82] Chem Age 1926, *15,* 392

It is recorded that 72 tons of iodine were recovered from 180,000 tons of seaweed in 1924, and 50 tons from 125,000 tons of seaweed used in 1925

In the United States during the 1914-18 war large quantities of seaweed were harvested mechanically, pulped and allowed to ferment, producing acetic acid The residue, after extraction of calcium acetate, was worked for potash and iodine

The seaweed industry has experienced three periods of economic prosperity, once when worked for alkali, once for iodine, once for potash, but has, each time, had to give way to superior methods of making its products and ceased to operate There is a hint in the air once more of the industry being resuscitated and winning success, this time because of its organic rather than its inorganic constituents It is at least remarkable and no compliment to the ingenuity of man that a material of which there are many millions of tons produced each year round the coastline of the several nations is allowed to go almost entirely to waste

The discussion of the general nature of seaweeds is not outside the scope of our title, and it is proposed to give some brief consideration to the subject, largely with the hope of giving some stimulation to its future progress

The large fixed algae or seaweeds are confined to a comparatively narrow belt round the coasts not more than a few hundred yards from the shore, where they are distributed in zones The green algae grow on the upper part of the strip between high and low water, generally where a certain amount of fresh water enters the sea The brown algae, mostly *fucoidae,* which constitute the main mass, are likewise inter-tidal They merge at the lower levels into the red algae, which are always submerged by the tide It is these that are the richest sources of iodine

The depth of their growth depends on the amount of illumination, being greatest in such clear warm waters as in the Mediterranean

A universal use of algae is as manure In Britain farmers cart it off accessible beaches after a storm, but transport costs restrict the application to fields near at hand Driftweed is largely collected for the purpose, but where the coast is suitable harvesting the cut weed is also practised The value is probably due to the organic constituents Algae are also used as fodder

The use of seaweeds as food for man goes far back into history, especially in the East They are used on the North and North-West coasts of Europe, in Ireland, Scotland and South Wales, but, except in the East, the total quantity is very small The names laver, dulse, murlins, carrageen suggest the edible kinds

In so large a family there are many variations, the ash, for example, varies from 17 7 to 52 per cent, the protein content calculated on the dry matter is reported as between 29 and 9 3 per cent Some species have no iodine There are a large number of analyses of different species on record[83]

Apparently seaweeds must be harvested at different times of year according to the compound desired The percentage of iodine is greatest at periods of most intensive light, the ash content is some 33 per cent in the spring and only 18 per cent in the autumn

The amount of mannitol is highest in July and August when temperature is high and sunlight plentiful, it is low in the spring after a cold dull winter

The powers which the algae have to extract all the scarcer elements from the sea should give special value to their use as manures , they serve to restore these to the earth This may have significance now that the value of trace elements in the soil is being appreciated

An important seaweed product is agar-agar, which is almost universally used as a basis for bacterial and fungal cultures because of its very convenient liquifying and solidifying properties The production of this has long been a Japanese monopoly, but efforts are now being made in California, New Zealand, Russia and elsewhere

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[83] See T Dillon, Chemistry and Industry 1938, *57*, 616, E C Stanford, J Roy Soc Arts, 1884, *32*, 717, E M Delf, *Ibid,* **1943. *91,*** 505

to find a substitute The difficulty is to make a sufficiently pure product Agar has other uses in connection with foods and medicines

Agar comes from red algae—*Gelidium*—in Japan and E. M Delf[84] has given a list of agar-contaning red algae The freshly-collected algae are bleached in the sun, boiled with water and strained through cloth The clear liquid is poured into shallow troughs to set and the jelly cut into narrow strips When this is done in cold conditions the strips contract, expelling water Agar is a carbohydrate derivative based on galactose, and has many features of interest

The yield from Japanese *Gelidium anansit* is high, as much as 25-35 Per cent The general term agar probably includes many closely related substances

The agar of North America, a war product, is a mixture of the extractives of several seaweeds The weed is dried in the sun and a crude gel extracted by a simple process of boiling and filtering The water and impurities are then removed by freezing Only some 18 per cent of the imports of agar go into media, the rest being used for dental materials, laxatives, emulsifiers, confections, also for meat packing

Efforts are being made in New South Wales to produce no tons of agar per year from *Gracilaria* The seaweed is boiled with live steam in open vats at a pH between 6 5 and 5 The use of iron or copper equipment results in discoloration and a high ash residue This agar is viscous and has a high setting point, qualities which are of no detriment to the food industries, but are a disadvantage for poured plates Organisms, however, grow well on it

In Western Australia a similar agar is made from *Eucheuma Spectosum,* whilst a superior bacteriological agar with low viscosity and setting point has been prepared from *Hypnea Musciformis*

Carrageen or Irish moss grows abundantly on rocky shores all round Britain and provides a continual supply for various commercial purposes it is a red Algae named

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[84] Proc Roy Soc Arts, 1943, *91*, 505

Chrondrus crispus and usually grows together with another species, *Gigartina stellata* It has abundant uses, for ages especially in Ireland it has been in demand as a specific against all sorts of bronchial and intestinal ailments It is a source of jelling substances used in medicines, for textile dressings, in cosmetics and shaving soap and for making agar It has long been the practice of many brewers to use it in very small quantities as a fining agent, so as to induce a good "break'' in the flocculation of wort

At present the methods of preparing it are crude and give the product a very uneven quality It is collected by hand, washed and sun dried for 10-14 days and after another wash dried off and marketed Experiments are in hand as with other seaweeds to provide a continual supply Amongst other details studied are the extent to which plants whose tops have been torn off and collected can regenerate a second crop The rate of growth in relation to environment is of importance, particularly the tidal factor

In the United States firms are now selling a purified extract of carrageen, known as "carrageenin" which is prepared apparently by boiling the seaweed in fresh water for 3-5 hours, filtering off the residue and drying the extractive American uses include it as an agent in the susp as a clarifying agent for beverages and quite widely as a suspending agent

One of the most interesting products is alginic acid This is a carbohydrate, a polymer of mannuronic acid It is either extracted directly from the washed seaweed—*Laminaria* species being the most suitable—by means of sodium carbonate of suitable concentration, or after preliminary treatment of the weed with dilute hydrochloric acid followed by extraction with soda What is sought is a clear solution which can be filtered from impurities The algin in the seaweed is a very large molecule, acid treatment degrades it somewhat, but the molecule is still large The compound is characterised by its high viscosity

The algmic acid is mainly responsible for the tensile strength and elasticity of the seaweed plants, probably because it provides the cell wall with a framework of substance which can be pictured as made up of long chain like molecules joined together by short cross strands every few links As an acid, algmic acid forms calcium salts, and there is evidence that the plants have a protecting outside layer of calcium alginate The continuous swelling of the algae under certain laboratory conditions involves the formation of a soluble alginate, i e , a sodium salt of the acid Some species are found on analysis to contain sufficient minerals to warrant the assumption that the algmic acid in them is present in the form of salts, and not as free acid

Whilst both *Laminaria* and *Fucales* species contain alginic acid, the former is at present regarded as the most satisfactory industrial source The alginate in the *Fucales* would appear to be more stable and perhaps the parallel chains in the molecules have a greater number of cross linkages uniting them The number of cross links may explain some of the remarkable changes in the viscosity of algin as the molecule is simplified

Both the free acid, the sodium and the calcium salts are used and special merits have been claimed for various other salts The algmic acid can be dissolved and spun just like rayon to give a textile for which unusual properties have been claimed, chief among which is resistance to fire due to the calcium unit in the molecule This field of enquiry is likely to be actively investigated after the war—a thread analagous to cellulose, into which metallic or other radicals can be introduced at regular intervals, has all sorts of potentialities

The alginates have other uses. They can be foamed and made into boards which are very light in weight They replace pectms in the making of jams, jellies and cosmetics, in fact anything which is required to set This material, sodium alginate, has the trade name "Manucol" it dissolves in water to form extremely viscous solutions which are tasteless, odourless and almost colourless

Added to milk previous to the manufacture of milk powders it is claimed that the milk can be reconstituted without sedimentation

The chief American use of algm is said to be as a stabilizer in the manufacture of ice cream , 2½ lbs are used to stabilize 300 gallons It serves as a creaming agent in the treatment of latex, in finishing leather, fireproofing wood and camouflage materials, and has a wide variety of uses [85]

Manucol is sold in Britain in two grades differing in viscosity and can be used to replace most imported gums to make emulsions, as a thickener, to form gels or make films and coatings It is competitive in price with these

It is clear that the colloidal properties of alginates may make them of the greatest value in a number of industries, particularly where they behave as "protective" colloids helping to keep particles in suspension or emulsion Pectins are also carbohydrates which are built up from hexuronic acid, but it is not easy to obtain them in any quantity Alginates, on the other hand, could be manufactured in very considerable quantities should their uses justify this

It is only of recent years that the study of the algae, both marine and fresh water, has been seriously undertaken From the chemical point of view a number of interesting carbohydrate derivatives replace the cellulose of green plants in them and they have peculiar pigments and sterols As they are mostly unicellular and therefore primitive forms of life these organic compounds may also be regarded as primitive forms **I M Heilbron** has described **the lipoid pigments and** sterols of 7 of the 11 classes into which the botanists divide the algae, **including the *Phaeophyceae* and** *Rhodophyllae,* which are mostly marine [86]

If the seaweeds are to have a commercial future a careful study will have to be made of the methods of

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[85] Chemistry and Industry **1944, 79**

[86] J Chem Soc 1942, 79

collecting and harvesting them The renewed interest taken in them under war conditions may well continue in peaceti is beginning of the distribution of marine algae, their properties, improved methods of extraction and new applications for their use in the food, drug and technical industries

