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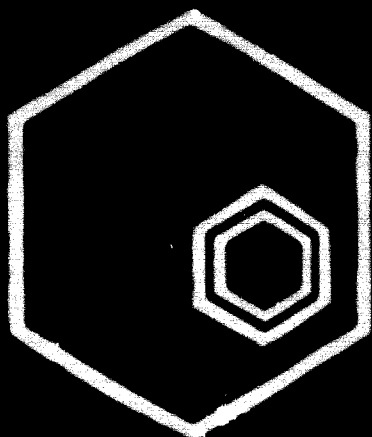
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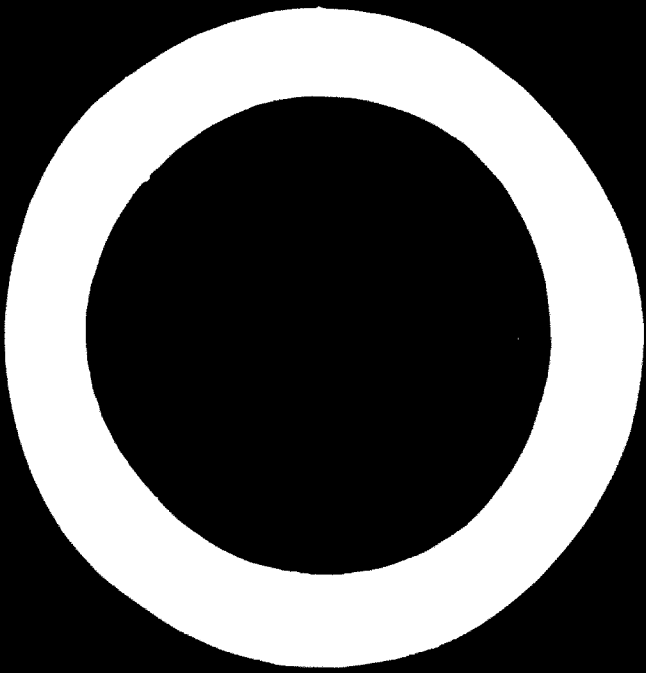
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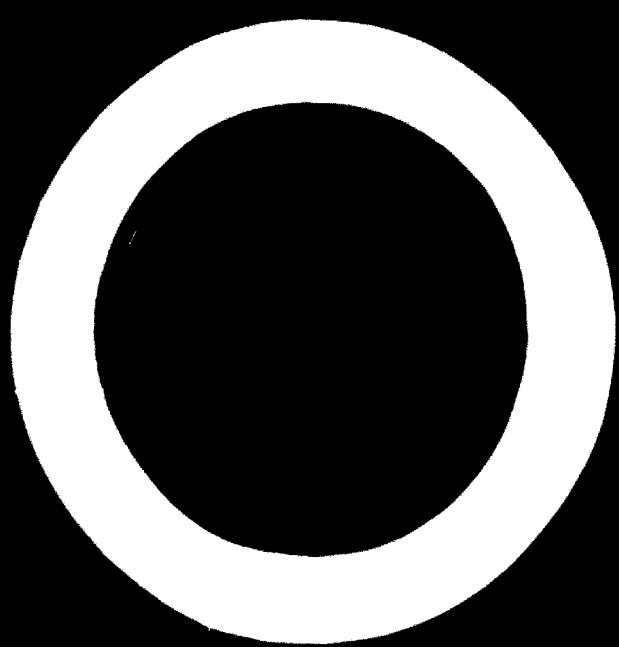


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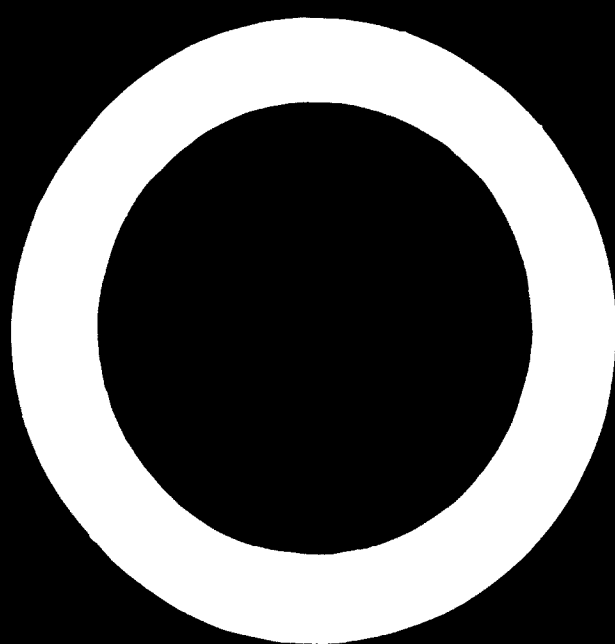


UNITED NATIONS





**EXTRACTION OF CHEMICALS FROM SEAWATER,
INLAND BRINES AND ROCK SALT DEPOSITS**



**UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
VIENNA**

**EXTRACTION
OF CHEMICALS FROM
SEAWATER,
INLAND BRINES
AND ROCK SALT DEPOSITS**



**UNITED NATIONS
New York, 1972**

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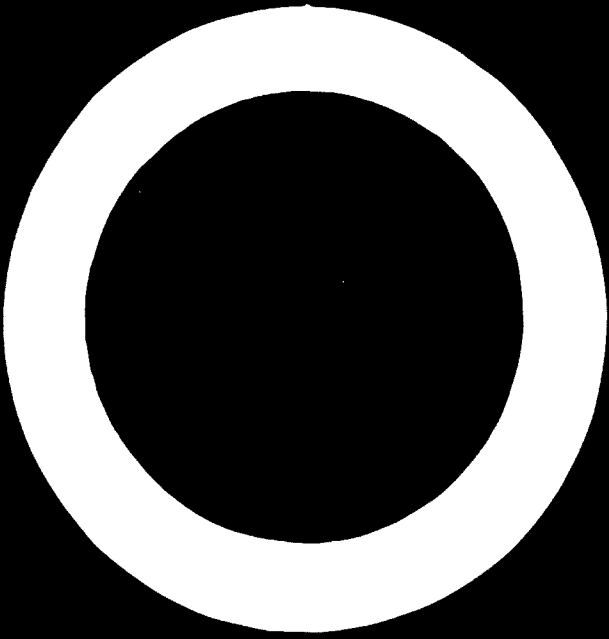
PREFACE

This study covers:

- The range of primary chemicals obtained at present from seawater, inland brines and rock salt deposits;**
- A review of established plants;**
- Process flow diagrams;**
- Process descriptions;**
- Material and energy requirements of the major processes;**
- Capital and operating costs and personnel requirements;**
- Probable future trends of production, with special reference to bromine production as a consequence of existing and proposed restrictions on automobile exhausts and atmospheric pollution, and alternative utilization of bromine;**
- The development of secondary industries based on the primary chemicals specified above.**

The study further examines the possibility of producing chemicals from seawater and other brines in conjunction with the desalination of seawater. The steps that would be necessary to initiate such a chemical complex are outlined. Excluded from the study are mineral deposits on the ocean floor, sulphur, and petroleum and natural gas.

The study was prepared for the United Nations Industrial Development Organization by Chemical and Technical Services, Kingston-upon-Thames, Surrey, England. The views and opinions expressed in this publication are those of the consultant and do not necessarily reflect the views of the secretariat of UNIDO.



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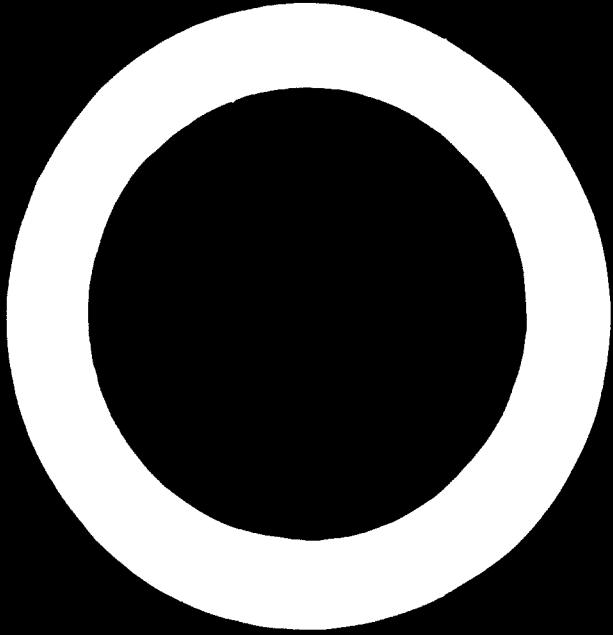
EXPLANATORY NOTES

Dollar (\$) refers to US dollar unless otherwise specified.

Ton refers to metric ton (1,000 kg) unless otherwise specified.

The following abbreviations are used in this publication:

A	= ampère
Btu	= British thermal unit
C. V.	= caloric value
DC	= direct current
kcal	= kilocalorie
kW	= kilowatt
kWh	= kilowatt hour
Nm	= normal cubic metre
NPK	= nitrogen, phosphorus, potassium
ppm	= parts per million
TDS	= total dissolved solids
TEL	= tetraethyl lead
TML	= tetramethyl lead



Chapter 1

SEAWATER AS A SOURCE OF CHEMICALS

Approximately 71 per cent of the earth's surface is water, [1]¹ most of which is seawater. The total volume of the sea is approximately 1,325 million km³, each containing about 30.4 million tons of salts. [2] This total includes approximately 28.8 million tons of common salt (NaCl), equal approximately to 25 per cent of the world's consumption of 113 million tons in 1968. [3]

Such figures cannot be readily grasped and have little meaning except as they indicate that, for six chemical elements (sodium, chlorine, magnesium, potassium, bromine and boron) the sea represents a commercial source that can compete with other sources. For bromine, seawater is the major source.

In addition to these 6 elements, and the hydrogen and oxygen of the water itself, the sea contains many others, 66 of which are shown in table 1. [4] However, the concentration of most of these is so small as to make their detection and estimation, to say nothing of their extraction, difficult; thus, for them seawater is of slight economic importance as a source.

TABLE 1. CONCENTRATION OF DISSOLVED SUBSTANCES IN SEAWATER

Element	Symbol	Concentration (ppm)	Principal chemical form
Chlorine	Cl	19,353	Cl ⁻
Sodium	Na	10,760	Na ⁺
Magnesium	Mg	1,294	Mg ²⁺ ; MgSO ₄
Sulphur	S	812	SO ₄ ²⁻
Calcium	Ca	413	Ca ²⁺ ; CaSO ₄
Potassium	K	387	K ⁺
Bromine	Br	67.3	Br ⁻
Carbon	C	28	HCO ₃ ⁻ ; H ₂ CO ₃ ; CO ₂ ⁻² ; organic compounds
Strontium	Sr	8.0	Sr ²⁺ ; SrSO ₄
Boron	B	4.6	B(OH) ₃ ; B(OH) ₄ ⁻
Silicon	Si	3	Si(OH) ₄ ; Si(OH) ₃ ⁻
Fluorine	F	1.3	F ⁻ ; MgF ⁺
Argon	A	0.6	A(g)

¹ Figures in square brackets refer to references listed at the end of this paper.

TABLE 1 (continued)

Element	Symbol	Concentration (ppm)	Principal chemical form
Nitrogen	N	0.5	NO_3^- ; NO_2^- ; NH_4^+ ; $\text{N}_2(\text{g})$; organic compounds
Lithium	Li	0.17	Li^+
Rubidium	Rb	0.12	Rb^+
Phosphorus	P	$7 \cdot 10^{-2}$	H_2PO_4^- ; HPO_4^{2-} ; PO_4^{3-} ; H_3PO_4
Iodine	I	$5 \cdot 10^{-2}$	IO_3^- ; I
Barium	Ba	$3 \cdot 10^{-2}$	Ba^{2+} ; BaSO_4
Indium	In	$2 \cdot 10^{-2}$	—
Aluminium	Al	$1 \cdot 10^{-2}$	$\text{Al}(\text{OH})_3$
Iron	Fe	$1 \cdot 10^{-2}$	$\text{Fe}(\text{OH})_3$
Zinc	Zn	$1 \cdot 10^{-2}$	Zn^{2+} ; ZnSO_4
Molybdenum	Mo	$1 \cdot 10^{-2}$	MoO_4^{2-}
Selenium	Se	$4 \cdot 10^{-2}$	SeO_4^{2-}
Copper	Cu	$3 \cdot 10^{-2}$	Cu^{2+} ; CuSO_4
Arsenic	As	$3 \cdot 10^{-2}$	H_2AsO_4^- ; HAsO_4^{2-} ; H_3AsO_3 ; H_2AsO_3
Tin	Sn	$3 \cdot 10^{-2}$	—
Uranium	U	$3 \cdot 10^{-2}$	$\text{UO}_2(\text{CO}_3)_2^{4-}$
Vanadium	V	$2 \cdot 10^{-2}$	$\text{VO}_2(\text{OH})_2^{2-}$
Manganese	Mn	$2 \cdot 10^{-2}$	Mn^{2+} ; MnSO_4
Nickel	Ni	$2 \cdot 10^{-2}$	Ni^{2+} ; NiSO_4
Titanium	Ti	$1 \cdot 10^{-2}$	$\text{Ti}(\text{OH})_4$
Cobalt	Co	$5 \cdot 10^{-3}$	Co^{2+} ; CoSO_4
Antimony	Sb	$5 \cdot 10^{-3}$	$\text{Sb}(\text{OH})_6^{3-}$ (?)
Caesium	Cs	$5 \cdot 10^{-3}$	Cs^+
Cerium	Ce	$4 \cdot 10^{-3}$	Ce^{3+}
Krypton	Kr	$4 \cdot 10^{-3}$	—
Yttrium	Y	$3 \cdot 10^{-3}$	—
Silver	Ag	$3 \cdot 10^{-3}$	AgCl_2^- ; AgCl_2^0
Lanthanum	La	$3 \cdot 10^{-3}$	—
Cadmium	Cd	$1 \cdot 10^{-3}$	Cd^{2+} ; CdSO_4
Neon	Ne	$1 \cdot 10^{-3}$	—
Xenon	Xe	$1 \cdot 10^{-3}$	—
Tungsten	W	$1 \cdot 10^{-3}$	WO_4^{2-}
Germanium	Ge	$7 \cdot 10^{-3}$	$\text{Ge}(\text{OH})_4$; $\text{Ge}(\text{OH})_6\text{O}^-$
Chromium	Cr	$5 \cdot 10^{-3}$	—
Thorium	Th	$5 \cdot 10^{-3}$	—
Scandium	Sc	$4 \cdot 10^{-3}$	—
Gallium	Ga	$3 \cdot 10^{-3}$	—
Mercury	Hg	$3 \cdot 10^{-3}$	HgCl_2 ; HgCl_2^{2-}
Lead	Pb	$3 \cdot 10^{-3}$	Pb^{2+} ; PbSO_4
Bismuth	Bi	$2 \cdot 10^{-3}$	—
Niobium	Nb	$1 \cdot 10^{-3}$	—
Thallium	Tl	$1 \cdot 10^{-3}$	Tl
Helium	He	$5 \cdot 10^{-4}$	—
Gold	Au	$4 \cdot 10^{-4}$	AuCl_4^-
Neodymium	Nd	$2 \cdot 10^{-4}$	—
Dysprosium	Dy	$7 \cdot 10^{-5}$	—
Praseodymium	Pr	$6 \cdot 10^{-5}$	—
Erbium	Er	$6 \cdot 10^{-5}$	—
Beryllium	Be	$6 \cdot 10^{-5}$	—
Gadolinium	Gd	$6 \cdot 10^{-5}$	—