It has recently been announced that a Government-aided research organisation is ready to begin work to determine whether Scottish seaweed resources are sufficient to build up a substantial Scottish industry in the extraction and use of seaweed chemicals

A few notes regarding the methods of harvesting will be found of interest There is a belief that supplies are inexhaustible, but this is probably ill-founded, and it is more likely that like land crops they are subject to serious fluctuations unless proper precautions are taken[87]

In places where the utilisation of seaweed has been long an industry of local importance as on the coasts of Brittany, harvesting seaweed has been subject to strict regulation The *Fucus* farms of Northern Ireland which grow weed for manuring the fields use sheltered bays where, at low water, there is a flat stretch of sand strewn with stones of several sizes The species of algae varies with the position in regard to the tidal range

In Japan close supervision and vigilance are practiced If beds of *Laminaria* are harvested too often they become overgrown with a rapidly spreading flowering plant which must be cleared by hand Farms for the cultivation of *Fucus* and of *Porphyra* have been established[88]

In the U S A kelp is harvested on the Atlantic Coast with a grapple hauled at a depth of 12 to 15 feet from a power boat and to a lesser extent by hand dragging or sickling from a dory The season extends from June to December On the Pacific Coast the kelp is mowed by giant harvesters cutting 3 to 4 feet below the surface and carrying as much as 300 tons in a single load A sustained yield is obtained by selection of the beds and

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[87] **E M Delf, Nature 1944, *153*, 223**

[88] **K Yendo, Proc Roy Soc Bot , Dublin, 1914, *2*, 105**

gathering takes place in calm weather throughout the year

Agar weed is collected on the Atlantic Coast by divers who work in a complete suit, crawling over the rocks on their knees and pulling the weed off by hand In Australia the seaweed *(Gracilaria)* is harvested by special grapnels, or in very shallow water by hand This species is found for a distance of 850 miles along the coasts of New South Wales and Queensland and grows in shallow flats in lagoons, estuaries and bays where conditions are favourable There is a seasonable rhythm in its abundance[89]

Carrageen is fairly abundant in the cooler waters along the rocky shores of Massachussets, Maine and Eastern Canada It grows at moderate depths and is gathered with lead weighted rakes some 15-20 feet long from dories A man can rake some 400 Ib of the wet moss a day

Little is understood about the large deposits of driftweed which occur from time to time

Plant growth must be related to the presence of nitrates and phosphates, which have been shown in Chapter 3, to undergo seasonable variations *Laminaria* flourish in quantity on submerged reefs away from human habitation, they will be sensitive to new factors such as sewage or oil films The cumulative effect on our Northern Atlantic coasts of the removal periodically of many thousands of tons of seaweed is quite unknown

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[89] E J F Wood and V M Jones, Nature 1944, *154,* 262

CHAPTER 8

POTASSIUM SALTS

Potassium, the element, is associated with the name of Davy, who obtained it by electrolysis of the fused hydroxide in 1808 , potassium as hydroxide from wood ashes is probably the earliest known source of alkali, potassium nitrate or saltpetre for explosives was first mentioned in the eighth century, the method of Agncola for extracting it in 1546 does not materially differ from the present process , potassium chloride as an important artificial fertiliser was the basis of the great Stassfurt salt industry

Before the 1914-18 war the production of potassium salts was a German monopoly The war showed the evil of this and production was developed in America and in Russia from salt deposits, as well as in small quantities from all kinds of raw materials The Alsace deposits were discovered in 1904 and only partially developed by the Germans When they came into French hands they became an important source In 1930 the development of the potash and other salts in the Dead Sea began under British influence

The treaty of Versailles gave the Alsatian Potash deposits to France and those in Galicia to Poland In 1924 Germany and France came together and agreed to share the American market The world search for potash led to its being found in Spain, Russia, Palestine and the United States The Potash Cartel was extended to cover Poland in 1932, Spain in 1935 and, later, made an agreement with Russia and with Palestine In 1938, 3 J million tons of potash (K_2O) were sold When war came the cartel controlled 80 per cent or, according to Bergmann, 85 2 per cent, of the entire output of the world, of this 20 per cent came from deposits largely developed since 1918

In the period 1921-39 the American production of potash increased thirty-fold from 10,000 tons to 300,000 tons At first natural brines were the major source, then came the development of the New Mexico potash beds, which now give two-thirds of the total In 1939 the U S A supplied half its own requirements the production is still increasing both at Searles Lake and in New Mexico The Palestine production may have 'reached 80,000 tons in 1940, expressed as 50 per cent potassium chloride, and has certainly further increased

During this war the Dead Sea deposits have no doubt been largely developed and have a great future The working of the American and Russian deposits has probably been similarly extended

Before giving any more detailed description of the deposits it is worth while referring to the possibilities of winning potash salts direct from the sea, where the percentage expressed as potassium amounts to o 037 per cent and as potassium chloride to o 072 per cent Potassium sulphate is considered to be better as a fertiliser than the chloride, while magnesium chloride in the free state is injurious to vegetable life Hence Kamite ($KC1, MgS0_4, 3H_2O$) and Schoemte (K_2SO , MgSO., $6H_2O$) are most usually employed as manures, but low-grade potassium chloride is also largely sold

If a cheap process based at first on solar evaporation can be worked out, whereby the presence of magnesium chloride can be largely avoided, there should be a wide use for low priced potash fertilisers, for example, in Australia, which is remote from the present sources of production Fertilisers are bulky and must be cheap, consequently they will not bear heavy transport charges

From this point of view the Niccoh process requires fuller investigation The original patents covering this process were taken out in 1925 and 1926[90] Sea

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[90] French Patent 594,903 British Patents 247, 405 and 261, 991

water is evaporated in pans by solar heat It is first evaporated to a specific gravity of 1 25 , during the evaporation most of the sodium chloride precipitates out Further evaporation to specific gravity 1 31 deposits other unimportant salts The liquor is then decanted to another pan, where it evaporates to specific gravity 1 345 —1 36 A mixture of sodium, potassium, and magnesium salts is here deposited

This mixture, known as mellakite, varies somewhat in composition but it is approximately as follows potassium chloride 18-21 per cent, sodium chloride 17-22 per cent, magnesium sulphate 29-33 per cent, and magnesium chloride 2-4 per cent The mellakite is usually left on the ground in heaps for two or three months, after which it is ground and washed with sea water at a suitable concentration and temperature Crude schoenite (K_2S0_4 $MgS0_4$, 6H2O) is produced which, when freed from water in a centrifuge, gives a product containing about 38 per cent potassium sulphate and 1 per cent only of potassium chonde After treatment in a dehydrator at I70 ^{0}C the water of crystallisation is lost, the product being " Niccoh potash salt " with 50 per cent of potassium sulphate This material closely resembles the German potash fertiliser " Kali-magnesia," which has been widely used for a long time it contains rather more magnesium sulphate

A third stage of the Niccoh process involves the solution of the schoenite before dehydration in a large volume of fresh water From this magnesia and any calcium sulphate present are precipitated by milk of lime After filtration and evaporation a potassium sulphate product of 95 or 96 per cent purity can be recovered This stage is only of limited interest as at the places where the Niccoh process is worked no supplies of fresh water are available

For the complete economic success of the process special climatic conditions are required At Massawa, in Eritrea, for example where the erection of a plant was begun in 1933 in conjunction with the salt works already established there by the Societa Italiana Saline Entree, the liquors were circulated by gravity and all the evaporation carried out by solar heat It is said that the process might be operated on the Atlantic coast of Columbia but not in the United States

The process was tried out experimentally near Naples and the larger plant completed in 1936[91] The installation was intended to deal with the whole of the mother liquors from the salt extraction works and to have an annual production capacity of between 15,000 and 20,000 quintals of the double potassium magnesium sulphate It was hoped to make Italy independent of imported supplies by extending the process

It is evident that if potash salts are to be separated from the enormously larger quantities of sodium compounds present in sea water, it is desirable to find a reagent which reacts selectively to precipitate an insoluble potassium compound while leaving the sodium salts in solution Such a reagent exists, namely, dipicrylamine or hexamtrodiphenylamine, which gives an insoluble orange red potassium compound in a slightly alkaline solution It was first proposed by Polucktoo[92] as an analytical reagent for the detection of potassium when present in small quantities

The use of dipicrylamine[93] has now been applied to the recovery of potash from sea water and a patent[94] has been taken out by the Norsk Hydro Elektnsk Company[96] All the metals, except potassium, present in sea water form soluble compounds with the reagent In the application of the process one of the soluble salts of dipicrylamine, preferably the calcium compound, although the sodium, magnesium, or lithium silts may be used, in slightly alkaline solution, is added to sea water or other saline solution in quantity a little below that theoretically required to react with all the potassium present The insoluble potassium salt is precipitated, filtered off and

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[91] La Chim e l'Ind 1936, *18,* 557

[92] Microchemie 1934, *14,* 265

[93] These particulars are condensed from an account in the Bulletin of the Imperial Institute tl940, *38,* 109)

[94] B P 22, 025

[95] Chem Tr J 1940, *106,* 241

washed The filtrate is acidified in order to precipitate any unused reagent, which is recovered

The insoluble potassium dipicrylammate is treated with an acid, preferably nitric acid, giving a solution of potassium nitrate and precipitating the dipicrylamme, which is recovered for re-use Sulphuric, hydrochloric or acetic acids can also be used, while by the employment of carbon dioxide under pressure, potassium carbonate can be obtained

An experimental plant is stated to have been erected at the Heroya works of the Norsk Hydro Elektnsk Company

The following is an example of a process for the production of 5,000 tons of potassium per annum 1750 cu metres (approx 8,000,000 gs) of sea water containing 0 43 Kg of K_2O/cu m (0 356 gm K/Litre) is pumped into a tank and treated with 50 cu metres (225,000 gs) of a solution of the calcium salt of dipicrylamme (containing about 5 6 tons of dipicrylamme) 75 per cent of the potassium is precipitated at the rate of 0 57 tons K_20 per hour

The preparation of the dipicrylamme reagent is carried out HI two main stages In the first place, aniline and aniline hydrochloride in equi-molecular proportions are heated in an autoclave, forming diphenylamine The product is boiled with dilute hydrochloric acid, which removes the unchanged aniline and leaves the diphenylamine as the free base, which is separated and purified by distillation

Dipicrylamme is hexamtrodiphenylamine

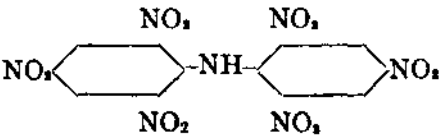

PLATE XVI. DEAD SEA. HAND HARVESTING CARNALLITE.
(Courtesy of Palestine Potash Ltd.).

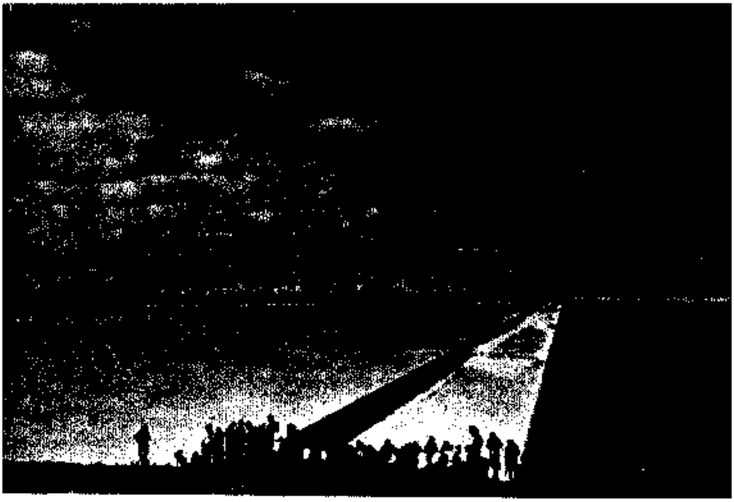

PLATE XVII. CARNALLITE PANS -SOUTH END OF DEAD SEA.
(Courtesy of Palestine Potash Ltd.).

The use of such organic reagents is growing more general and if the recovery of the reagent for each operation is high, a process of this type has possibilities At the present time the price in Britain is very high, since it is only made on a small scale as a laboratory reagent On a commercial scale the cost would undoubtedly be much less, and since the reagent is to a very large extent recovered and used again, a continuous heavy expenditure for its replacement would not be necessary

In 1937 it was reported that Japan had discovered a process for making potassium sulphate from bitterns by treating them with aluminium sulphate, which can be recovered and used again

The outlook for making potassium compounds direct from sea water appears to be hopeful in spite of the enormous quantities available in the Dead Sea and elsewhere In a scientifically organised state monies derived from the profits made on the deposits should be utilised to work out the newer processes based on solar evaporation so as to avoid for all time the repetition of monopolies

Previous to the working of the Stassfurt deposits the chief source of potash was kelp—that is the ashes of sea weed These were produced on the coasts of Scotland and Normandy as described in a previous chapter During the great shortage of potassium salts in 1914-18, a large plant was installed in California, primarily for the purpose of making acetone with potassium chloride and iodine as by-products[96] The seaweed was cut by a Harvester boat, chopped up and loaded into barges, from which the material was transferred to vats, where it fermented for 18-25 days, forming acetic acid The mass was boiled with lime, filtered and concentrated by evaporation in a vacuum Potassium chloride of high quality crystallised out at various stages

The war conditions prevented any full disclosure of essential manufactures in allied countries In consequence we are restricted in regard to describing the Dead Sea operations of the Palestine Potash Company, and still

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[96] Chem Met Eng 1918, *18*, 11

more in regard to Russian deposits The Stassfurt deposits and their technical working have been already the subject of many books, so that a brief description will suffice

In past geological times a large area of the sea has evaporated over Central Europe, leaving salt deposits under France, Central Germany and Poland, which originally joined one another Most of these deposits, as elsewhere in the world, consist of anhydrite and salt only but, exceptionally, in two localities, Stassfurt and Alsace, the mother liquors remained to dry up Under England, in Cheshire and Durham, we have large areas of salt only—perhaps the new technique of geophysical exploration will be able to detect potassium salts in some corner of the salt area

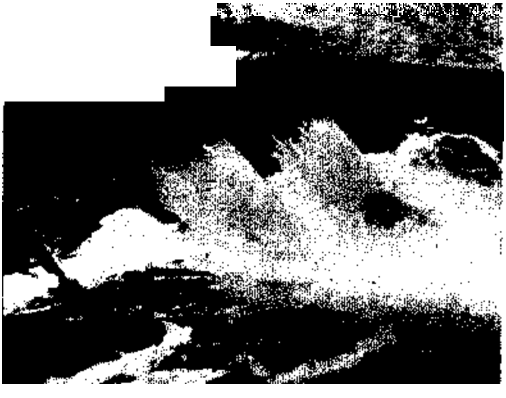
The course of events which led to the Stassfurt deposits is pictured somewhat as follows The influx of water was intermittent and there were several geological elevations and depressions The basin or valley communicated at one end with the ocean over a shallow bar, over which, in autumn, gales and high tides carried large quantities of water There was steady evaporation during most of the year

For a long period only gypsum was deposited, then came common salt as well and the gypsum was converted to anhydrite Later the concentration increased and the yearly crusts of salt became thicker For some thousands of years, each year was marked by a thin string of anhydrite, deposited when the strong brine first came in contact with fresh sea water, followed by a few inches of salt

As concentration increased the salt deposited was mixed with magnesium sulphates and later, for a short period of 500 years, the deposit was mainly potassium and magnesium sulphates in the form of double salts During the last period of perhaps another 500 years the remaining mixed potassium and magnesium chlorides, i e , carnallite, were deposited Finally a mass of clayey mud formed a layer over the whole and protected the strata from being redissolved

PLATE XVIII. Above: EXPERIMENTAL PANS—SOUTH END OF DEAD SEA.
(Courtesy of Palestine Potash Ltd.).

Below: LARGE PIPES FOR DELIVERY OF DEAD SEA WATER
(Courtesy of Palestine Potash Ltd.).



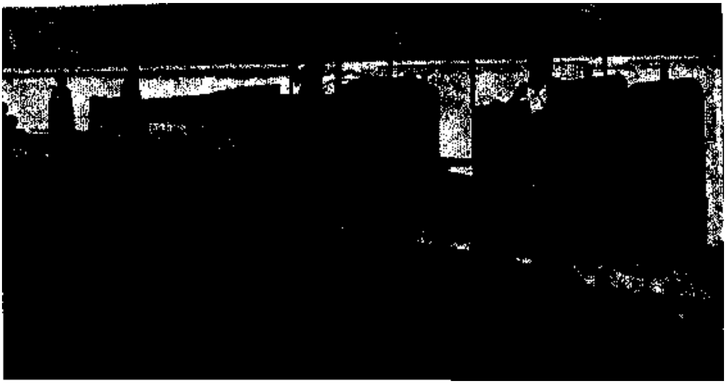


PLATE XIX. *Above*: TRANSPORTING CARNALLITE FROM PANS TO FACTORY

(Courtesy of Palestine Potash Ltd.)

Below. EVAPORATING PANS.

(Courtesy of Palestine Potash Ltd.)

The four Stassfurt regions are —

I	Anhydrite		$CaSO_4$
2	Salt	91%	$NaCl$
	Polyhahte	7%	$CaS0_4$, $MgSO_4$, K_2SO_4
3	Salt	65%	
	Kiesente	17%	$MgS0_4\ H_20$
	Carnailite	13%	
4	Carnailite	53%	$KC1$, $MgC1_2$, $6H_20$

The total thickness of the salt strata is estimated at 2500 feet and the time necessary for their formation at some 8,000 years

The Stassfurt brine springs are mentioned as far back as 1227, and salt was mined there throughout the 18th century In 1843 salt was struck at a depth of 850 feet and the boring was continued for another 1080 feet, without getting out of the salt The brine pumped up was exceedingly impure and it was some time before its value was realised—by Dr A Franck in 1860 Only the rock salt and the carnallite regions are of technical importance

The main product is potassium chloride, the by-products are kieserite ($MgSO_4$, H_20), Glauber's salt (Na_2S0_4, $10H_20$), magnesium chloride and bromine Large quantities of potassic manures are made particularly from kamite by grinding, calcining and effecting a proper mixture with the guaranteed content of K_20 Potassium sulphate is better for this purpose than the chloride

The Alsace deposits near Mulhouse were first discovered in 1904 They have been described by Kestner[97] and consist of 2 beds, the lower with an average thickness of 4 metres and potash (K_20) content of 30-35 per cent, whilst the upper, which is not so thick, has 22-25 per cent potash They are more recent geologically than the Stassfurt beds, and the borings are deep, which entails a high working temperature The mineral is mainly sylvimte ($KC1$, $NaCl$) with a little calcium sulphate

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[97] J Soc Chem Ind 1918, *37*, 409 R

and no magnesium salts, so that the preparation of potassium chloride from it is simple The crushed potash salts are fed direct into a tank containing hot saturated sodium chloride solution This dissolves potassium chloride, which has a greater solubility hot than cold, whereas the solubility of sodium chloride does not alter with temperature The clear filtered solution is run to crystallising tanks where the potassium chloride crystallises out on the sides, the solution is pumped round to be reheated and used again

Enormous deposits of carnallite and sylvmite have been discovered in Russia at Solikamsk on the western slope of the Urals An area of over 700 square miles has been explored by deep boring and it is said that the reserves there amount to 80 per cent of the world's resources Even those at Stassfurt are dwarfed in comparison Production was started in 1932 , by 1937 as much as 2 million tons of crude salts had been produced The reserves of potassium are at least 15 million tons, of magnesium 18 million tons, together with many million tons of rock salt