TABLE 1 (continued)

Element	Symbol	Concentration (ppm)	Principal chemical form
Ytterbium	Yb	$5 \cdot 10^{-7}$	—
Samarium	Sm	$4 \cdot 10^{-7}$	—
Holmium	Ho	$2 \cdot 10^{-7}$	—
Thulium	Tm	$1 \cdot 10^{-7}$	—
Europium	Eu	$1 \cdot 10^{-7}$	—
Lucentium	Lu	$1 \cdot 10^{-7}$	—
Protactinium	Pa	$2 \cdot 10^{-9}$	—
Radium	Ra	$1 \cdot 10^{-10}$	Ra^{+2} ; $RaSO_4$
Radon	Rn	$6 \cdot 10^{-10}$	—

Source: J. P. Riley and G. Skirrow (1965) *Chemical Oceanography*, Academic Press, London

In most seawaters the concentration of total dissolved solids (TDS) varies between 32,000 and 38,000 ppm, with a mean of 35,000 ppm (so-called standard). Proximity to land can cause significant deviations from this value, either downwards, owing to influx of fresh water from rivers, underground springs and run-off from the land, or upwards by evaporation in excess of dilution by precipitation. An example of high concentration is at San Diego, California, USA, where the salt concentration reaches 5 per cent (50,000 ppm). [1] Here, the annual evaporation rate is 1,525 mm per year, compared with a precipitation rate of 25 mm per year. This large excess of evaporation over precipitation permits yields as high as 1,230 to 1,570 tons of salt per hectare by solar evaporation to be obtained compared with a more normal rate of 38 tons per hectare. [3]

Although the concentration of total salts in seawater varies, their relative concentrations are remarkably constant. This may be seen from table 2, [5] which gives the ratio of the seven listed chemicals to the chlorine concentration.

TABLE 2. RATIO TO CHLORINE OF SEVEN CHEMICALS IN FIVE BODIES OF SALT WATER

	North Atlantic	Atlantic	North Pacific	Indian	Mediterranean
Na		0.5544—0.5567	0.5553		0.5310—0.5528
Mg		0.0667	0.06632—0.06695		
K 0.02026		0.01953—0.0263	0.02096		
Ca		0.02122—0.02126	0.02154	0.02099	
Sr		0.000420		0.000455	
SO ₄		0.1393	0.1396—0.1397	0.1399	
Br 0.00337—0.00341		0.00325—0.0038	0.00348	0.0038	

Source: R. A. Hoens (1969) *Marine Chemistry*, Wiley-Interscience, New York.

A notable exception is a recently discovered localized area of the Red Sea, which has a temperature of 45°C and a TDS of 43,000 ppm compared with the 35,000 ppm standard, and whose major components in relation to chlorine are shown in table 3. [5]

TABLE 3. RATIO TO CHLORINE OF SIX CHEMICALS IN THE RED SEA BRINES AND IN NORMAL MID-OCEAN SEAWATER

	<i>Red Sea brines</i>	<i>Normal mid-ocean seawater</i>
Na	0.598	0.55
K	0.0139	0.021
Ca	0.0303	0.021
Mg	0.0052	0.067
SO ₄	0.0048	0.140
Br	0.00079	0.0035

Source: R. A. Howe (1969) *Marine Chemistry*, Wiley-Interscience, New York.

These Red Sea brines show considerable enrichment with Na⁺ and Ca⁺, which, together with the high evaporation rate in the area, would make them an excellent source of salt and calcium carbonate and calcium sulphate. Another highly saline seawater is found at Kuwait in the Persian Gulf, where the seawater contains 45,000 ppm of salt. The water is fed to a desalination plant. [6]

Seawater provides a significant proportion of the total world requirements of common salt, magnesium metal, magnesium compounds and bromine. Table 4 gives the estimated annual world production of these chemicals from seawater, and table 5 the estimated figures for United States production.

TABLE 4. ANNUAL WORLD PRODUCTION OF FOUR IMPORTANT CHEMICALS

	<i>Total (million tons)</i>	<i>From seawater (million tons)</i>	<i>Per cent from seawater</i>
Salt	113	32.7	29
Magnesium metal	0.188	0.123	65
Magnesium compounds	10.1	0.635	6.3
Bromine	0.148	0.10	68

TABLE 5. ANNUAL PRODUCTION OF FOUR IMPORTANT CHEMICALS IN THE UNITED STATES

	<i>Total (million tons)</i>	<i>From seawater (million tons)</i>	<i>Per cent from seawater</i>
Salt	37.4	5.0	13.4
Magnesium metal	0.136	0.118	87
Magnesium compounds	1.27	0.454	36
Bromine	0.139	0.0675	46

Common salt, gypsum and potassium salts are recovered from seawater by evaporation and precipitation. Bromine and magnesium are normally recovered from unconcentrated seawater if they are not produced

in conjunction with salt. If production of these two chemicals is carried out together with salt production, it is more economic to recover them from the residues (bitterns) after evaporation of the seawater and precipitation of the gypsum and salt: lower power costs for pumping can be distributed among more salable products; and the equipment needed for bromine and/or magnesium production will be smaller and therefore cheaper, owing to the reduction in volume.

For example, the residual mother liquor from the production of 100,000 tons of salt contains: [1]

	<i>Tons</i>
KCl	2,800
MgCl ₂ · 6H ₂ O	27,300
MgSO ₄ · 7H ₂ O	16,000
Br ₂	0,240

The initial quantity of seawater required for the production of 100,000 tons of salt is 3.7 million tons and will, in the course of evaporation and precipitation of the salt, be reduced to less than 300,000 tons, that is, a reduction of more than 90 per cent in mass. This smaller quantity will contain all the magnesium and bromine still in solution, but in a much higher concentration.

The sequence of precipitation of salts from seawater depends largely on the temperature of evaporation and whether the seawater is allowed to remain in contact with the precipitated salts. Table 6 gives the deposition sequence at 27°C. [7]

TABLE 6. SEQUENCE OF DEPOSITION OF SALTS FROM SEAWATER AT 27°C

<i>Original seawater remaining (per cent of weight)</i>	<i>Salt beginning to precipitate</i>	<i>Composition of salt</i>
100	Calcite	CaCO ₃
32.22	Gypsum	CaSO ₄ · 2H ₂ O
12.13	Halite	NaCl
2.45	Astrakhanite	Na ₂ SO ₄ · MgSO ₄ · 4H ₂ O
2.18	Epsomite	MgSO ₄ · 7H ₂ O
1.96	Kainite	MgSO ₄ · KCl · 3H ₂ O
1.63	Hexahydrate	MgSO ₄ · 6H ₂ O
1.22	Kieserite	MgSO ₄ · H ₂ O
1.18	Carnallite	KCl · MgCl ₂ · 6H ₂ O
0.93	Bischofite	MgCl ₂ · 6H ₂ O

Source: W. F. McIlhenny and M. A. Zeitoun (1969) "A chemical engineer's guide to seawater", *Chemical Engineering* Vol. 76, No. 25, pp. 251-256.

A further factor affecting the production of chemicals from seawater is the net rate at which water evaporates, which is directly proportional to the yield of chemicals. This net evaporation rate is a function of liquid

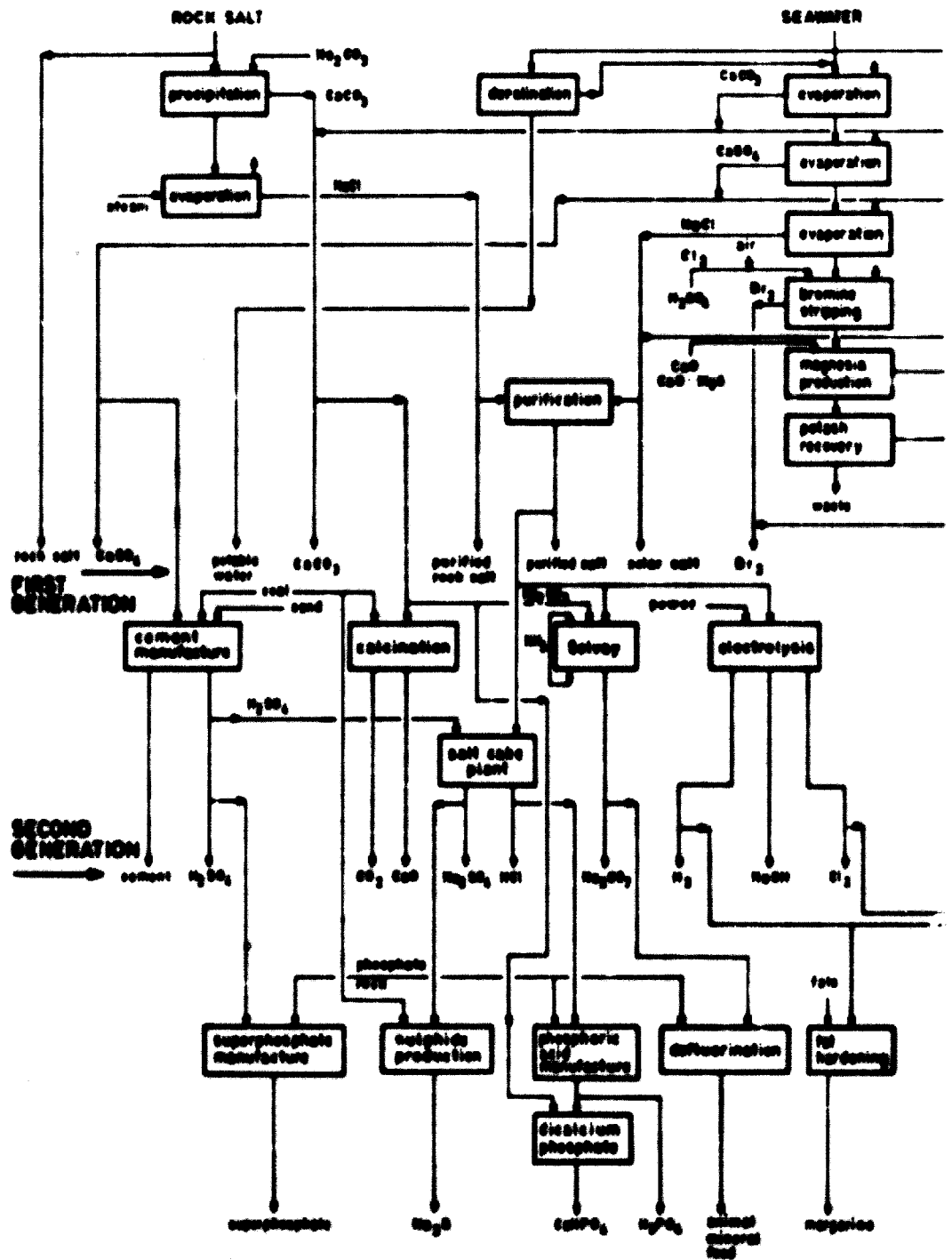
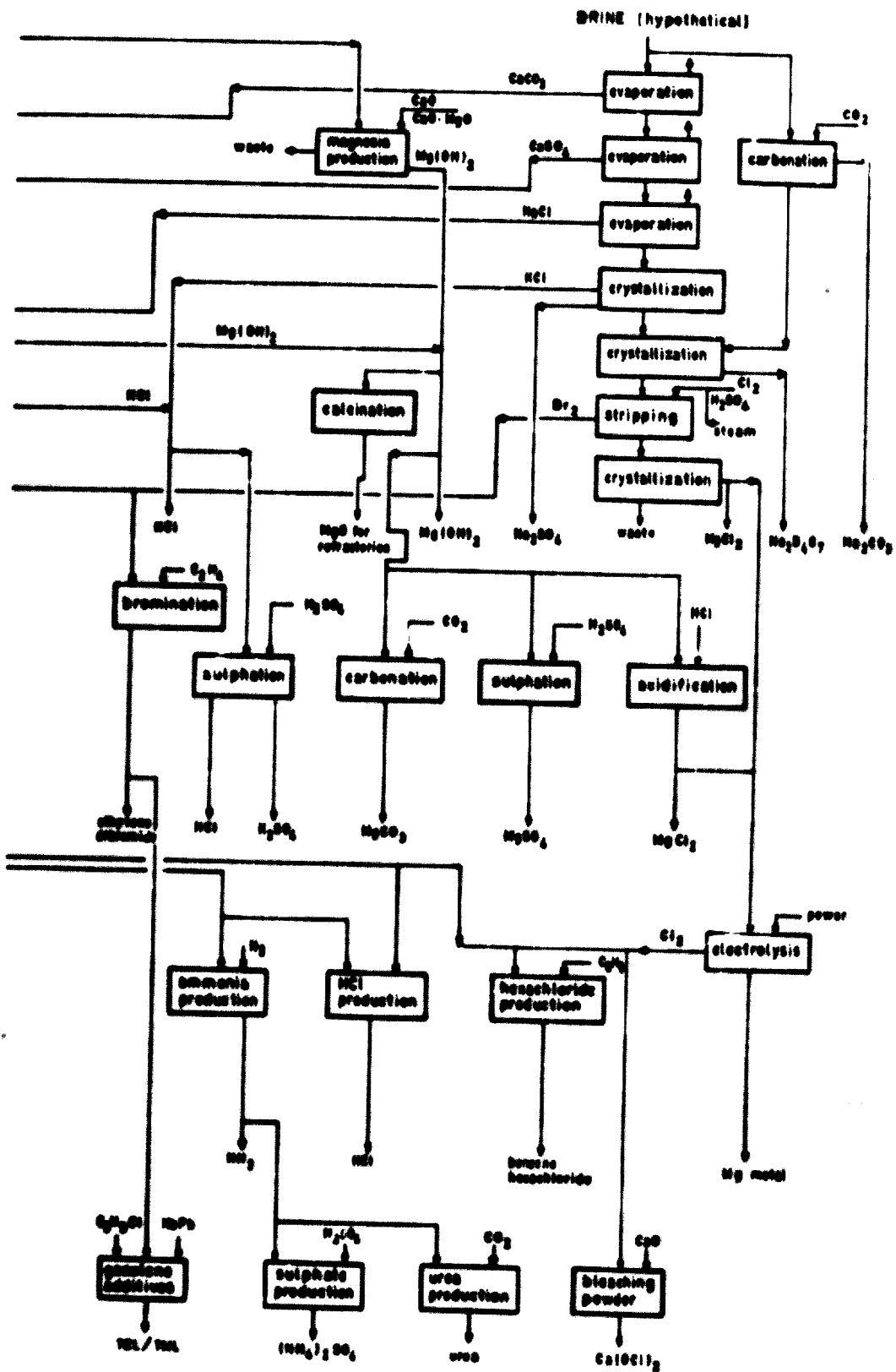