Whereas the Germans had a monopoly of potash in 1914, their production in 1922 was some 700,000 tons as potash (K_2O), compared with 200,000 tons from Alsace In 1935 Germany and France between them made 77 per cent of the world's production, as against 8 per cent by America According to Bergmann, 85 2 per cent of the world production was in Axis hands in 1940 Hence the political and strategical importance of the Dead Sea

The work of the Palestine Potash Company has been described by Novomeysky[98] and by E Bergmann [99]

The Dead Sea is 47 miles long and has an average breadth of about 9 miles Its surface is 1300 feet below that of the Mediterranean and its maxium depth is about 1300 feet Lying as it does in a great depression it has no outlet The river Jordan discharges into it some 1,400 million gallons of water daily This represents

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[98] **Trans Inst Chem Eng 1936, *14*, 60**
[99] **Advancement of Science, 1942, *2*, 225**

about three-quarters of the total inflow which is made up by smaller rivers and streams and also by subterranean springs The hot dry climate favours evaporation, which is about two and half times that on the neighbouring Mediterranean shores Geologists estimate that the present Dead Sea and the Sea of Galilee are what remains of a very much bigger inland sea that was some 190 miles long with four or five times the present volume of the Dead Sea and filled the entire Jordan valley The Dead Sea absorbs 630 calories of heat per square centimetre per 12 hours This means that the water temperature is greatly above the air temperature, and this greatly favours evaporation One observation records a water temperature of 62 °C when the air temperature was 37°C The specific gravity varies between 1 15 and 1 24 with the depth and the time of year

The total salts in the Dead Sea vary between 23 and 33 per cent, with an average of about 30 per cent compared with from 3 3 per cent to 3 7 per cent in the Atlantic Ocean The absolute salt concentration increases with the depth, but the ratio of the various salts remains constant

The salt concentration must also be increasing with time as the Jordan and its tributaries bring in 40,000 tons per annum of potassium chloride alone

The total content of the Dead Sea is approximately —

TABLE 21

Potassium Chloride	KC1	2	x 10^9	tons (metric)
Sodium Chloride	NaCl	n 9	X 10^9	„
Calcium Chloride	$CaCl_2$	6	X 10^9	,,
Magnesium Chloride	$MgCl_2$	22	X 10^9	,,
Magnesium Bromide	$MgBr_2$	0 98	x 10^9	,,
Total Magnesium	Mg	5 8	x 10^9	tons
Total Bromine	Br	0 85	x 10^9	„
Total Potassium	K	1 05	x 10^9	„

The differences in the ratio of the salts from that in ocean water cannot entirely be explained in geochemical terms It has been calculated that if all the salts present have been carried by the Jordan and other rivers it would have taken some n thousand years to supply the sodium and calcium, but 50 to 60 thousand years to supply the potassium and magnesium Perhaps a certain and variable part in the history is played by the hot springs which discharge into the bottom of the Sea of Galilee As elsewhere noted, all the bromine is derived from these

The first laboratory experiments on the production of chemicals from the Dead Sea were begun in 1911 It was then shown that 90 per cent of the sodium chloride, over 80 per cent of the potassium chloride, and much of the magnesium chloride could be recovered by evaporation and fractional crystallization In 1921 concentration experiments were begun using shallow evaporating pans and in 1925 these were made on a very much more extensive scale, when a pump and three small concentrating tanks were erected on the northern shore of the lake All concentration was carried out by solar evaporation

The technicians of Palestine Potash, Ltd have successfully applied a new method for the acceleration of solar evaporation by adding certain dyes to the evaporating brine, which absorb a greater proportion of the heat rays of the sun

In the first tank the brine was allowed to concentrate from a specific gravity of about 1 15 to 1 29 During this stage over 90 per cent of the sodium chloride settled out In the second pan the brine was concentrated from specific gravity 1 29 to 1 33 Here the remainder of the sodium chloride was precipitated and potassium chloride and magnesium chloride came out in the form of carnalhte ($KC1$ $MgCl_2$ $6H_20$) In the third pan the specific gravity was raised to 1 37 and magnesium chloride crystallised out In later work stage 2 was sub-divided into two parts in order to get a purer carnalhte

In 1930 Palestine Potash, Ltd began to construct a commercial scale plant to produce potash and bromine A year later the first bromine producing plant was in operation In February, 1932 the first few hundred tons of potassium chloride were despatched By the end of 1932 the plant was working at the rate of 10,000 tons of potassium chloride and 250 tons of bromine per annum, and in 1936 at the rate of 25,000—30,000 tons of potassium chloride and 1000—1,200 tons of bromine per annum.

The plant has since been enlarged and now the flat land at both the northern and southern ends of the sea is in use for concentrating At the north end the water is pumped up from a depth of 175 feet (the concentration of bromine and potash being twice as much at this depth as on the surface) through a steel pipe line of 30 inches diameter and with a capacity of over half a million gallons per hour According to the official description of the process " The pans are separated from one another by wooden dams filled with earth The bottoms of the pans have been left in their natural condition to receive the sea water as the impermeability of the soil forming the floor of the pans has proved satisfactory The system of pans is so arranged as to allow a constant slow movement of the brines from one pan into another in a zig-zag, downward flow along the slope falling towards the Dead Sea The pans are provided with sluices permitting regulation of the flow or the temporary shutting off of any of the pans when needed In the course of such tardy flow the sea brine becomes more and more concentrated Common salt is the first salt to be deposited in the pans " At the end of November or early in December, when the evaporation season is at an end, fresh water from the Jordan is directed into these pans to dissolve away the unwanted common salt

The liquor then passes to the carnallite pans, where it is further concentrated in two stages The carnallite is collected mechanically by floating suction dredges as soon as 3-4 inches have been deposited and conveyed to field mixers in the refinery and mixed up with water (½-ton water to 1 ton carnallite) This washes out much of the more soluble magnesium chloride Thus a carnallite containing—

Potassium Chloride	22 23 per cent
Sodium Chloride	8 96 per cent
Magnesium Chloride	29 59 per cent

after treatment for 1½ hours with water at 15°C gives an artificial sylvinite (a mixture of sodium and potassium chlorides) with the composition —

50 38 per cent	Potassium Chloride
20 75 per cent	Sodium Chloride
7 65 per cent	Magnesium Chloride

The sylvinite is filtered off on rotary filters The mother liquor goes back to the carnallite pans and the sylvinite then goes to settling tanks, where it is purified by washing with cold water to give a high-grade potassium chloride The mother liquors from this stage are returned to the sodium chloride pans

The brine left after carnallite separation or final brine contains the entire bromide in a concentrated form, which is conveyed by pumping to the bromine factory, where liquid bromine of very high purity is extracted from the bromide in a continuous process involving treatment with chlorine gas and steam Another portion of the final brine is left to concentrate further in pans until a specific gravity of 1 37 is reached during the hottest part of the summer At this point crystals of magnesium chloride separate out

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further treated for the market The remaining brine contains all the calcium chloride which can also be extracted by a fairly simple method

This process sounds simple, but in practice, as with the Searles Lake brines, the process depends essentially on an ingenious use of the solid-liquid equilibria of the salts concerned and requires constant vigilance and strict control

PLATE XX. THE PANS.

(Courtesy of Palestine Potash Ltd.

The mines in New Mexico are at Carlsbad, 170 miles north of El Paso They contain potassium chloride ores with 16-26 per cent K_2O which are easily refined The mines are of relatively recent development At first America only produced potassium chloride in quantity The production of potassium sulphate began in 1939

Searles Lake is situated in the Mohave desert in California, about 185 miles north-east of Los Angeles in a valley about 25 miles long and 10 miles wide It and the other salt lakes in the district are all that remains of an ancient sea, which has since been cut off from the ocean by the throwing up of a range of mountains It is about 1,600 feet above sea level It has a surface area of about twelve square miles and is now almost dry, consisting of a mass of crystals with brine standing about 6 inches above crystal level in winter and about 6 inches below in summer The surface is so hard that a car can be driven over it in safety The crystals extend to a depth of about 50 to 75 feet, below which is mud The lake is surrounded by about 100 square miles of mud flats and is all that remains of a lake once nearly 40 times the area and 20 times the depth Searles Lake now contains mineral constitutents from the neighbouring Owens Lake which used to overflow into Searles Lake until evaporation lowered its level The annual rainfall is only between 3 and 7 inches and no surface rivers flow into the lake, though it is fed by underground rivers

The lake was first worked in the 1870's for borax by several groups of miners headed by J W Searles, who is reputed to be the discoverer of borax there Borax working ceased in 1895 as it was then being produced by other and cheaper methods After commercial vicissitudes a plant to make potassium chloride was put in -operation in 1916 and has worked ever since, being re-erected in 1925-27 In 1919 the manufacture of borax was begun again In 1933 plants were erected by the American Potash and Chemical Corporation, to make sodium sulphate and carbonate, and at the present time potassium sulphate, sodium bromide, bromine, and crude lithium salts are also produced Another company, the West End Chemical Company, also works the Searles Lake brines, producing soda ash and borax.

The solid matter in the lake is almost entirely composed of the following six crystalline salts —

Common salt	$NaCl$
Trona	$Na_2C0_3, NaHCO_3, 2H_2O$
Hanksite	$9Na_2S0_4, 2Na_2C0_3, KC1$
Borax (Tincal)	$Na_2B_4O7, 10H_2O$
Glasente	$3K_2SO_4, Na_2SO_4$
Sulphohahte	$2Na_2S0_4, NaCl, NaF$

The top 15 to 20 feet is composed very nearly completely of sodium chloride, but below that the salts are mixed in a very erratic manner and the composition vanes greatly at different places The brine has a more uniform composition but contains more sodium chloride near the surface than at greater depths

TABLE 22

A typical analysis of the brine, which has a specific gravity of 1 30 and a pH of 9 48, is as follows —

		Per cent
Total potassium	as $KC1$	470
Remaining chlorine	as $NaCl$	1635
Total carbonate	as Na_2C0_3	470
Total sulphate	as Na_2S0_4	696
Total borate	as $Na_2B_4O_7$	150
Total phosphate	as Na_3PO_4	0 16
Total fluorine	as NaF	0 01
Other salts		030
		3468
Water		65 32

It is remarkable that there is no magnesium and only infinitesimal amounts of calcium in the lake, although both are present in the mud under the lake

The problem of obtaining specific salts from such a complex mixture is primarily one of determining the solubilities of every salt in the presence of many other salts These solubilities have been worked out by following the principles of the phase rule and by plottmg equilibrium diagrams[100]

With such a highly complicated system it is obvious that to describe the steps by which the various constituents of the brine are separated would take a large book The reader is referred to Teeple's monograph and to articles by R. W Mumford[101] and G Ross Robertson[102] for descriptions of the processes worked by the American Potash and Chemical Corporation The separation of the potash and soda salts and the borax is essentially done by careful adjustments of temperature, pressure, and concentration, and by the mixing of various liquors, but no raw materials are used other than those present

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be said to begin with the raw brine which is pumped from wells in the crystal body of the lake The brine is used as a cooling material in various condensers and for washing various filter cakes before it enters the process proper, where it is mixed with various mother liquors The raw material is first concentrated at a high temperature This results in the crystallization of common salt and of burkeite, a double salt of sodium sulphate and sodium carbonate, (Na_2CO_3, $2N_2,SO_4$) The common salt crystallises as coarse crystals, but the burkeite crystallises in very fine crystals and is washed away with the mother liquor before settlement, by this means the common salt is removed The burkeite is then

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[100] The reader who is interested is referred to Dr John E Teeple's monograph in the American Chemical Society series, in which many of the equilibrium diagrams are given

[101] Ind Eng Chem 838. *30,* 872

[102] *Ibid,* 1942. *34,* 133

dissolved in distilled water to give a saturated solution at 27°C On cooling this to 22°C much of the sodium sulphate is precipitated as the decahydrate, Glauber's salt The mother liquor is heated to 70°C and treated with sodium chloride containing much burkeite and a little sodium carbonate (a mixture formed at another stage in the process) More of the sodium sulphate is removed as burkeite and cooling the resulting liquor from 30°C to 5°C (using a liquid ammonia cooler) results in the precipitation of washing soda, ($Na_2CO_2^{-}$ $10H_2O$)

The hot brine after the sodium salts have been removed is essentially a saturated solution of potassium chloride which is precipitated by cooling rapidly in vacuum coolers down to about 40°C Rapid cooling is essential in order to stop precipitation of the borax with which the liquor is super-saturated The borax is obtained by further cooling the liquor to about 20°C , again using liquid ammonia for cooling The crude borax is then refined and bone acid is also made from it

Potassium sulphate is obtained by treating potassium chloride with burkeite which gives the relatively insoluble double salt glasente, $3K_2SO_4$, Na_2SO_4 Treatment of the glasente with more potassium chloride then gives potassium sulphate and sodium chloride The production of potassium sulphate is important because this salt is preferred by many people, particularly citrus and tobacco growers, as a fertilizer, to potassium chloride

The sodium carbonate and the sodium sulphate produced at Searles Lake are largely used locally, the latter chiefly in crude form by sulphate paper milk The potassium chloride is used on a national scale, the output in 1938 being about 40 per cent of the total U S production The total production of all chemicals at the Trona plant in that year was at the rate of about 400,000 tons per annum

The production of bromine from the Searles Lake brines has already been discussed in chapter 5

LITHIUM

Lithium in the form of **a** crude phosphate was first recovered from the Searles Lake brines in 1938 It has been stated that Searles Lake now supplies the raw material for half the total world production of lithium salts, the pnncipal uses for which are for alkahne storage batteries, in air conditioning and in medicinal products Lithium metal is a very efficient scavenger , at least one major electric railway in the U S A uses high purity copper and high strength bronze which have been deoxidized with metallic lithium Lubricating greases, based on lithium stearate, which have many new, unexpected and potentially important features have been developed by the Foote Mineral Company

Not least among the problems of Searles Lake is that provided by its geographical position It is situated nearly in the middle of an area of 5,000 square miles containing no other town or village and the population of 2,200 are therefore all connected with the company either directly or indirectly The company owns not only the plant but the town, the roads, the railway, the school, the swimming pool, the public utility services, the hospital, and the gaol

The Searles Lake brines produce nearly half of the world's total production of borax, and most of the remainder is obtained from ores only 60 miles away

BORAX

The West End Chemical Company extracts borax from Searles Lake by a rather different process to that described above Sodium bicarbonate is precipitated by treating the brine with carbon dioxide, obtained by calcining limestone The bicarbonate is filtered off and the filtrate is mixed with approximately an equal quantity of untreated brine This converts the more acid borates in the brine to the tetraborate ($Na_2B_4O_2$), with which the liquor is now supersaturated The solution is sprayed into open air cooling ponds where the sodium borate crystallizes This is thickened in Dorr thickeners and filtered and used to produce both the anhydrous salt and the decahydrate, borax

Another salt lake worked for soda ash and borax is Owens Lake Unlike the semi-sohd Searles Lake, this is an alkaline water lake, into which flows the Owens River The river is however often diverted to supply water to Los Angeles and this causes a variation in the salt content which interferes with satisfactory working The Pacific Alkali Company has a plant at Owens Lake at which soda ash and borax are recovered by a process similar to that of the West End Chemical Company The brine is concentrated and then carbonated with carbon dioxide made by calcining dolomite Sodium carbonate is precipitated and removed by filtration and the mother liquor is chilled to precipitate borax, which is filtered off on an Oliver rotatory filter The crude borax is then recrystallized[103]

The total production of borax in the United States rose from about a hundred thousand tons in 1924 to over double that figure in 1934

The chief uses for borax are in the production of glass and enamels, as a flux in soldering and as a mordant in the textile and tanning industries It is used as a disinfectant and preservative and has many other minor uses Boric acid is largely used as a preservative and in medicinal preparations

COURSE OF EVAPORATION

In order to understand the presence of pockets of particular salts in oceanic deposits it is necessary to make some study, necessarily limited here, of the course of evaporation

Such studies were begun some 45 years ago by Van't Hoff and his pupils with the explanation of the various deposits at Stassfurt as the ultimate objective They involve determinations of solubility, etc of salts taken first one, then two, and finally three or more at a time,

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[103] See P D V Manning, Chem Met Eng 1941,45,96

having regard to the new salts which are formed by their interaction This work of Van't Hoff has formed a model for all subsequent work on these questions

It is before all things essential to bear in mind in the first place that a solution can only be spoken of as saturated with a given substance or mineral when the substance is present in the solid state in contact with the solution A solution, for example, is not saturated with magnesium sulphate but with the particular hydrate which can remain in contact with it at a particular concentration In general, as the amount of water grows less, a hydrate containing fewer molecules of water will be the substance with which the solution is saturated

The branch of physical chemistry known as the phase rule is but an expression of the fact that in the case of solutions in volatile solvents, equilibrium—that is saturation—is attained at a particular pressure at a particular temperature and *vice versa* when *n* substances are present n + I states or phases separable as such, each such state being technically a phase A phase is not a radical of a salt The real difficulty that occurs in practice is to know what are the possible phases—in other words, to determine the nature of the single salts, distinct hydrates or double salts that may be formed

As an example, the critical temperature for sodium sulphate is 32 65°C , below that temperature only the decahydrate can exist, above it only the monohydrate crystallises When a solution is saturated with two salts whose basic and acidic radicals are different and which therefore can interact, as for example, potassium chloride and magnesium sulphate, the problem is more complicated At temperatures about 25 ^{0}C seven substances in all may be formed, viz , $KC1$, K_2SO_4, $MgCl_2 6H_2O$, $MgS0_4 7H_2 0$, $MgS0_4 6H.O$, Schoemte K_2SO_4, $MgS0_4 6H_2O$ and Carnalhte $MgCl_2 KCl\ 6H_2 0$

In practice, however, K_2SO_4 and $MgSO_4$ cannot exist together but always form the double salt schoemte, and

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As the result of the determination by experiment of the constitution of saturated solutions of the seven first-named salts, taken one at a time, then two at a time and, lastly, three at a time, in all 16 measurements, diagrams can be drawn on which every solution is[4] represented During each determination the solution must be stirred with solid crystals of all the salts with which it is saturated.