Figure 1: Extraction of industrial chemicals from



seawater, rock salt deposits and inland brines

temperature, wind velocity, relative humidity of the air, precipitation and rate of absorption of solar radiation. All of these can vary widely over the time required for the precipitation of salts. Table 7 gives data on absorption of solar radiation.

From table 7 it can be calculated that an evaporation rate of 1 cm/day requires an average solar radiation absorption rate of 4,180 Btu/ft² · day (11,300 kcal/m² · day). From this table it is also clear that evaporation rates of economic significance are not restricted to tropical and subtropical regions; even in temperate regions the rates are within the limits of economic viability.

TABLE 7. INCIDENCE OF SOLAR RADIATION ON HORIZONTAL SURFACES AND EVAPORATION RATES IN TEN LOCATIONS

	Incident solar radiation		Evaporation rate (cm/day)
	Range (Btu/ft ² · day) ^a	Average (Btu/ft ² · day) ^a	
Dead Sea	—	6,270	1—2 (accelerated)
El Paso, Texas	1,200—2,730	2,030	0.485
Algeria	1,460—2,400	2,000	0.477
Poona, India	1,430—2,690	1,980	0.473
Phoenix, Arizona	1,061—2,710	1,925	0.460
Messina, South Africa	1,340—2,320	1,875	0.447
Nice, France	571—2,525	1,500	0.358
Salt Lake City, Utah	443—2,192	1,442	0.345
Boston, Massachusetts	502—1,938	1,240	0.296
London	181—1,740	882	0.210

^a To convert to kcal/m² · day, multiply by 2.7125.

The over-all range of chemicals obtainable from seawater, brines and rock salt deposits, together with second-generation products, is shown in figure 1.

Chapter 2

CHEMICALS FROM SEAWATER, INLAND BRINES AND ROCK SALT DEPOSITS: GENERAL CONSIDERATIONS

LAKES, WELLS AND OTHER INLAND BRINES

In contrast with salts in seawaters, which have a basically uniform composition and vary only in concentration, salts in salt lakes, wells and dried-up deposits are characterized by the wide variety of both their composition and concentration. No central index of such lakes exists for any country, and data for individual lakes, wells etc. are scattered widely through the literature. The most comprehensive single source of data is the compilation by Clarke (1924). [8] Other chemical analyses are given in Meglis (1961). [9] The absence of such data on a country basis presents a major problem in the selection of the most suitable locations and sources of recovery of chemicals.

Clarke [8] gives data on lakes in North, Central and South America, the USSR, Africa, India, Australia and the Dead Sea (Israel). Also given are data on wells, ranging from predominantly NaCl brines through Na_2SO_4 and FeSO_4 and mixed sulphate, chloride and carbonate brines. These waters are classified as:

- Chloride waters (containing Na and Ca);
- Sulphate waters (containing Na, Ca, Mg, Fe or Al);
- Sulphato/chloride waters;
- Carbonate waters (containing Na or Ca);
- Sulphato/carbonate waters;
- Chloro/carbonate waters;
- Triple waters;
- Siliceous waters;
- Boron waters;
- Nitrate waters;
- Phosphate waters;
- Acid waters.

In contrast with seawater, the total concentration of salts in landlocked bodies of water and, more particularly, the relative concentrations of different salts, can vary widely, as shown in table 8. [10]

TABLE 8. CONCENTRATIONS OF MATERIALS IN WATER FROM THE OPEN SEA AND FROM THREE LANDLOCKED BODIES OF SALT WATER
(Parts per million)

	Seawater (from Table 1)	100 m below surface of Dead Sea	Great Salt Lake	Caspian Sea
Na	10,760	32,000	67,300	3,200
Mg	1,294	35,700	5,600	7,3
Ca	413	12,700	300	297
K	387	6,400	3,400	70
Cl	19,353	178,600	112,900	5,500
SO ₄	2,436	400	13,600	2,970
HCO ₃	140	trace	200	48
Br	67.3	5,200	100	
Li	0.17		40	
Others	18.3			
TDS	35,000			
Specific gravity	1.0243			

Source: K. S. Speigler (1962) *Salt Water Purification*, Wiley, New York.

Because of the wide variations in their concentration and composition, there cannot be a standard method for treating lake water and well brines; each source must be evaluated individually. While an approximate assessment of the yields and composition of the various fractions can be deduced theoretically, the presence of a number of chemical species and varying concentrations necessitates practical studies on evaporation and crystallization for the proper assessment of the technology needed to exploit these sources efficiently.

ROCK SALT DEPOSITS

Extensive deposits of rock salt are found throughout the world, and about 30 per cent of the total salt production in the United States in 1968 was from this source. [3] The two principal methods for recovering rock salt are:

By direct dry mining of the strata, if they are relatively close to the surface;

By wet mining, i. e. dissolving the salt *in situ* by pumping in fresh water and pumping up the resultant brine.

The purity of the mined rock salt varies widely, according to the locality, and can reach 98.5 per cent, as compared with 98 per cent for salt derived from seawater. The salt produced by either method can be crystallized, recrystallized or sold in the raw state, or it can be used as a feedstock in the chemical industry. The use of Na, Cl₂ etc. as a feedstock is discussed further in chapter 3.

The transport of salt as brine for further processing is being practised on an increasing scale and over increasing distances. Its transport by long pipelines of 80 km and more in length is not uncommon on the Gulf Coast of the United States. An 80-km pipeline of 25-cm diameter is being installed by Hooker Chemicals from a ten-well brine-producing unit to carry brine to its Niagara Falls chlorine/caustic soda manufacturing facility. The brine is obtained from the wet mining of rock salt deposits. The pipeline will deliver 95 per cent saturated brine solution at the rate of 13.55 m³/hour.

DESALINATION OF SEAWATER

In the production of salts from seawater, over 90 per cent of the water initially present must be evaporated before precipitation takes place in economic quantities. Obviously, great economies can be realized if such salt production is associated with desalination plants that produce drinking water from the sea.

This dual function is being implemented in at least one desalination plant (Kuwait), where the concentrated brine leaving the plant is utilized to produce, daily, 4 tons of chlorine, 7 tons of common salt, 4 tons of caustic soda and 2 tons of hydrochloric acid. The production of 300 tons of common salt per day is contemplated in Aruba (Netherlands Antilles). [6]

Potable water should contain not more than 500 ppm TDS, but levels up to twice this value are tolerated, and in some cases water of up to 2,000 ppm TDS is consumed where no other source is available. Upper limits of 5,000 ppm for cattle and 8,000 ppm for sheep are indicated. Water for agricultural use is limited to 2,500 ppm, with a limit of half this quantity for most crops. [11]

The largest desalination plant in the world, at Tijuana, Mexico, has a capacity of 28,400m³/day. Plants with a capacity of about 113,000 m³/day are under construction in the USSR. Designs for a 757,000 m³/day plant are now being prepared for the US Office of Saline Water (OSW). [12] Plans for 378,500 m³ and 576,750 m³/day units already exist. In all of these large plants, water is recovered by distillation; that is, the seawater is heated and evaporated, and the water vapour produced is condensed and represents the product of the plant. If no pretreatment of the feedwater is carried out, the residual water from the plant will contain all the original salts at a higher concentration, which will be a function of the percentage of water evaporated. The desalination plant at Freeport, Texas, recovers 67 per cent of the seawater feed as distillate, and the concentration of salts in the residual water is therefore increased by a factor of 3.0 to 3.3. [13] If the residual water were not returned to the sea but were used for recovery of chemicals, the economic benefit would be twofold:

The cost of power for pumping water from the sea to the desalination plant could be apportioned between the desalinated water and the chemicals produced from the residual water.

The capital cost of the plant for treating water having 116,000–149,000 ppm TDS would be considerably lower than that for a plant for treating 35,000 ppm seawater.

A plant to produce 757,000 m³/day, with 70 per cent recovery as desalinated water, would require a feed of 1,080,000 m³/day of seawater, and the concentrated feed for the chemicals plant would be 323,000 m³/day. With 70 per cent recovery of the salts, the plant would have an annual production as shown in table 9.

TABLE 9. TYPICAL YIELD OF CHEMICALS FROM DESALINATION PLANT WITH FEED OF 1,080,000 m³/DAY

<i>Product (tons)</i>	<i>Per cent US production, 1968</i>
8.25 million NaCl	{ 22 % of total salt production 165 % of evaporated salt production 65 % of rock salt production
590,000 MgO	92 %
206,000 KCl (128,000 K ₂ O equivalent) ..	4.8%
18,200 Br ₂	11.3%

This output is so great that it is most unlikely to be implemented in full owing to the distance from the markets for most of the MgO and NaCl. The total quantity of KCl could probably be marketed in the immediate future, but disposal of the Br₂ would encounter difficulties because of the expected overproduction of this material in the next few years. However, it would be useful to consider the market potential of desalination plant effluent as a source of chemicals.

Since the concentration of salts in the desalination plant effluent would be three times that of seawater, the equipment to handle the equivalent of 1,080,000 m³/day would be smaller by a factor of 3, and the power consumption required for the initial daily feed of 1,080,000 m³ would be halved if allocated equally between the desalination plant and the chemical complex. Assuming that the cost of this chemical complex follows the six-tenths rule for capital costs, its cost, relative to the cost of a conventional chemical complex to handle 1,080,000 m³ of normal seawater per day, would be

$$\frac{1}{3^{0.6}} = 0.49.$$

This calculation refers only to those sections of plant whose size is proportional to the volume of seawater handled, such as:

Seawater pumps, pipelines and primary evaporation pans for solar evaporation of seawater up to NaCl precipitation;

Seawater pumps, pipelines and primary chlorination of seawater for bromine recovery;
Seawater pumps, pipelines, pretreatment, reaction and settling sections of magnesia from seawater installation.

The cost of power would be 50 per cent of that for the conventional chemical complex, as would the cost of power for the desalination plant. However, if the scale of operation of the chemical complex were less than the full output of available chemicals in the desalination plant effluent, the cost-scale factor would still apply, as it is independent of absolute size, but the saving in power costs would vary and would be less for a smaller plant.

The power required per 1 m³/hour of desalinated water at 15 m head and 60 per cent pump efficiency is 0.1 kW and, at \$0.0051 per kWh, represents a cost of \$0.0005/m³. The cost of demineralized water from a 189,000 m³/day desalination plant is estimated at \$0.0872/m³. The percentage reduction will, therefore, be 0.6 per cent on the cost of the water, which is not significant. For the 757,000 m³/day desalination plant, the power required for pumping the equivalent amount of seawater would be 3,050 kW, and at the above price would represent an annual cost of \$123,000 per year of 330 days, up to 50 per cent of which could be charged to the chemical complex.