From this diagram it is possible to predict the order of deposition of the salts from a solution of any particular composition[104]

It is possible as a solution is continuously evaporated for the salt which is first deposited, e g , K_2SO_4, if not removed, to be dissolved again and deposited as the double salt schoenite At a later stage KC1 comes down as welt as schoenite, which last salt is next replaced

A chemist wishing to isolate particular salts from the mixtures he encounters must prepare his own solubility diagrams at the temperatures chosen and carry out his evaporations accordingly he can remove deposited salts or let them re-dissolve again to make something else

When a sea evaporates undisturbed the salts at first deposited are not removed and the pockets of salts which are found represent the salts, perhaps several of them, appropriate to the particular composition of the solution More often the evaporation is disturbed, fresh water finds access to the deposits, a solution of quite different composition arises and this, in turn, evaporates again to deposit another group of salts

It will be seen how complex the problem is and how it is possible for the chemist, having worked out his solubility diagram in the laboratory beforehand, to exercise his ingenuity to simplify it This has been accomplished at the Dead Sea, Searles Lake and elsewhere

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[104] For further details see £ F Armstrong, British Association Reports Glasgow 1901

CHAPTER 9

POTABLE WATER FROM SEA WATER

The question of obtaining fresh water on lifeboats has become of real importance in war and its solution in a practical form, if that were possible, is much to be desired A good deal of work has been done on the problem which it is proposed to summarise here it is far more difficult than the lay press and the public suppose and certainly not to be solved by adding tablets of undisclosed composition to sea water

Compared with drinking water, from which it is often the practice to remove the hardness by chemical treatment to render it more suitable for a wide variety of purposes, sea water is quite a strong solution The concentration of salts is about 35 parts per thousand parts, of which some 80 per cent is common salt This compares with a concentration of about 9 parts per thousand for the saline fluids of the body and is perhaps one hundred times as much as the salts in a typical hard water Moreover, those salts which produce hardness are the bicarbonates and sulphates of calcium and magnesium, which are easily removed by chemical precipitation or by the modern methods of base exchange Sodium chloride is not so amenable to chemical precipitation and its removal in whole or in part presents a major chemical problem outside a laboratory

The obvious method of treatment is by distillation, which requires apparatus, fuel and a cooling agent Water has a very high latent heat of vaporisation, so that much heat is required to turn it into steam A fair-sized apparatus of simple design will produce a ton of distilled water for each ton of coal or oil burnt, an elaborate apparatus will produce as much as 10 tons of water for every ton of fuel consumed

The figures are different when it is desired to make something of the order of a pint of water per hour under the best conditions some 5 volumes of distilled water per volume of spirit or oil are all that can be expected The conditions to be met are stringent and they must take into account the space occupied by the equipment and the fuel and the weight in relation to the quantity According to press statements 3 types of specially designed stills have been under practical trial, which includes their testing in standard lifeboats several miles out at sea The various stills were operated continuously for several hours, the fuel used being scraps of wood, paraffin or kapok There are other possible methods

Silica gel, for example, when exposed to moist air will absorb water vapour up to one-fifth of its weight This absorbed water can be removed by heating the gel and cooling the vapour obtained to condense it The gel can then be used again Such a method simulates distillation but it is less efficient and more difficult to operate

An alternative is to freeze sea water till it deposits ice crystals, separate these and melt them But this demands a simple practical refrigeration plant suitable for a boat

Methods of osmosis and electro-osmosis, whereby salts diffuse through a semi-permeable membrane, are not applicable as they require large volumes of fresh water It has been suggested that if a pressure greater than the osmotic pressure of water, viz, 450 lbs /square inch, could be applied to a solution bounded by a semipermeable membrane, pure solvent would go through the membrane The difficulty here is to discover a suitable membrane, a quest in which success is most unlikely

There remains for discussion the methods of base and acid exchange which in recent years have been much extended in applicability by the discovery of the exchange renins, first made in 1934 at the Chemical Research Laboratory, Teddmgton

It has been known for a considerable time that certain alummosilicates, often called zeolites, which may be either natural or artificial, possess base exchanging properties, that is they can remove calcium and magnesium from water The principle has been applied for many years with success to household water softeners and also on a much larger scale in softening water for industrial purposes and public water supply When hard water is passed through a bed of granules of the sodium compound of the zeolite, the calcium and magnesium bicarbonates and sulphates in the water are replaced by soluble sodium salts, whilst the calcium and magnesium replace the sodium of the zeolite The action goes on until the whole of the replaceable sodium has gone into solution, which may take many days or weeks The material is then regenerated within an hour or so in a very simple manner by treating it with a strong solution *6i* sodium chloride and running the effluent to waste The reverse action takes place, calcium and magnesium pass into solution and sodium alummosilicates are reformed Such a treatment softens hard waters, a process which involves the replacement of soap-destroying and scale-forming calcium and magnesium by relatively innocuous sodium

The zeolites proper form a well known group of chemically related minerals , they were so-called because they fuse characteristically with intumescence, i e swelling up, in a blow pipe flame The artificial zeolites possess the base exchanging property in a marked degree Another mineral, which is quite unrelated, though has the same property, is glauconite The term zeolite has become accepted both in commerce and in scientific literature to connote the many substances used as ion exchange materials

One class in particular of these substances—the so-called carbonaceous zeolites—has been developed with considerable success , they have passed the experimental stage and are now available commercially These products, which may be made from coal, have many advantages over the silicate softeners They possess high exchange values, are of rugged constitution and can act as exchangers either of sodium or of hydrogen according to whether they are regenerated with common salt or dilute acid Since these carbonaceous products are non-siliceous, their special field of usefulness lies in the treatment of boiler-feed water, where dissolved silica from other types of base exchangers is a nuisance.

They are made by treating coal or lignite with strong reagents such as fuming sulphuric acid, sulphur trioxide, chromic acid, etc The process is one of sulphonation and the active group is believed to be a sulphonic acid group Little is yet known of the reactions which occur or what physical and chemical characters are desirable in the coals One method digests the coal for 3 hours at 100°C with concentrated sulphuric acid Another saturates coal with sulphur trioxide at 150°C for 3 to 7 hours.

Since they exchange hydrogen for calcium or magnesium the dissolved salts can be removed altogether instead of being merely replaced

The base-exchanging properties of the synthetic resins were first described by B A Adams and E L. Holmes.[105] These polyhydric phenol formaldehyde resins contain hydrogen in an hydroxyl group which readily goes into solution to replace calcium or sodiums ions and so forms acids Such resins are reported as physically more stable and faster in action than the other softeners mentioned and they have the advantage over the aluminosilicates that they are insoluble in dilute solutions of the mineral acids

What is equally important is that another group of resins, described as amine-formaldehyde resins, has acid

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[105] J Soc Chem Ind 1935, *54,* I T, see also Annual Reports of the Water Pollution Research Board for 1935-38

exchange properties The mechanism of their action is obscure but it may include both surface absorption and reaction of the acids with the amine group Using both resins in turn, an ordinary hard water may be converted into something approaching distilled water By treating the saline water first with the base exchange resin, which has been previously regenerated with a solution of sulphuric or hydrochloric acid the sodium in sodium chloride in solution is replaced by hydrogen, forming hydrochloric acid, and the sodium is abstracted and held by the resin When this water is now treated with an acid exchange resin, that has been regenerated with a solution of an alkali, the hydrochloric acid is removed because the chlorine ion is replaced by an hydroxyl ion, leaving water These base and acid exchange resins are now under trial in many places for the removal of salts from waters not nearly as concentrated as sea water and for the recovery of valuable materials from trade waste waters The process is one of growing economic significance in connection with the recovery of very small quantities of a salt

Theoretically the whole of the salts can be removed from the saline water and the equivalent of distilled water recovered But in the sea the concentration of the salts

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materials required would be as great as the volume of water obtained, so that it would be easier to carry fresh water and dispense with the apparatus

The Permutit Company are now advertising a "Sea-Water Desalting Kit" as used by the U S forces It consists of a plastic bag and a supply of salt-removing briquets The instructions are to fill the bag with sea water and then add a briquet. The briquet is broken up by kneading and the water is kept in contact with it for twenty minutes or longer, after which water fit for drinking can be sucked through the outlet tube

Normally one expects to regenerate a base or acid exchanging zeolite and use it many times but the problem becomes rather different and indeed simplified when the material is only used once It then becomes possible to incorporate substances such as silver oxide which have an avidity for chlorine or barium oxide with an avidity for sulphate These bring about the precipitation of the dissolved solids in the sea water The time of reaction becomes considerable as indicated but in favourable circumstances it should be possible to remove most of the chlorine and have a water barely alkaline and not containing too much magnesium sulphate which last has medicinal action Such a kit will not be too large and afford useful quantities of drinking water Security reasons prevent further information being given at present, but it is understood that a similar kit has been devised in this country

Zeolites are being used at the large nitrate works of the Norsk Hydro Elekrisk Company at Heroya, in Norway, to extract the sodium ion from the sea The sodium is required there to convert calcium nitrate into sodium nitrate This process is an illustration of how it may be economically of advantage to take a single ion out of the sea for manufacturing purposes

We have elsewhere made brief reference to the use of carbonaceous zeolites to recover small quantities of copper from solution This matter has been fully studied by Beaton and Furnas[106] and is worth mention as an example of what can be achieved Of course, metals similar to copper would be absorbed on the zeolite at the same time but these would be recovered with the copper and could be separated later Such a recovery plant might form a profitable addition to a works with an effluent containing a valuable mineral in traces, such, for instance, as zinc, chromium, tin, gold, silver, lithium or potassium, which are all worth recovering from dilute process waste liquors

The ideal conditions of working when using carbonaceous zeolites have been determined The absorption for copper is a function of the ratio of copper ions to hydrogen ion concentrations, or, in more simple language, there are ideal conditions of acidity favouring the transfer of copper from solution to zeolite

[106] Ind Eng Chem 1941, *33*, 1500

The storage capacity of a zeolite does not alter with the Tate of flow of dilute solutions, but it does change with the concentration of the influent becoming less as this increases The average transfer co-efficient decreases as the height of the zeolite column is increased, owing to the fact that the released hydrogen ions begin to interfere with the exchange reaction over an increased portion of the bed.