CHEMICALS FROM THE PRETREATMENT OF DESALINATION PLANT FEEDWATER

If raw seawater is fed to a desalination plant using the evaporative process, scale consisting of calcium sulphate (CaSO₄) and calcium carbonate (CaCO₃) very quickly forms a coat on the water side of the tubes of the evaporator and reduces the flow of heat from the steam to the boiling seawater by reducing the heat-transfer coefficient. The first method used to control this scale was the addition of polyphosphates, their effect being to convert the previously hard scale to a sludge, which was periodically removed by acid treatment. This procedure permitted the temperature of the brine to be raised from approximately 82° to 88° C, with a resultant higher efficiency. A further development was the continuous injection of acid to control the pH of the brine; this acid treatment permitted brine temperatures of up to 120° C to be employed. This was effected by converting CaCO₃ to CaSO₄ and de-gassing the CO₂ produced. Further work on descaling to permit higher brine temperatures, approaching the optimum of 175° C, [13] has produced a variety of methods for scale prevention, some of which result in the production of by-product chemicals of economic importance.

The lime-magnesium carbonate process was devised to remove the bulk of the calcium from seawater. It effectively removes 88 per cent of the calcium from the water and increases the magnesium content by approximately 15 per cent. The process has already been tested on a pilot-

plant scale and is now being incorporated in the full-scale plant at San Diego. However, it offers little in the way of producing salable chemicals from seawater, except perhaps in areas of limestone deficiency.

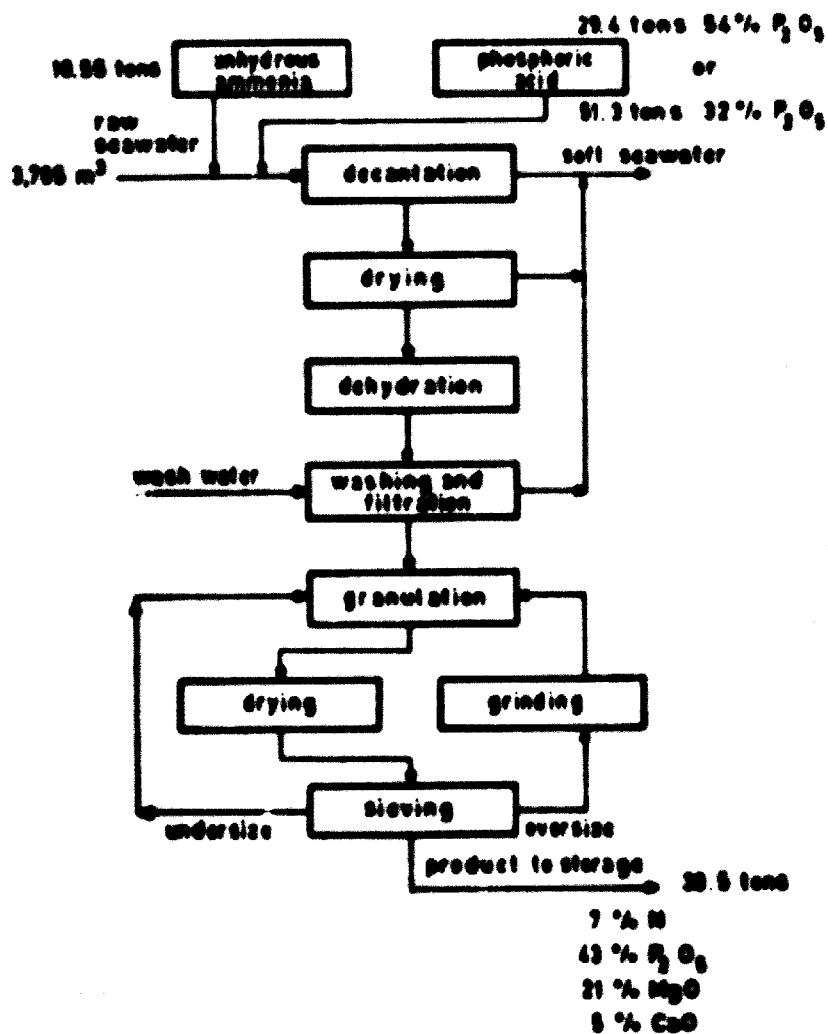


Figure 2: Production of fertilizers from seawater: the Grace process

A method of reducing scale-forming materials from the seawater feed, and at the same time producing salable by-products, is the Grace process for the production of chemicals from seawater as shown in figure 2. [14, 15] The process consists of adding the requisite proportions of ammonia and phosphoric acid to seawater. These precipitate an ammonium-magnesium-calcium-phosphate complex that is settled out from the bulk of the seawater by decantation. The seawater, which has been softened by the removal of the calcium and magnesium, is now a suitable feedstock for the desalination plant. The settled salt complex is washed with fresh water to remove residual occluded seawater, filtered, granulated, dried and sieved ready for packing and shipping. The undersize from the sieve is returned to the

granulator, as well as the oversize, which is recycled through a crusher. The production per 3,785 m³ of seawater is 33.5 tons of a salable fertilizer with the following composition: 7 per cent N, 43 per cent P₂O₅, 21 per cent MgO, and 5 per cent CaO.

On this basis the process will recover 70 per cent of the magnesium and 93 per cent of the calcium originally present in the raw seawater and thus reduce the scale-forming potential of the water going to the desalination plant. The 757,000 m³/day desalination plant considered above would have an annual production of about 3.2 million tons of chemical fertilizer, which would be a considerable contribution to the fertilizer production of any country. Furthermore, if the desalination plant were coupled to a chemical complex as outlined above, the production of potassium salts from the seawater complex would permit production of a wide range of NPK fertilizers, suitable for many agricultural purposes.

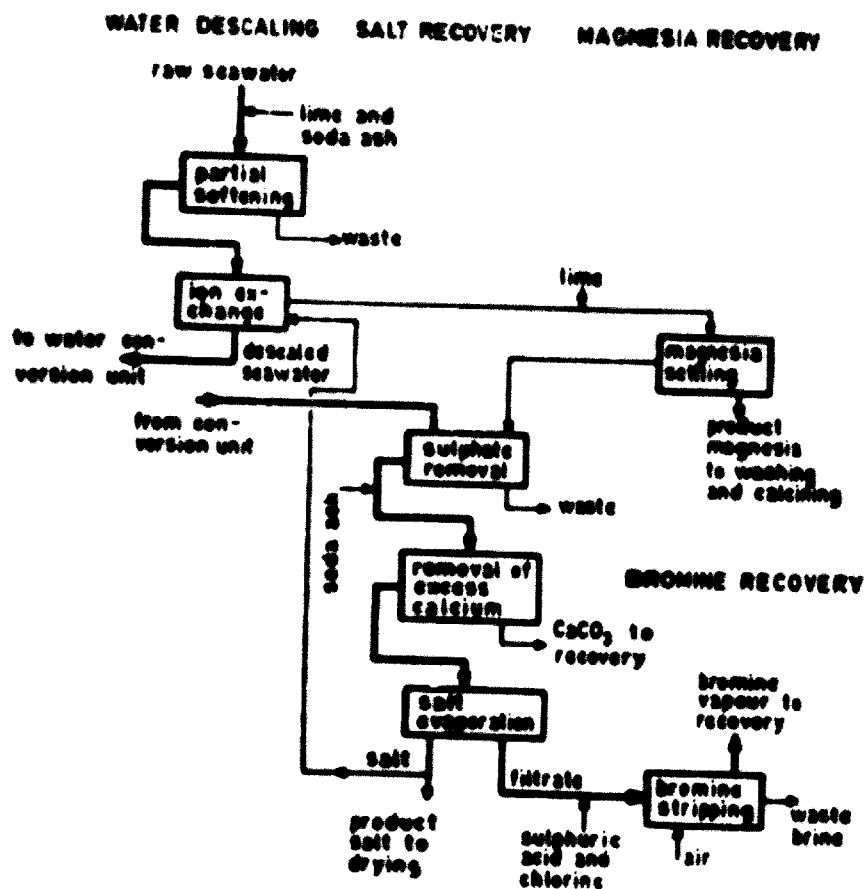


Figure 3: Recovery of chemicals from seawater: scheme 1

Two other processes for pretreating the feed to desalination plants to remove scale-forming compounds, and at the same time for treating a concentrated effluent from the desalination plant, are described by Weinberger and de Lapp [16] and are shown diagrammatically in figure 3 and figure 4. The process shown as scheme 1 (figure 3) softens the water

feed to the desalination plant by converting the relatively soluble calcium bicarbonate to the insoluble calcium carbonate, together with precipitating metals such as iron and aluminium. After settling, the treated water goes to an ion-exchange resin, where magnesium and the residual calcium are absorbed and replaced in the water by sodium, this treated water being the feed to the desalination plant.

Regeneration of this ion-exchange resin by a sodium chloride solution will yield a solution rich in magnesium chloride from which the magnesium can be recovered as the hydroxide by treating with lime and/or dolomite. The precipitated magnesium hydroxide is then treated in the conventional way for the production of magnesia. The effluent from the magnesium-recovery unit contains calcium and sodium chlorides and is mixed with the concentrated effluent from the desalination plant containing sulphates. (On mixing, calcium sulphate is precipitated and removed by settling. The clarified liquor remaining after removal of the sulphate is treated with sodium carbonate to precipitate the remaining calcium as carbonate, which is washed, dried and preferably sold or, alternatively, in the absence of a supply of local limestone calcined and used for magnesium recovery. The calcium-free brine is then evaporated to produce purified salt and distilled water. After the salt recovery, the brine can be treated for bromine recovery by acidification and chlorination.

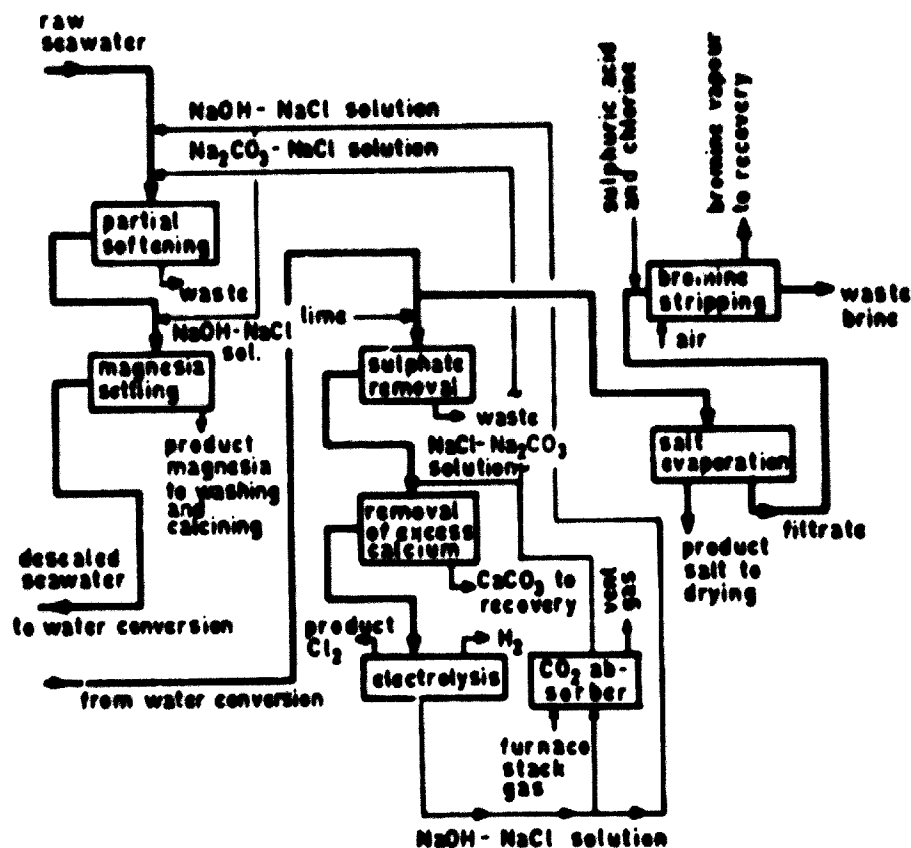


Figure 4: Recovery of chemicals from seawater: scheme 2

The process shown as scheme 2 (figure 4) also descales the seawater by the addition of sodium carbonate and caustic soda to precipitate the calcium as carbonate. After settling out the carbonate, the treated water is mixed with an additional hydroxide solution to precipitate the magnesium as hydroxide, which is then treated in the normal way for magnesia recovery; the settled water from this operation is used to feed the desalination plant.

The concentrate from the desalination plant is divided into two streams: one going for bromine recovery in the conventional way or, alternatively, for the production of salt; the other being treated, first, with lime to precipitate calcium sulphate and then, after settling, with sodium carbonate to remove the residual calcium as carbonate. This purified solution, if of the right concentration, can be fed directly into the electrolytic cells for conversion to chlorine and hydrogen or, if dilute, be used to dissolve additional solid purified salt to bring it up to the correct concentration for electrolysis. The residual liquor from electrolysis is then concentrated to produce strong caustic soda. The sodium chloride precipitated during the concentration of this caustic soda is either recycled to the electrolytic cells or dried and sold as such. Alternatively, as is shown in figure 4, some of the caustic soda could be recycled back to the raw seawater.

According to Weinberger and de Lapp [16], the economics of the process are shown in table 10, and the credits shown for the by-products should be offset against an estimated cost of approximately \$0.265/m³ for desalinated seawater at 1964 prices.

TABLE 10. ECONOMICS OF BY-PRODUCT RECOVERY FOR A 37,850m³/DAY SEAWATER CONVERSION PLANT^a

<i>Alternative (Maximum recovery of magnesia and bromine is assumed for all three alternatives)</i>	<i>By-product credit (\$/ton fresh water)</i>	<i>By-product recovery plant investment (\$)</i>
1. All salt sold as refined product	0.129	14,000,000
2. 40% of salt sold as refined; remainder as brine (\$ 3.70/ton)	0.052	11,000,000
3. 40% of salt sold as refined; remainder as brine (\$ 1.85/ton)	0.052	11,000,000
4. Bitterns	0.025	

^a See figure 3.

Source: A. J. Weinberger and D. F. de Lapp (1965) "Saline water conversion and its by-products", *Chemical Engineering Progress*, Vol. 60, No. 11, pp. 56-59.

The most recent process to be studied for the treatment of feedwater for desalination plants is the desulphating process, which was originally developed by the Metallurgy Research Center of the Bureau of Mines, which is part of the US Department of the Interior, in Salt Lake City, Utah. The process, covered by a US patent, [17] was originally developed for the removal of sulphates from brines of the Great Salt Lake as a first step in the recovery of mineral values from these brines. It has subsequently

been adapted to the desulphation of seawater [18] and has reached the pilot-plant stage. This pilot plant has been in operation at the Office of Saline Water (OSW) testing station at Wrightsville Beach, N. C., since early 1970. A commercial plant design for desulphating 283,000 m³/day of seawater has been developed by Catalytic Inc., Philadelphia, Pa. [19] A block flow diagram of this process is shown in figure 5. It consists of six stages, as follows:

1. Bringing the brine into contact with the barium form of cation-exchange resin. This removes the sulphate ions and carbonate ions as barium salts, converting the resin to the sodium form.
2. Separating the desulphated and decarbonated brine from the resin and precipitated salts. The separated brine is the feedwater for the desalination plant.
3. Converting the barium precipitate by roasting in a reducing atmosphere to a soluble barium form. For this purpose, the barium precipitate is compounded with carbon (e. g. pulverized coal).
4. Leaching the calcine to dissolve the soluble barium salts, forming barium hydrosulphide and barium hydroxide. By conducting this operation in a hydrogen sulphide atmosphere, all the barium present is converted to the hydrosulphide.
5. Regenerating the sodium form of the resin with the soluble barium salts.
6. Recovering by-product hydrogen sulphide and sodium bicarbonate from the solutions leaving the regeneration step.

The chemistry is as follows:

Step

1. $\text{Na}_2\text{SO}_4 + \text{BaR}_2 \rightleftharpoons \text{BaSO}_4 + 2\text{NaR}$, where R = resin
3. $\text{BaSO}_4 + 4\text{C} \rightleftharpoons \text{BaS} + 4\text{CO}$
4. $2\text{BaS} + 2\text{H}_2\text{O} \rightleftharpoons \text{Ba}(\text{HS})_2 + \text{Ba}(\text{OH})_2$
5. $\text{Ba}(\text{SH})_2 + \text{Ba}(\text{OH})_2 + 4\text{NaR} \rightleftharpoons \text{BaR}_2 + 2\text{NaOH} + 2\text{Na}(\text{HS})$
6. (a) $2\text{NaHS} + 2\text{CO}_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{NaHCO}_3 + 2\text{H}_2\text{S}$
 (b) $2\text{NaHCO}_3 \rightleftharpoons \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$
 (c) $2\text{H}_2\text{S} + \text{O}_2 \rightleftharpoons 2\text{S} + 2\text{H}_2\text{O}$
 (d) $\text{H}_2\text{S} + 2\text{O}_2 \rightleftharpoons \text{H}_2\text{SO}_4$

An economic assessment for a 189,000 m³/day desalination plant based on this process indicates that the treatment plant can generate sufficient revenue from the sale of the by-products to defray all the operating costs of both the treatment and seawater distillation plants. [18] An additional advantage claimed for the desulphating process is that the elimination of the sulphate facilitates the recovery of potassium and magnesium chlorides from the bitterns formed after the precipitation of NaCl by eliminating the formation of complex single and double sulphates during solar evaporation.

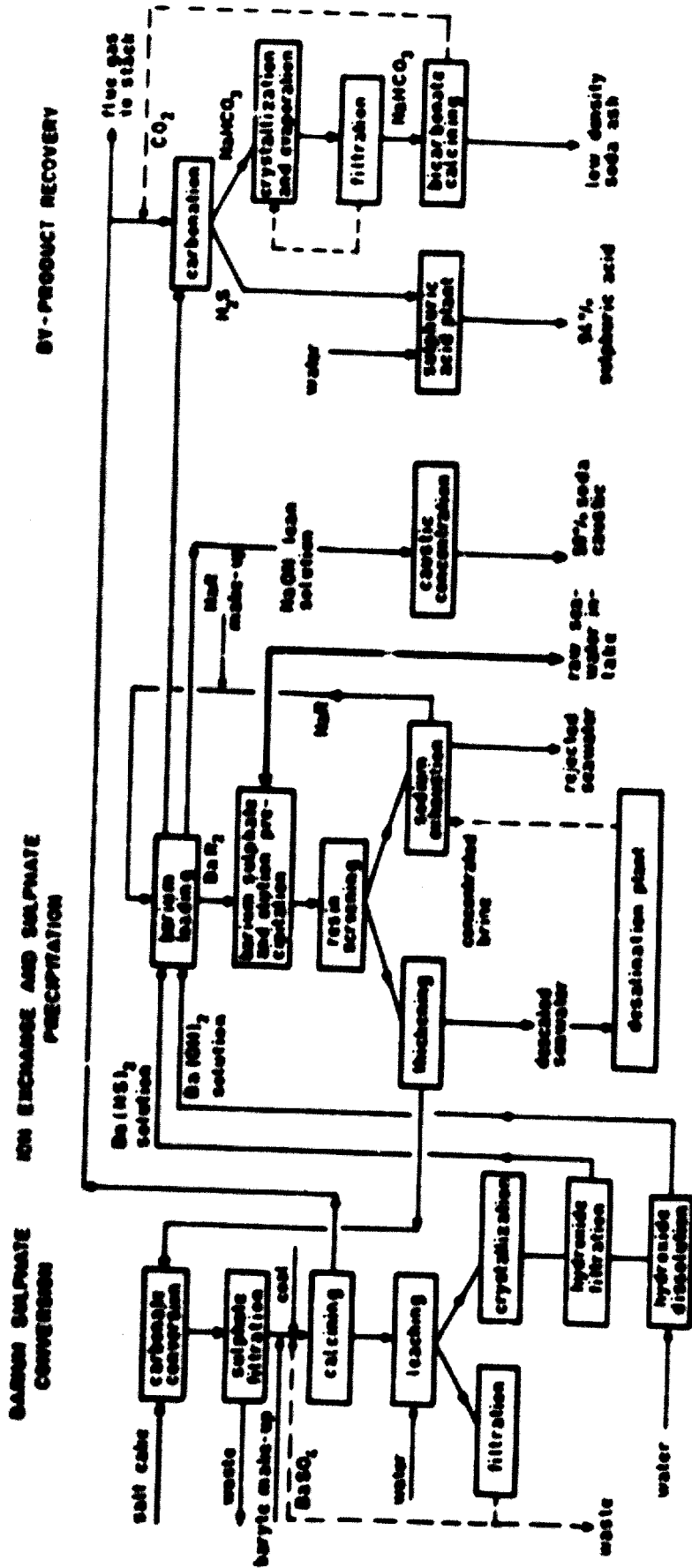


Figure 5: The brine desulfating process

Chapter 3

CHEMICALS FROM SEAWATER, INLAND BRINES AND ROCK SALT DEPOSITS: FIRST GENERATION

SODIUM CHLORIDE

In addition to being a basic nutrient for humans, animals and plants, sodium chloride (NaCl) is probably the most widely used industrial chemical. It is used directly in the dairy and pickling industries and in the preservation of meat and fish, in water-softening plants, and in ice and snow removal. It is also used as the basic raw material in the production of such chemicals as NaOH, Na_2CO_3 , Na_2SO_4 , Cl_2 and HCl, which in turn are starting materials or intermediates for a host of other applications.

The sodium chloride produced is used approximately as follows:

- 60 per cent for the chemical manufacturing industry, of which 42 per cent is for NaOH and Cl_2 ;
- 17 per cent for synthetic soda ash (Na_2CO_3);
- 6 per cent for other chemicals;
- 14 per cent for ice and snow removal;
- 3 per cent for table salt.

Table 11 gives the world production of sodium chloride and the United States production of both sodium chloride and rock salt during the five years 1964—1968.

TABLE 11. WORLD AND US PRODUCTION OF SODIUM CHLORIDE AND US PRODUCTION OF ROCK SALT, 1964—1968
(Thousand tons)

	Sodium chloride		Rock salt
	World production	US production	US production
1964	98,500	28,600	7,760
1965	108,200	31,400	8,800
1966	110,000	32,200	9,100
1967	119,000	35,300	10,550
1968	113,000	37,400	11,200

Source: Bureau of Mines, United States Department of the Interior (1969), *Minerals Yearbook, 1968*, Government Printing Office, Washington, D. C.

Table 12 gives the breakdown of the US production of sodium chloride during 1967 and 1968 according to method of recovery.

TABLE 12. US PRODUCTION OF SODIUM CHLORIDE IN 1967 AND 1968 ACCORDING TO METHOD OF RECOVERY
(Thousand tons)

Method	1967	1968
Evaporation of seawater	4,780	5,000
Mining (wet and dry) of rock salt	10,550	11,280
Evaporation of inland brines	19,970	21,120
Total ...	35,300	37,400

Source: Bureau of Mines, United States Department of the Interior (1969), *Minerals Yearbook, 1968*, Government Printing Office, Washington, D. C.

SALT FROM SEAWATER BY EVAPORATION

As shown in table 4, only a relatively small proportion (29%) of the world's total salt production is based on seawater. For countries with warm climates and a seasonal or annual evaporation exceeding precipitation, the production of solar salt is practicable; in fact, this method has been used since prehistoric times and is practised throughout the tropical and subtropical regions of the world.

To produce salt from seawater approximately 90 per cent of the water present must be evaporated, and the only large-scale economic method available for such dilute solutions is the use of solar heat. An evaporation rate of 1 cm/day requires an absorption rate of 4,180 Btu/ft²·day (11,300 kcal/m²·day), which indicates a thermal efficiency of approximately 50 per cent. This evaporation rate can be increased by the addition of black sand or dye, [20] with consequent increases in the yield per unit area of evaporation surface.

Commercial exploitation of seawater for salt and/or chemical products requires a supply of seawater with a constant composition close to (or if possible, higher than) the mid-ocean value and free of any sources of dilution, such as springs or rivers. In addition, a large area of level land adjacent to the sea with a relatively impervious structure is necessary in order to minimize the loss of water by seepage.

As shown in table 6, the evaporation of seawater results initially in the precipitation of CaCO₃ and further concentration of the water precipitates CaSO₄.

If sodium chloride is allowed to precipitate without the prior removal of the precipitated carbonate and sulphate, the resultant salt will be a crude, dark-coloured product contaminated with these materials, together with iron and suspended matter present in the original seawater. Although such salt may be suitable for curing fish etc., it would be of little value for

table use or as a chemical raw material. Reference to table 6 shows that if, following precipitation of the sodium chloride, the mother liquor is not removed, the salt will be contaminated by mixed salts of potassium, sodium and magnesium, all of which would result in further contamination.

The production of solar salt with optimum purity thus requires the following six stages:

1. Pumping of the brine from the sea into primary evaporating lagoons.
2. Concentration of the brine in these lagoons to precipitate calcium carbonate and calcium sulphate.
3. Removal of the brines to fresh lagoons and the continuation of evaporation.
4. Precipitation of salt in these lagoons.
5. Removal of the mother liquor from the lagoons before precipitation of the mixed sulphates of sodium and magnesium for recovery of further salts or for return to the sea.
6. Harvesting of the salt from the lagoons.

Figure 6 shows a typical plant for the production of high-grade, unrefined solar salt. Such plants are described in detail in the literature, [1] and their operation is summarized below.

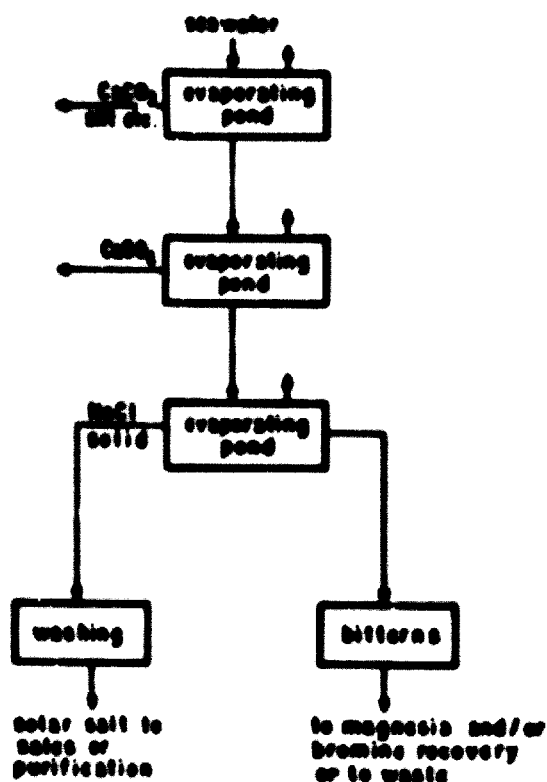


Figure 6: A typical plant for the production of high-grade, unrefined solar salt from seawater

Seawater is pumped to primary evaporators/settlers at the beginning of the hot, dry season. Here any suspended matter, such as silt, clay and silica, settles out and evaporation commences. After settling is complete, the brine is decanted to secondary ponds, where evaporation continues. When the brine reaches a specific gravity of approximately 1.057, precipitation of the calcium carbonate begins and proceeds until the brine reaches a specific gravity of 1.068. At this point the brine is drawn off to additional ponds and evaporation continues until the brine reaches a specific gravity of 1.193.

During this period most of the calcium sulphate in the brine has been precipitated, and the calcium sulphate-free brine is again decanted to the crystallizing ponds proper, where the precipitation of relatively pure sodium chloride proceeds and evaporation continues until the brine reaches a specific gravity of 1.257.

If the brine were allowed to continue to evaporate in this pond, the salt produced would become contaminated with magnesium sulphate, so at this stage the evaporation is interrupted by drawing off the brine into the bitterns pond. The precipitated sodium chloride remaining in the pond is reasonably pure, with a small percentage of magnesium and calcium chlorides.