The collection of copper is complete and takes place at a rapid rate of flow of the very dilute solution over the columns of the exchanger The recovery of the copper when the zeolite is saturated is effected by fairly strong solutions of sulphuric acid at the same time the zeolite is regenerated for another cycle Thus normal sulphuric acid will concentrate the copper 200 fold, whereas 4 times normal acid effects an 800 fold concentration There remains as final product a strong solution of copper sulphate

Putting the results in plain figures rather than in the form favoured by the chemist, it appears that a solution which contained 1 Ib of copper in 6,ooo Ib of water is turned into one of copper sulphate containing 1 Ib of copper in 6 87 lbs of water To do this 1 54 Ib of sulphuric acid (100 per cent strength) are necessary, and simple arithmetic indicates that 1 Ib of acid performs the same duty as the evaporation of 4,200 lbs of water. This illustrates the tremendous difference in energy requirements between the base exchange process and evaporation for the concentration of very dilute solutions, and is evidence of the unique possibilities of the use of zeolites Thus by their agency the ash content of sugar beet syrup is being reduced from o 87 to 0.008 per cent, in a single operation, whilst working with gelatine in 5 per cent solution the ash is brought down from 2 6 to 0 09 per cent. Demineralising installations of this type, using basic and acid resins in series, are described by H. L. Tiger and S, Sussman[107]

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[107] Ind Eng Chem 1943, *35*, 186

APPENDIX

ANALYTICAL METHODS

Figures have been given in Chapter 2 for the quantities of many elements present in sea water These amounts are often extremely small and it may well be asked how reliable and how accurate are the figures given, more particularly as in the past widely differing results have been obtained by different investigators One of the surest methods of showing the reliability of the figures is to give details of or references to the actual methods of analysis employed This is one of our reasons for collecting together these analytical methods Another reason lies in the intrinsic interest of the methods Sea water is one of the most complex mixtures that could be devised for analysis and although there is no difficulty in rendering the material soluble such as troubles the analyst of ores , the analysis of sea water bristles with almost all the other analytical difficulties, not the least of which is the estimation of one element in presence of a great excess of very similar elements Furthermore, these analytical methods for sea water have, we believe, never been collected together before, and many of them are not easily to be found

But an analyst is not going to look up details of procedure except in original papers unless he can help it, and in many instances these papers are long and contain details of intricate apparatus It would not have been possible to give greater details without unbalancing this book and turning it into a textbook of sea water analysis For this reason we have tried to give sufficient details to convince the reader of the reliability and accuracy of the methods employed and have given references to the original papers for those further interested The elements are treated in alphabetical order purely as a matter of convenience

Aluminium.

H M Haendler and T G Thompson[108] determine the aluminium content of sea water by precipitation with oxme at pH 6-7, followed by solution of the precipitate

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The oxine is then coupled with diazotized sulphanihc acid, treated with caustic soda and estimated colounmetrically against a standard

Boron.

E G Moberg and M W Harding[109] estimated boron

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with slight modifications This method[110] depends on the fact that boric acid titrates as a reasonably strong acid in the presence of mannitol The solution is brought to neutrality to bromothymol blue, mannitol is added and the amount of standard alkali to bring back the pH to the original figure is determined This is a measure of the bone acid present

Bromine.

A suitable method for estimating bromides in the presence of much chlorides as in sea water is given by I M Kolthoff and H Yutzy in The bromide is oxidised to bromate with sodium hypochlorite, the excess hypochlorite is removed with sodium formate and the bromate determined by adding potassium iodide and titrating with sodium thiosulphate

[108] J Marine Research, Sears Foundation 1939, *2*, 12
[109] Science, 1933, 77/510
[110] Ind Eng Chem Anal 1932, *4*, 38.
[111] Ind Eng Chem Anal 1937, *9*, 75

Calcium.

Calcium is estimated in the usual way by precipitation as the oxalate, but as the magnesium/calcium ratio is so high very special precautions have to be adopted A summary of the methods used is given by T. G Thompson and C C Wright,[112] and a detailed description of an accurate method by P L Kirk and E G Moberg[118] The calcium figure, obtained by all these methods, includes strontium and barium[114] J D Robertson and D. A. Webb[116] used a semi-micro modification of Kirk and Moberg's method involving two precipitations with oxalate, treating the final precipitate with cenc sulphate and back titration with ferrous ammonium sulphate

Carbon Dioxide.

The carbon dioxide in sea water can be determined by acidifying and heating and estimating either gasometncally or by absorbtion in baryta

Chlorine.

The analytical methods are of great importance owing to the fact that the salinity is based on the chlorinity measurement The sea water is titrated against silver nitrate preferably standardized against normal sea water of known chlorinity at the same temperature Oxner and Knudsen[116] have developed a method accurate to 1 part in 100,000 in which 10 to 15 ce of sea water are titrated with standard silver nitrate solution using potassium chromate as an internal indicator Such methods naturally give the total halogen content, to get the true chlorine figure the result must be multiplied by 0 9985

Coppftr

W R G Atkins[117] discusses various methods for estim-

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[112] J Amer Chem Soc 1930, *52*, 915

[113] Ind Eng Chem Anal Ed 1933, *5*, 96

[114] See D A Webb, Nature 1938, *142*, 751

[115] J Exp Biol 1939, *16*, 155

[116] Bull Comm Internat pour l'Expl sci de IaMer Mediterrane* eneNo 3, April 1920

[117] J Marine Biol Assoc U K 1932, *IS*, 193

ating copper in sea water including a direct colounmetric method with sulphide, Scott's potassium ethyl xanthate method, and Callan and Henderson's method using sodium diethyl dithio carbamate He considers the best method is one involving electro-deposition One litre of sea water is heated nearly to boiling and a potential difference of 2 volts applied for an hour Copper is deposited on a platinum gauze The gauze is then replaced by another one and the electrolysis repeated twice more The copper is dissolved off the gauzes with sulphuric acid and determined colounmetrically

Fluorine.

T G Thompson and H J Taylor[118] estimated this element by a colounmetnc method Zirconium nitrate and sodium ahzann sulphonate react to give a brilliant reddish violet lake This is stable in acid solution except in the presence of fluorides, when it fades to the pale yellow colour of the sodium ahzann sulphonate The sea water is acidified, a solution of the mixed reagents is added and the solution then boiled and left to stand for four hours The colour is then compared with that given when known amounts of fluoride have been added References to earlier less satisfactory methods are given in this paper These depended on precipitation as calcium and banum fluondes, but precipitation was not complete

Gold.

W E Caldwell[119] reviews the methods for obtaining gold from the sea The methods of analysis are sub$tantially the same as these, in that gold is finally weighed as the metal Caldwell took 40 litres of sea water and added 400 ce of 0 iM mercunc chloride, 40 gm of magnesium powder, and 400 ce of concentrated hydrochlonc acid The nascent hydrogen reduces the mercunc chloride to give a semi-colloidal mercury-mercurous chloride precipitate This absorbs the gold and silver It is allowed to

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[118] Ind Eng Chem Anal 1933, 5, 87

[119] J Chem Educ 1938, *15*. 507

settle , the supernatant liquor is decanted and filtered off To the precipitate is added some very pure lead and 10 mg. of silver and the mixture is heated in a furnace The mercury and lead evaporate off and the silver is then removed by solution in nitric acid The gold is annealed by heating to redness and then weighed Caldwell obtained from o 004 to o 04 mg of gold from different 40 litres samples Even these figures he considers err on the high side owing to the presence of gold as an impurity in the reagents He believes the results of many other workers are too high for the same reason

Iodine.

Methods of estimating the iodine content of sea water are discussed by J F Reith [120] He considers that Winkler's standard method is probably the most satisfactory

Iron.

Iron is present in sea water in three forms, ferrous, ferric and organically bound Various methods have been used and are referred to by N W Rakestraw, H E Mahneke and E F Beach in The authors use a method in which the iron is removed from solution with ammonium sulphide, this precipitation being rendered complete by the large amounts of insoluble magnesium salts which are precipitated at the same time The iron is redissolved in hydrochloric acid and oxidized with bromine, reprecipitated, and then determined colounmetncally with potassium thiocyanate in presence of ethylene glycol monobutyl ether which stabilizes the colour

T G Thompson, R W Brenner and I M Jamieson[122] estimated the iron directly with thiocyanate after ashing with sulphuric acid Subsequent slight alterations to this method are described by Thompson and Brenner[128]

[120] Rev trav chim 1930, *49,* 142
[121] Ind Eng Chem Anal 1936, *8,* 136
[122] Ind Eng Chem Anal 1932, *4,* 288
[123] J Conseil intern exploration mer 1935, *10,* 33

L. H N Cooper[124] uses 2 2 ' 2" **tripyridyl.** This gives **a violet colour** with iron which is detectable in **a** concentration as low as 1 mg per cubic metre The better known 2 2" dipyndyl reagent is only half as sensitive Ferrous iron is estimated by acidification with 2 drops of 4 normal acid and after standing for 24 hours Ferric iron is estimated after treatment with sodium sulphite and total iron including that present in organic compounds after treatment both with bromine and sodium sulphite It is necessary to leave the mixture standing for 24 hours, as the presence of fluoride slows the development of the colour

Lithium.

B D Thomas and T G Thompson[125] determine the lithium content of sea water by taking one litre and removing most of the calcium and magnesium with sodium carbonate They then evaporate, filter off more magnesium carbonate, acidify with hydrochloric acid and go on concentrating until sodium chloride begins to crystallize An equal quantity of alcohol is then added and the sodium chloride filtered off More sodium chloride is removed by saturating with hydrochloric acid gas All precipitates are redissolved and reprecipitated in order to remove absorbed lithium The solution is finally evaporated to dryness, dissolved in 50 per cent alcohol, and any residual magnesium removed with sodium carbonate The lithium is then estimated spectroscopically

J Bardet, A Tchakinan and R Lagrange[126] also concentrate down the sea water and progressively remove other constituents before determining the lithium spectroscopically

Magnesium.