The primary evaporators/settlers are refilled with fresh seawater, as the previous settled batch has been transferred to the secondary ponds, and thus there is a continuous intake of seawater to the plant. Similarly, as soon as the secondary ponds are emptied, they can be refilled in turn from the evaporators/settlers, with further evaporation and precipitation of the calcium carbonate and calcium sulphate. At the end of the season the accumulated deposits of calcium carbonate and calcium sulphate are removed, either by washing them back into the sea with seawater or by scraper conveyor for stockpiling as starting materials for second-generation products. The calcium carbonate can be dried and calcined for lime, possibly for use in precipitating magnesia from the seawater or for building purposes; the calcium sulphate finds uses in agriculture, building, or, in areas without sulphur (such as India), as a source of sulphuric acid and cement.

The precipitated sodium chloride from the final salt pond is removed by mechanical scrapers or shovels and dumped into washers where the salt is washed, in a countercurrent process, with a flow of brine from the sulphate-free pond having a specific gravity of approximately 1.094, the washing liquor being returned to the pond. The salt is washed again with seawater and finally with fresh water. The washed salt, containing approximately 99.8 per cent NaCl on a dry-weight basis, contains traces of calcium, magnesium and sodium sulphates and calcium and magnesium chlorides. This wet product is then dried, bagged and is ready for shipment as unpurified solar salt.

The number of times the ponds can be filled in each season varies from two to five, depending on the depth of the initial filling, the concentration of the seawater feed and the evaporation rate. The frequency of removal of

the calcium carbonate, calcium sulphate and sodium chloride is determined by the capacity of the equipment for further processing of the salts and on the number of basins employed at each stage of evaporation, but it is usually on a once-per-season basis.

The solar salt produced from the evaporating ponds is usually discoloured, contains insoluble matter and is hygroscopic, owing to the presence of calcium and magnesium chlorides that make it unsuitable for most purposes. Solar salt must be refined to make it suitable for table, dairy and chemical use. Refining is carried out either by dissolving and recrystallizing, using either of the two methods (vacuum panning and graining) described in the next section, or by rewashing.

Rewashing is carried out in a revolving screen partly submerged in an alkaline solution of sodium chloride. After washing, the salt is screened to separate the coarse from the fine grains, the latter being sold as fish salt, the coarse salt being used for the preparation of table and dairy salts. The washing solution, which is a solution of high-grade salt in fresh water, dissolves part of the magnesium salts and other impurities from the crude salt. The washings are made alkaline by the addition of lime and/or sodium carbonate and bicarbonate. The washed salt is dried by heating to 90° to 100°C in a stream of hot air and then ground. Additions to the salt are made for various purposes; for example, magnesium carbonate and borate are added to salt for table use to prevent caking.

The bitterns remaining after the precipitation of sodium chloride form the raw materials for the production of potassium, magnesium and, possibly, bromine; their recovery is discussed later in this chapter.

SALT FROM ROCK SALT DEPOSITS

Rock salt deposits can reach up to 99.5 per cent purity, and salt of this purity can be used directly in meat and fish preservation, pickling, water-softening plants and ice and snow removal. For human consumption and for most chemical uses, however, rock salt requires purification. Rock salt deposits contain all the components of seawater, but, owing to the differences in solubility, differential crystallization leads to stratification.

Most rock salt deposits, and especially deep deposits, are exploited by "wet", or "hydraulic", mining; that is, the salt is recovered as a solution in water and not as a solid. Hydraulic mining is normally carried out by sinking a well into the layer of salt. The well shaft contains two concentric pipes, which protrude into the salt layer at different depths. Water is pumped down the annulus between the pipes and dissolves the surrounding rock salt. The saturated solution of brine formed is pumped up the inner pipe.

The composition of this artificial brine depends upon the composition of the rock salt and the impurities in the water, and these, as well as the purpose for which the salt is intended, determine whether the brine will require pretreatment before salt production. Methods of pretreatment include air blowing to remove dissolved H_2S , if present, followed by

injection of chlorine to convert a residual H_2S to sulphur, the addition of caustic soda or soda ash to precipitate calcium as calcium carbonate, magnesium as magnesium hydroxide and iron and aluminium as their hydrates. A typical method of recovery of salt of over 99 per cent purity from rock salt deposits is shown in figure 7 and described in detail in the literature. [21]

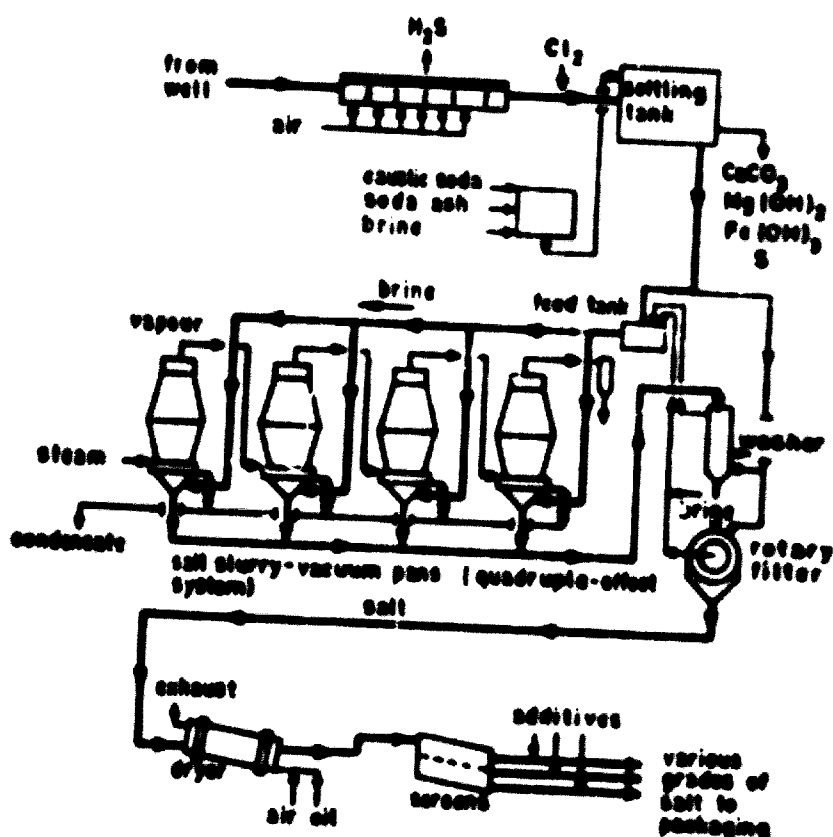


Figure 7: Salt production from rock salt deposits: vacuum-pan method

The production of granulated, or vacuum-pan, salt is achieved by feeding the settled brine from the settling tank, after removal of the precipitated matter, to a series of multiple-effect evaporators operating in parallel on the brine side and in series on the steam side. The first effect is fed with steam and operates at the highest pressure. The cold, concentrated brine solution enters the base of the evaporator, which consists of a series of steam-heated tubes inside which the brine is boiled. The boiling mixture of steam, brine and suspended salt crystals shoots up the tubes at high velocity into the space where the vapour and liquid separate, with the brine and suspended crystals returning to the base of the evaporator via a central down-comer and being recirculated through the tubes with further evaporation and concentration. The vapour separated from the brine is then fed to the steam side of the evaporator tubes on the second effect, where more water is boiled away from the brine. The process is repeated throughout the entire series of effects, the vapour from the final effect at the lowest

pressure being condensed in a condenser, thus producing the vacuum in the system.

The recirculation of the suspended crystals and the brine through the evaporator tubes results in increased evaporation of water and growth of the crystals in contact with the supersaturated brine. At a certain size the crystals are too heavy to be recirculated, and they sink to the bottom of the evaporator and are removed as a brine slurry. This slurry is washed with fresh brine to remove any precipitated calcium sulphate, and the washings, consisting of mother liquor and precipitated calcium sulphate, are returned to the feed tank. The washed salt crystals, together with brine, are then fed to rotary vacuum filters. The salt crystals are dewatered, and the filter cake is again washed with fresh brine. The filtrate and the brine washings are returned to the feed tank. Alternatively, centrifuges can be used in place of the filters. The washed filter cake is then dried in rotary dryers using oil or gas firing. The dried product, usually between 20 and 100 mesh, is screened into various grades, and additives are introduced if required for various specific uses. The product is used extensively for table salt and in many food-processing operations.

The calcium sulphate washed out of the salt is returned to the evaporators as a suspension, and nuclei of the sulphate crystals prevent scaling of the tubes for extended periods, as the nuclei form growth points for freshly deposited calcium sulphate. The suspension of salt crystals likewise prevents supersaturation of the brine solution and deposits of salt on the tubes as scale. This process produces a fine-grained product and represents the major production of salt.

For other uses, a salt crystal having a greater surface area, a lower bulk density and a faster dissolving rate is required, and for this product (grainer salt), open pans are used, as shown in figure 8. The process consists of allowing salt to crystallize slowly in a grainer, which is a long, shallow pan. The brine, slightly supersaturated, is fed to the grainer at 140°C and, during its passage along the grainer, cools to 96°C , and in doing so precipitates salt. Air is circulated over the exposed surface of the brine to assist evaporation. This method of slow cooling produces large crystals, which ultimately settle and are removed.

The cooled, separated brine at 96°C is mixed with purified make-up brine and pumped through a steam-heated exchanger, where the temperature is raised to 110°C . The hot brine is then passed over a bed of small stones on which brine supersaturated with calcium sulphate can deposit this salt on the stones, which form nuclei for crystallization of the sulphate. The bed of stones is removed periodically and washed with water to remove the calcium sulphate deposits. After passing through this stone bed, the brine is flashed down to 104°C by reducing the pressure, and the flashed vapour is removed. The brine at 104°C is slightly supersaturated when it enters the grainer, and the crystals of sodium chloride present in the grainer act as nuclei for the crystallization of the added sodium chloride and grow in the process.

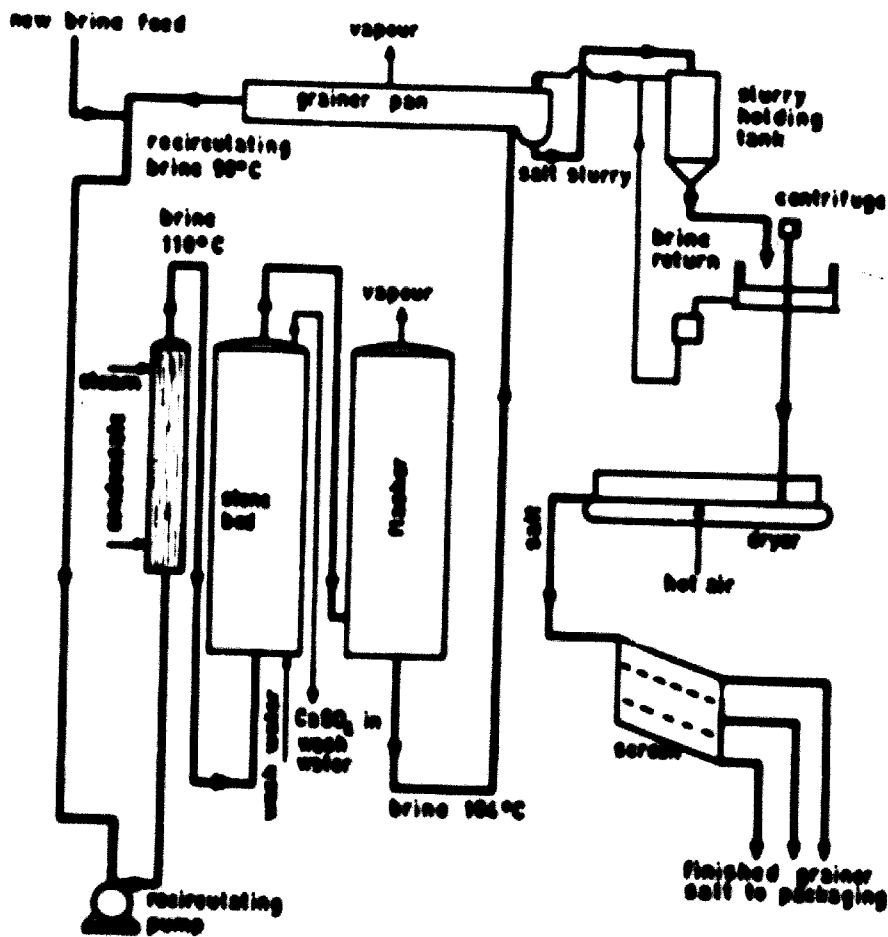


Figure 8: Salt production from rock salt deposits: grainer method

A single grainer 36.5 m long, 4.9 m wide and 0.6 m deep will produce 27.2 tons of salt per day with a brine circulation rate of 0.95 to 1.9 m³/minute. The salt from the grainer is then pumped with a special pump to minimize crystal breakage to batch centrifuges for dewatering, the brine being returned to the grainer. The centrifuged salt is dried on a deck-type dryer in a current of hot air. The dried salt is then screened and graded according to size and then bagged.

SALT FROM INLAND NATURAL BRINES AND MIXED DEPOSITS

Owing to the wide variation in the nature and composition of possible compounds of brines, there is no single method of recovering salt from them. Each source must, of necessity, be treated individually. The usual procedure consists of:

- Analysis of the constituents of the brine;
- Generalized predictions of the sequence of crystallization;

Verification of these predictions, on both laboratory and pilot-plant scales;

Commercial exploitation.

Of the many variants, one is described below as indicative of the methods adopted.

Great Salt Lake, Utah

Great Salt Lake covers an area of 2,600 km². Its dissolved salts content is shown in table 8. The brine from the lake has been used for many years for the recovery of sodium chloride by solar evaporation; at present, about 270,000 tons are produced annually. [22] Recovery of further chemicals from the bitterns after solar evaporation of the brine has, until recently, been restricted by the difficulty of separating salts from brine of such a high sulphate content.

When Great Salt Lake brine is subjected to solar evaporation, sodium chloride precipitates initially, and with further evaporation a mixture of sodium chloride, potassium chloride and the double sulphates of sodium, potassium and magnesium crystallize. Finally, kainite ($\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$) and carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) crystallize out. A considerable amount of work, both on the brine and the bitterns after salt recovery, has been carried out by the Bureau of Mines in Salt Lake City. One aspect of the desulphation of the brine before evaporation has already been noted above [17] and modified for the desulphation of seawater. [18] The main object of this work was the removal of sulphate to facilitate the later recovery of KCl from the bitterns after solar evaporation and precipitation of the sodium chloride. However, the plants now going into operation are based upon straight solar evaporation to produce K_2SO_4 and Na_2SO_4 . The process, as proposed by the Great Salt Lake Mineral and Chemical Corporation, is shown in figure 9. This proposed method is to pump brine from the lake to a 410-hectare pond and then to the main pond system, which consists of 77 ponds covering 5,100 hectares. The brine flow is controlled to precipitate mainly NaCl in the first 2,500 hectares; in subsequent ponds MgSO_4 and $\text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ are precipitated and used as feed for the salt cake (Na_2SO_4) plant. Finally, in the last group of ponds, a mixture of kainite and carnallite is precipitated and used as raw material for the potash plant. After removal of the potash, the final mother liquor is processed to obtain Na_2SO_4 .

The feed to the complex is at the rate of 230 m³/minute. The mother liquor from the solar ponds (bitterns) is finally processed for the recovery of bromine by treatment with chlorine, and, after removal of bromine, the liquor is treated by a solvent-extraction process to separate the lithium from the magnesium salts remaining in solution. These processes are yet to be proven on a large scale.

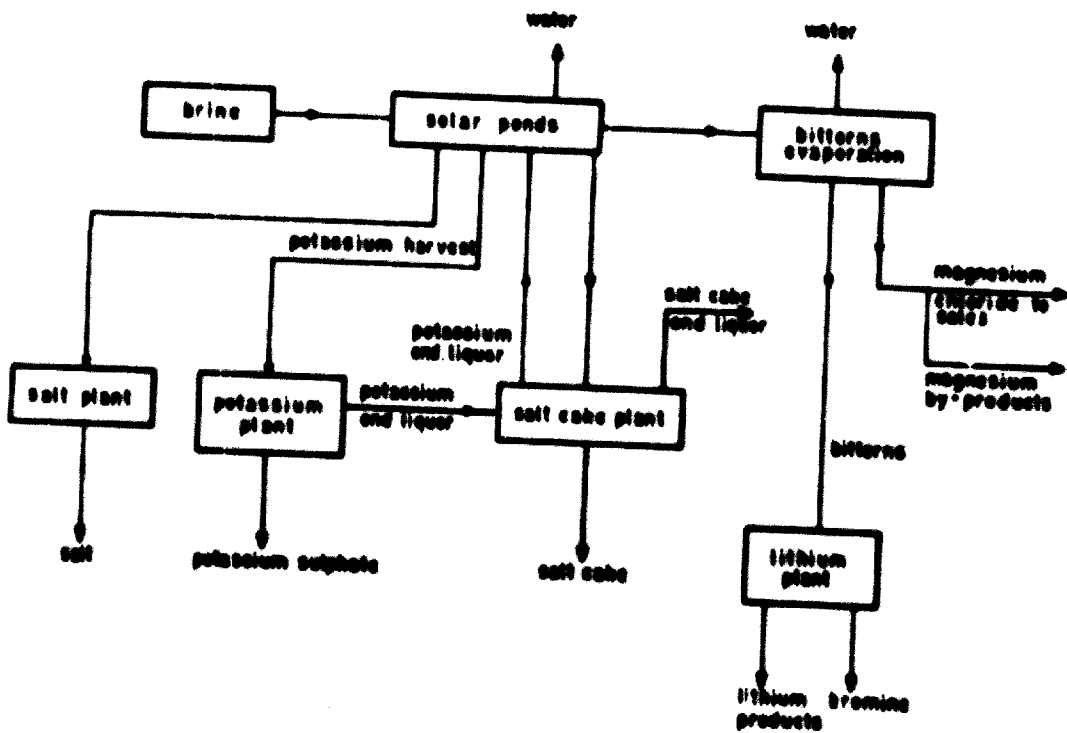


Figure 9: The Great Salt Lake Mineral and Chemical Corporation process for extracting chemicals from brine

The complex is expected to produce, annually, 180,000 tons of potassium sulphate, 90,000 to 135,000 tons of salt cake and up to 340,000 tons of magnesium chloride. The latter is subsequently converted to metallic magnesium, together with about 4,500 tons of lithium chloride and 1,800 tons of bromine annually. Subsequent operations with the brine are expected to produce, electrolytically, 41,000 tons of magnesium metal, 73,000 tons of chlorine and 43,000 tons of gypsum annually.

An alternative method of recovering potassium salts from these brines has been proposed by the Bureau of Mines. [23] This method is to recover the potassium directly from the brine or from the bitterns after the solar evaporation to product salt. These bitterns contain:

	<i>Grams per liter</i>
K	13.5
SO ₄	46
Cl	133
Na	66
Mg	22

The process proposed is shown diagrammatically in figure 10.

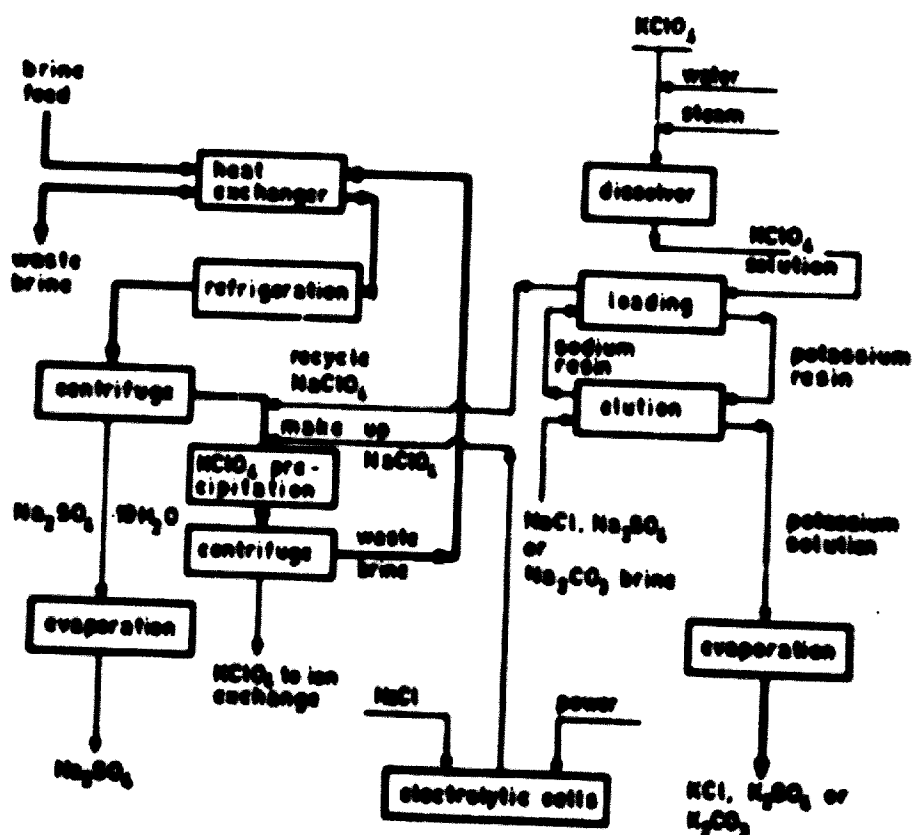


Figure 10: Method proposed by the Bureau of Mines to recover potassium salts from Great Salt Lake brines

MAGNESIUM AND ITS COMPOUNDS

The sea, certain brine wells and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) and magnesite (MgCO_3) rock provide the major sources of magnesium and its compounds. The 1968 world production of magnesite was 10.1 million tons, and that of the metal was 187,000 tons. [3]

The most important single use of magnesium compounds is for the production of magnesia (MgO). In 1968, world production, excluding that of Japan, amounted to 4.7 million tons. Japanese production amounted to 385,000 tons, giving a total world production of 5.1 million tons. The sources of the magnesia were: ores (67.7 per cent), seawater (24.9 per cent), brines (6.6 per cent) and bitterns (0.8 per cent). The major producers of magnesia are shown in table 13. [24]

In the United Kingdom, the total production of 254,000 tons of magnesia comes from one plant using seawater as a source. In the United States, seawater represents the source of 70 per cent of the annual production of 900,000 tons. In Asia and Eastern Europe, the major source of production is ore. Projects currently proposed for Ireland, Israel, Italy, Japan, Norway and Saudi Arabia are mainly based on seawater, [25] and a proposed plant to be located in the USSR on the Black Sea is also based on saline sources.

TABLE 13. SUMMARY OF WORLD PRODUCTION OF MAGNESIA
(Million tons)

<i>Africa</i>		
Total		0.060
<i>Americas</i>		
United States of America	1.096	
Mexico	0.082	
Brazil	0.072	
Canada	0.030	
	<hr/>	1.280
<i>Asia</i>		
Japan	0.400	
People's Republic of China	0.305	
People's Democratic Republic of Korea ...	0.205	
India	0.176	
	<hr/>	1.086
<i>Australia</i>		
Total		0.030
<i>Europe</i>		
Austria	0.691	
United Kingdom	0.256	
Greece	0.245	
Yugoslavia	0.245	
Czechoslovakia	0.155	
Bulgaria	0.055	
Italy	0.051	
Norway	0.051	
Spain	0.051	
Union of Soviet Socialist Republics	1.020	
	<hr/>	2.820
<i>Middle East</i>		
Turkey	0.118	
Israel	0.041	
	<hr/>	0.159
Grand total ...		5.435

Source: Fouse (1969) "World survey of deadburnt and caustic magnesia producers plant capacity", *Taihakutsu Kagaku* Vol. 21, No. 11, pp. 549-50.

Magnesia production from unconcentrated seawater

Magnesia is recovered from unconcentrated seawater in about ten plants in Europe, the United States, Mexico and Canada. The process consists of reacting either slaked lime ($\text{Ca}(\text{OH})_2$) or, preferably, slaked burnt dolomite ($\text{Mg}(\text{OH})_2\text{Ca}(\text{OH})_2$) with seawater to precipitate magnesium hydroxide. The advantage of using dolomite is that half of the magnesium

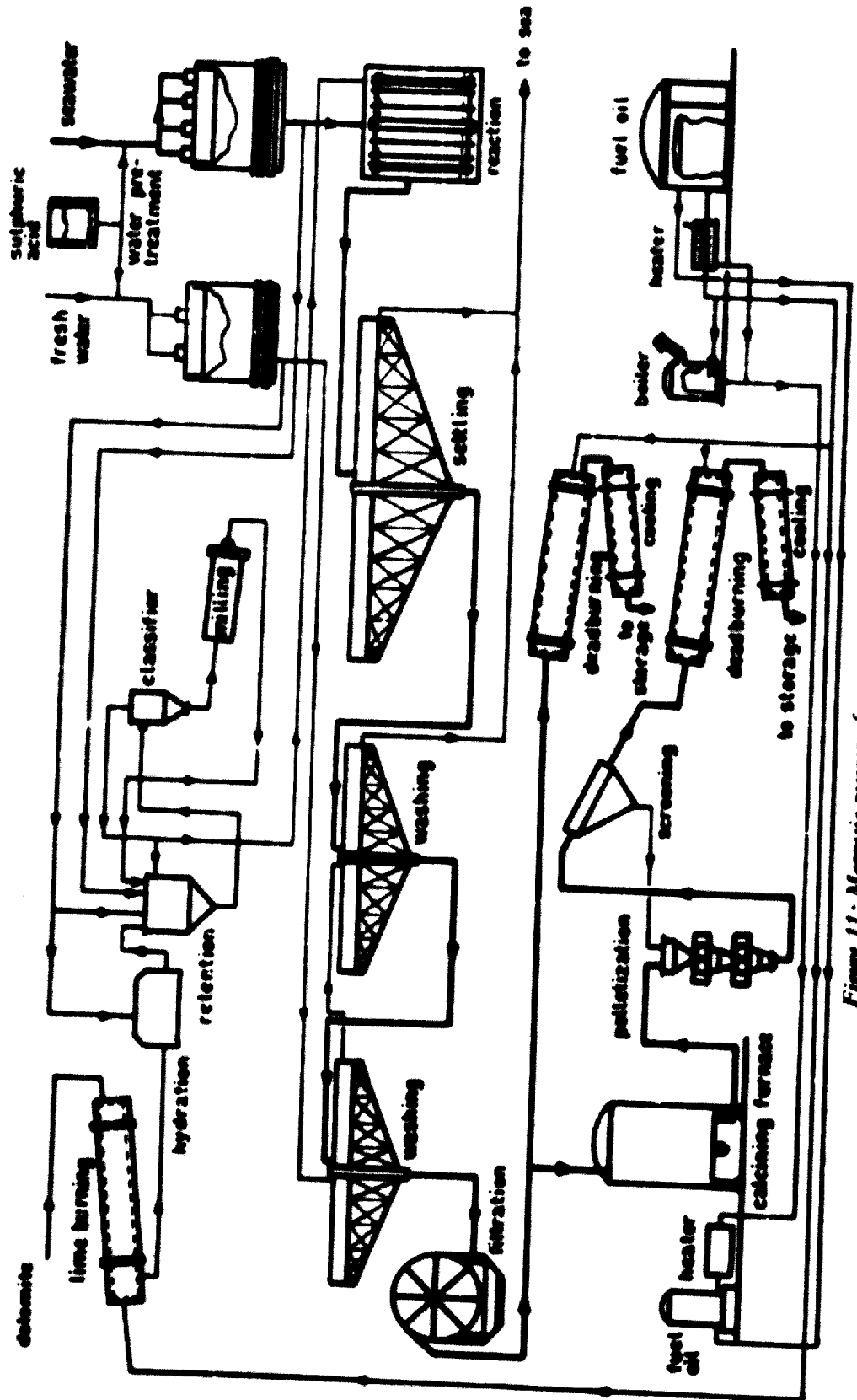


Figure 11: Magnesium recovery from seawater: the Soreby process

recovered is derived from the dolomite, and thus the volume of seawater required per ton of final product is only half that needed when lime alone is used.