T G Thompson and C C Wright[127] estimate magnesium in sea water by A E Epperson's method[128] The water is

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[124] Proc Roy Soc B 1935, *118*, 419
[125] Science 1933, *77*, 647
[126] Compt rend 1937. *204*, 443
[127] J Amer Chem Soc 1930. *52*, 915
[128] *Ibid*, 1928, *50*, 321

acidified with 5 ce of hydrochloric acid and methyl red is added as an indicator The solution is made up to 150 ce and 10 ce or excess is added of a saturated solution of diammomum hydrogen phosphate The solution is slowly neutralized with ammonia while stilting, 5 ce, more ammoma are added and the solution stirred for 10 minutes and then left to stand for 4 hours or longer The precipitate is then filtered off, washed with dilute ammonia, dissolved in dilute hydrochloric acid, 1 ce of diammomum hydrogen phosphate solution is added, and the magnesium ammonium phosphate reprecipitated The final precipitation is repeated once more, before the precipitate is finally dried and ashed

J D Robertson & D A Webb[12*] precipitate magnesium with oxme in ammomacal solution The precipitate is dissolved in hydrochloric acid and reprecipitated It is then redissolved and treated with a bromide—bromate solution which reacts with the oxme Uncombmed bromine is estimated with potassium iodide, and sodium thiosulphate

Manganese.

The most satisfactory method of estimation seems to be that of H H Willard and L C Greathouse[130] slightly modified by T G Thompson and T L Wilson in The water is freed from organic matter and halogens by concentrating to dryness and ashing in presence of sulphuric acid The manganese is oxidised to permanganate by treatment with sodium parapenodate and estimated colounmetncally Thompson and Wilson refer to and criticize other methods

Nitrogen.

(1) *as Nitrogen gas* A method for the determination of the dissolved nitrogen in water is given by N W Rakestraw and V M Emmel[132] The water is repeatedly

129 J Exp Biol 1939, *16*, 156
130 J Amer Chem Soc 1917, *39*, 2366
131 J Amer Chem Soc 1935, *57*, 233
132 Ind Eng Chem Anal 1937, *9*, 344

sprayed into an evacuated vessel and the gases are extracted The extracted gas is measured at constant volume, the oxygen is removed with phosphorus, and the nitrogen with metallic lithium Full details of the apparatus and manipulation will be found in the paper referred to

(2) *as Ammonia* H E Wirth and R J Robinson[133] have made a study of the methods for determining the ammonia content of sea water They consider the best method to be one in which the water is first treated by the Witting method with barium chloride and a mixed sodium hydroxide sodium bicarbonate solutiQn to remove interfering ions After standing for three days the supernatant liquor is decanted, Nessler reagent is added and the turbidity measured in a photometer

(3) *as Nitrate* H W Harvey[134] uses a colounmetnc method for estimating nitrates, using a reduced strychnine reagent by which a red colour is given The reagent is prepared by dissolving 0 5 gm of strychnine in 25 ce water and heating it with 2 ce hydrochloric acid and 4 square inches of zinc foil, previously amalgamated with mercuric chloride Potassium sulphate is also added Nitrites also give a red colour with the reagent

(4) *as Nitrite* A P Orr[135] uses the Gness—Ilosvay reagent for the colounmetnc determination of nitrites The reagent is made up in two solutions which are mixed in equal proportions when required One of these is prepared by dissolving one gramme of sulphamic acid in 14 7 gm of glacial acetic acid and making up to 285 ce , the other by dissolving o 2 gm napthylamme in 14 7 gm of acetic acid and making up 325 ce 100 ce of water, and 4 ce of reagent, give a pink colour if nitrites are present

Oxygen.

The dissolved oxygen in sea water is conveniently determined by Winkler's standard method described by

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133 Ind Eng Chem Anal 1933, 5, 293
134 J Marine Biol Assoc U K 1926, 14, 71
135 J Marine Biol Assoc U K 1926, 14, 55

Jacobsen and Knudsen[136], o 5 ce of a 40 per cent solution of manganous chloride and 1 ce of a 5 per cent solution of potassium iodide in 10 per cent sodium hydroxide are added to a known volume of water in a completely filled stoppered bottle and the bottle well shaken The oxygen oxidizes some of the manganous hydroxide formed to the manganic form The solution is then acidified with 4 ce of concentrated hydrochloric acid and the manganic chloride formed sets free iodine from the potassium iodide The iodine is determined with sodium thiosulphate and starch in the usual manner

Phosphorus.

Methods for estimating the phosphate content of sea water are reviewed by W R G Atkins[137] Atkins considers Florentine modification of Deniges' method to be the most satisfactory Two solutions are prepared Solution A is a mixture of 100 ce of 10 per cent ammonium molybdate and 300 ce of 50 per cent (by volume) sulphuric acid Solution B is a freshly prepared stannous chloride solution made by dissolving o 1 gm of tin in 2 ce hydrochloric acid, adding one drop of copper sulphate and making up to 10 ce 100 ce of sea water are taken and to it are added 2 ce of A and one drop of B An intense blue colour is given, which is compared with a standard This method will include arsenates but not silicates in addition to phosphates

Potassium.

The standard methods of estimating potassium are applicable to sea water D A Webb[138] precipitates as potassium silver cobaltinitnte 10 ce of sea water are taken and o 3 ce of sulphuric acid and the mixture is evaporated to dryness The residue is then dissolved in water and made up to 50 ce 20 ce are added of a solution of 125 gm of sodium cobaltinitnte and 5 gm of silver nitrate per litre at 75°C 10 ce Acetone are then added

[136] Bull del 'Institut Oceanogr Monaco, No **390. 1921**

[137] J Maine, Biol Assoc 1932, *13,* 119, 7C0

[138] J Exp Biol 1939, *16,* 178

and the mixture stood for at least 12 hours at 10°C It is then filtered and the precipitate washed with a saturated solution of potassium silver cobaltinitnte It is then treated with excess of a cenc sulphate solution and back titrated with ferrous ammonium sulphate using Lissamme green as an indicator

B Bullock and P L Kirk[189] find that a volumetric chloroplatmate method is suitable for estimating potassium in sea water. 1 or 2 cc are taken and evaporated to dryness with excess chloroplatimc acid The residue is then thoroughly washed with 80 per cent alcohol and with 20 per cent ammonium chloride solution, both saturated with potassium chloroplatmate, and then with 80 per cent alcohol The residue is then suspended in water and powdered magnesium is added This reduces the chloroplatmate to metallic platinum and frees the chloride The mixture is evaporated to dryness, redissolved and titrated with standard silver nitrate solution in presence of acetone and using dichlorofluorescem as an indicator

Selenium.

V M Goldschmidt and L W Strock[140] determined the concentration of this element by precipitating ferric hydroxide in sea water The selenium is absorbed on this and then determined by a modification of the hydrobromic acid distillation method of W O Robinson et al[141]

Silicon.

W. R G Atkins[142] estimated the silicates in sea water by taking 100 ce of water and adding 2 ce of a 10 per cent ammonium molybdate solution and 4 drops of 50 per cent (by volume) sulphuric acid The yellow colour is compared against a picne acid standard

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[139] Ind Eng Chem Anal 1935, 7, 178

[140] Nachr Ges Wiss Gottmgen, Mathaphysik Klasse 1935, 1 123

[141] Ind Eng Chem Anal 1934, *6*, 274

[142] J Marine Biol Assoc U K 1932, *13*, 151.

This method has been further studied and developed by T G. Thompson and H G Houlton[143] and by R. J. Robinson and A. J Spoor,[144] the latter using a photometer for the colour comparison They claim that potassium chromate is a better standard than picric acid and that the values obtained by earlier methods were too low

Sodium.

J. D Robertson and D A Webb[146] estimate the sodium

in sea wate

tion with zinc uranyl acetate The precipitating solution is made up as follows — 80 gm uranyl acetate are dissolved in 425 ce water and 14 ce glacial acetic acid added , 20 gm zinc acetate are dissolved in 275 ce water and 7 ce glacial acetic acid added , the two solutions are mixed hot and a trace of sodium acetate added The mixture is stood for at least 24 hours and filtered before using 20 ce of this solution are taken and 1 ce of sea water added After standing for an hour the precipitate is filtered off and washed with a saturated solution of sodium zinc uranyl acetate in 95 per cent alcohol The precipitate is dried and weighed The weight multiplied by 0 01495 gives the sodium content

Strontium.

Y Miyake[146] precipitates calcium and strontium from sea water as the oxalates, ignites these and dissolvesjthem in nitric acid The dry nitrates are separated in anhydrous alcohol-ether by the standard Fresemus method

Sulphur.

Sulphur as sulphate cannot be accurately determined by the normal gravimetric methods involving precipitation as barium sulphate J D Robertson and D A Webb[147] make use of the intense pink colour given by solutions of

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143 Ind Eng Chem Anal 1933, 5,417
144 Ind Eng Chem Anal 1936, *8*, 455
145 J Exp Biol 1939, *16*, 155
146 Bull Chem Soc Japan 1939, *14*, 55
147 J Exp Biol 1939, *16*, 155

banum salts with sodium rhodizonate A known excess of a banum chloride solution is added in presence of the indicator The solution is buffered at pH 3 o and standard sodium sulphate solution added until the pink colour vanishes From this the sulphate content of the sea water is calculated

Zinc.

W R G Atkins[148] estimated the zinc by concentrating the sea water and then determining it turbidometrically on adding 10 ce of a 0 1 per cent solution of sodium diethylthiocarbamate as described by him in the Analyst[149]

G Bertrand[160] concentrated 1 litre of sea water after adding 1 ce of hydrochloric acid, precipitated the sulphates with barium chloride and the zinc as calcium zincate with ammonium hydroxide and lime water The calcium zincate was redissolved and reprecipitated twice more before final determination

Publishers Note

> *The manuscript of this book was received from the Authors in September,* 1943, *but publication has been delayed owing to printing and paper supply difficulties caused by the war*

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148 J Marine Biol Assoc U K 1936, ***20,*** **625**
149 1935, ***60,*** **400**
150 Compt Rend 1938. ***207,*** **1137**

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