The Steetley process, as practised in the United Kingdom [26] and shown in figure 11, is as follows: Dolomite is quarried near the seawater plant and is crushed, graded and burnt in coal-fired rotary kilns to produce "dolime" ($MgOCaO$). The selection of the correct grade of dolomite (minimum 99.5 per cent purity) is of fundamental importance with regard to the purity of the final product, especially with respect to the silica, iron and aluminium content.

The calcined dolomite is transported to the seawater treatment plant, where it is slaked to a fine, dry powder by the addition of treated fresh water and is then slurried by mixing with treated fresh water and seawater. The slurry is classified to remove impurities.

The seawater is drawn by centrifugal pumps through pipelines extending approximately 600 m into the North Sea and is treated by the addition of sulphuric acid to remove the calcium bicarbonate. It is then degassed in towers, and the carbon dioxide-free seawater is mixed with the hydrated dolomite in reaction tanks fitted with agitators. The chemical reaction proceeds as follows:



The magnesium hydroxide is precipitated, and the slurry flows to a 98-m-diameter shallow settling tank fitted with a centre-drive rake mechanism. The overflow, which is rich in calcium ions, is returned to the sea; and the underflow, consisting of concentrated magnesium hydroxide slurry, is drawn to the centre well of the tank by the rakes and removed from the settling tank. It then flows to two washing and settling tanks in series with a countercurrent flow of fresh water to reduce the sodium chloride content of the liquor. The spent water is returned to the sea, and the thickened underflow from the final washing stage is filtered on rotary vacuum filters.

The filter cake, which contains approximately 50 per cent solids, is then fed either to rotary kilns or calcined in a multi-stage hearth furnace and formed into pellets by passing through pelletizing rollers, after which the material is screened, the undersize being returned to the pelletization rollers. The product goes to rotary kilns where it is dead burnt at temperatures above $1,650^{\circ}C$ to produce the pelletized refractory. The dead-burned product is stored in bunkers and used as the raw material for producing refractory bricks. Before calcining, additives are introduced for producing various grades of the refractories. More than 95 per cent of the magnesium present in the seawater is recovered as MgO . The filter cake, containing 50 per cent MgO , if not used for the production of refractories, becomes the starting material for second- and subsequent-generation magnesium-based chemicals such as magnesium carbonates, magnesium sulphate and

magnesium chloride, the chloride being used for the production of magnesium metal.

The minimum capacity of a unit for the production of refractory-grade MgO is considered to be approximately 50,000 tons/year, representing an investment of \$ 14.4 million. Such a plant would require an operating staff of approximately 100 people, of whom 80 would be process staff on shift.

The major seawater magnesia plants operate as single-product plants. As the production of bromine is, in its initial process stages, involved with the pumping of large volumes of seawater, the combination of a magnesia plant and a bromine plant, using a common seawater pumping unit, might offer some economies of operation. The non-existence of such dual-purpose plants appears to be due less to the technical difficulties than to the comparatively low output of bromine from a magnesia plant of a given size. For example, the minimum-sized magnesia plant of 50,000 tons/year output noted above would produce about 1,500 tons of bromine, and the flexibility of the operation would be limited to this extent. Furthermore, the present uncertainty as to the future scale of bromine production would militate against moves towards dual operation.

The integration of such processes into other chemical complexes, such as the processing of bitterns or effluents from large-scale seawater desalination plants, where the magnesia is concentrated twofold or threefold compared with seawater, has been noted in chapter 3. Such integration appears feasible and could lead to economies of operation, provided that the necessary technical problems associated with the corresponding increase of the other components of the seawater, and in particular sulphate, are taken into account. In the case of bitterns, the sulphate is removed on concentration, and in the case of effluent from desalination plants, this would depend on whether the sulphate has been removed as part of the pretreatment of the seawater feed to the desalination plant.

Magnesia production from concentrated saline solutions

The production of magnesia from concentrated saline solutions is based on a variety of sources, two of the most important of which are sea bitterns, after solar evaporation and salt recovery, and inland bodies of salt water such as the Great Salt Lake and the Dead Sea. The process selected for recovery of the magnesia depends upon the magnesium compound required (MgO or MgCl₂), and on the source. As with sodium chloride recovery, each source must be treated separately.

The most important magnesium compound produced from seawater bitterns is MgO, and the method of recovery is essentially the same as for its recovery from normal seawater, as described above. The major difference, and a pronounced advantage, is that the concentration of the MgO has been increased from the normal mid-ocean value of 1,300 ppm up to as high as 60,000 ppm after solar evaporation. [1]

This thirtyfold to fortyfold increase in concentration results in a corresponding decrease in the size of the plant required to handle the bitterns, precipitate the $Mg(OH)_2$ and separate it from the mother liquor. The remainder of the plant for the washing of the $Mg(OH)_2$, calcination etc. would be similar in size to a plant of equal capacity based on the use of seawater, as the size of this section of the plant is based on the output of magnesia. An integrated salt/magnesia plant could thus achieve significant reductions in both capital and operating costs as compared with a conventional magnesia seawater plant.

The typical methods of recovery of magnesia from inland bodies of salt water such as the Dead Sea and the Great Salt Lake have been described in connexion with the production of sodium chloride.

Magnesia production from wells and ores

Few of the magnesium compounds that can be used commercially originate from wells. The methods for the recovery of the magnesium from them would, as stated in chapter 3, depend on the concentration and composition of their brines. Most of the magnesium obtained from such wells is recovered either as $MgSO_4 \cdot 7H_2O$ (Epsom salts) or as MgO . The recovery of magnesium compounds from ores (brucite, dolomite, magnesite) is outside the scope of this report.

POTASSIUM

Potassium is an essential component of plant food; by far its most important use is for fertilizer. The most common form of potassium found in nature is the chloride (KCl), the world production of which in 1968 was 15.55 million tons as K_2O . [3] The corresponding production in the USA in the same year was 4.32 million tons (3.39 million tons as K_2O and 0.93 million tons as other potassium salts).

Little potassium is recovered from seawater, for the following reasons:

The concentration of potassium in seawater is low (387 ppm);

Large deposits of potassium-bearing salts exist throughout the world;

There are extensive potassium-rich inland aqueous sources, namely, Great Salt Lake bitterns (20,000 ppm); Searles Lake brines (15,500 ppm); Dead Sea (6,400 ppm); Great Salt Lake (3,400 ppm).

Solar evaporation of seawater would produce bitterns containing up to 10,000 ppm K, and if the effluent from a desalination plant with a concentration factor of 3:1 were considered, the effluent would reach more than 1,100 ppm. The recovery of potassium from seawater bitterns is complicated by the presence of high concentrations of sodium, sulphate and magnesium, and these bitterns are normally discarded after recovery of the salt, magnesium and bromine.

The recovery of potassium from seawater has been studied at length. One method proposed for the recovery of potassium from desalination plant effluent having a potassium concentration of 1,100 to 1,200 ppm is the conversion of the soluble potassium in the effluent to an insoluble potassium complex, filtration of the complex from the liquor, reacting this complex with acid to recover the potassium as a salt, and regenerating the chelating agent for reuse. [27]

A more recently proposed method is the precipitation of potassium as KClO_4 . It is shown diagrammatically in figure 10. [23] The process consists of producing NaClO_4 electrolytically from NaCl and adding it to chilled brine. The precipitated KClO_4 is recovered by filtration and dissolved in hot water. This solution is reacted with resin to convert the resin to its potassium form, releasing NaClO_4 for reuse. The potassium is recovered from the resin by elution with NaCl , Na_2CO_3 , Na_2SO_4 etc. The process has been tested on a small scale on bitterns from Great Salt Lake with a potassium content of 13.5 g/litre.

Neither of these two processes has yet been proved commercially.

The present sources of potassium are either solid underground deposits or inland brines and lakes, such as Searles Lake in California, which is a deposit of solid sodium salts permeated with a complex saturated brine, or the Dead Sea. The actual process steps required to recover the potassium depend on the nature and concentration of the other chemical species present.

Dead Sea brine is initially pumped into solar pans to a depth of approximately 1 m, and green dye is added to increase the evaporation rate to 1 to 2 cm/day. [20] During the course of the evaporation, NaCl crystallizes out, and the brine is then transferred to secondary evaporating pans, and evaporation and precipitation continue. When carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$) crystallizes it is slurried with its mother liquor and pumped to thickeners. The thickened slurry is filtered, the liquor being rejected or used for bromine recovery. The carnallite is decomposed by partially dissolving it in water and upstream brines to remove MgCl_2 , which can be processed.

The resulting sylvinite ($\text{NaCl} \cdot \text{KCl}$) slurry is then subjected to froth flotation by the addition of foaming agents and air, which carry the KCl to the surface and allow the NaCl crystals to sink. The froth containing KCl is skimmed off the surface and allowed to settle. It is then filtered, washed, centrifuged and dried; the product contains 98 per cent KCl . The residual NaCl can be removed from the flotation cell, washed to remove residual KCl and then filtered and dried as industrial salt. Recently, advantage has been taken of the shallowness of the southern end of the Dead Sea to build a dam that effectively converts the dammed area into a primary evaporating pond.

Searles Lake brine is processed differently. The brine is pumped from the lake body and concentrated in triple-effect evaporators together with recycled mother liquor. During evaporation and concentration, the double salt of Na_2SO_4 and Na_2CO_3 precipitates and is removed. The concentrated

liquor is then quickly cooled to precipitate KCl, which is filtered, washed, centrifuged and dried. The mother liquor is further cooled to crystallize crude borax, which is separated and purified. The mother liquor, after removal of the borax, is returned to the concentrators. Lithium (as Li_2NaPO_4), Na_2SO_4 , NaCl and Na_2CO_3 are also recovered.

BROMINE AND ITS COMPOUNDS

Seawater is the chief source of elemental bromine, other sources being natural well brines and lake brines (such as those of Searles Lake and the Dead Sea). More than 75 per cent of the bromine produced is used for the manufacture of ethylene dibromide, which is used in the production of tetraethyl lead (TEL) and tetramethyl lead (TML) for incorporation into motor and aviation fuels to increase their anti-knock ratings. Its function in these compounds is to react with the lead during combustion of the fuel to yield a volatile lead compound that does not deposit on the combustion chamber valves and ports.

Data on world production of bromine for 1967 and 1968 are given in table 14.

TABLE 14. WORLD PRODUCTION OF BROMINE IN 1967 AND 1968
(Tons)

	1967	1968
Elemental bromine (Br_2)	22,100	23,600
Ethyl bromide	175	190
Methyl bromide	7,000	7,260
Ethylene dibromide (including sodium bromide, potassium bromide etc.)	104,725	108,450
	134,000	139,500

Source: Bureau of Mines, United States Department of the Interior (1969), *Minerals Yearbook, 1968*, Government Printing Office, Washington, D. C.

The usual method of recovery of bromine from seawater (60 to 70 ppm) or other dilute sources is to acidify the water and then add chlorine. The water then flows down a packed tower into the base of which air is injected. The freed elemental bromine is stripped from the water by the air; a mixture of air and bromine vapours passes out through the top of the tower and is ducted into a second packed tower, down which a solution of SO_2 in water flows. The SO_2 reacts with the bromine to produce H_2SO_4 and HBr in solution. The air, depleted of bromine, is finally washed with fresh seawater to recover any traces of unreacted bromine. The HBr solution, now at higher bromine concentration than in seawater, is again reacted with chlorine to release bromine, which is stripped from the liquor by live steam. This mixture of bromine and water vapour is condensed, and the

resulting two-phase condensate is separated. The upper aqueous phase, containing dissolved bromine, is returned to the stripper; the lower phase, consisting of crude bromine, is purified by distillation.

For the recovery of bromine from more concentrated sources, such as bitterns, the stripping of the acidified and chlorinated liquor is carried out by steam alone. This process (the Kubiersky process) is shown diagrammatically in figure 12. The raw material, fuel and electrical power requirements per kilogram of bromine are as follows: [28]

H ₂ SO ₄	0.78	kg
Cl ₂	1.3	kg
S	0.3	kg
Fuel oil	0.12	kg
Power	2.8	kWh

Under European conditions, the capital cost of a plant to produce 20 tons/day of bromine from seawater would be approximately \$4 million.

BORATES

The production of crude borax (Na₂B₄O₇ · 10H₂O) as a by-product of the recovery of potassium chloride from Searles Lake brines has been noted above. Other commercial sources exist in southern, central and southwest Asia, in South America and elsewhere. The production of this material in the United States during the five years 1964—1968 is shown below in the table 15. [3]

TABLE 15. UNITED STATES PRODUCTION OF BORAX, 1964—1968
(Thousand tons)

1964	1965	1966	1967	1968
367	385	417	450	492

Source: Bureau of Mines, United States Department of the Interior (1969). *Minerals Yearbook, 1968*, Government Printing Office, Washington, D. C.

Borax and its derivatives are used in detergents, soldering materials and the manufacture of glazes and enamels. It is also used in the manufacture of sodium perborate (NaBO₃ · 4H₂O) by reacting sodium peroxide and hydrogen peroxide, as follows:



Sodium perborate has extensive uses as an antiseptic in medicine and dentistry.

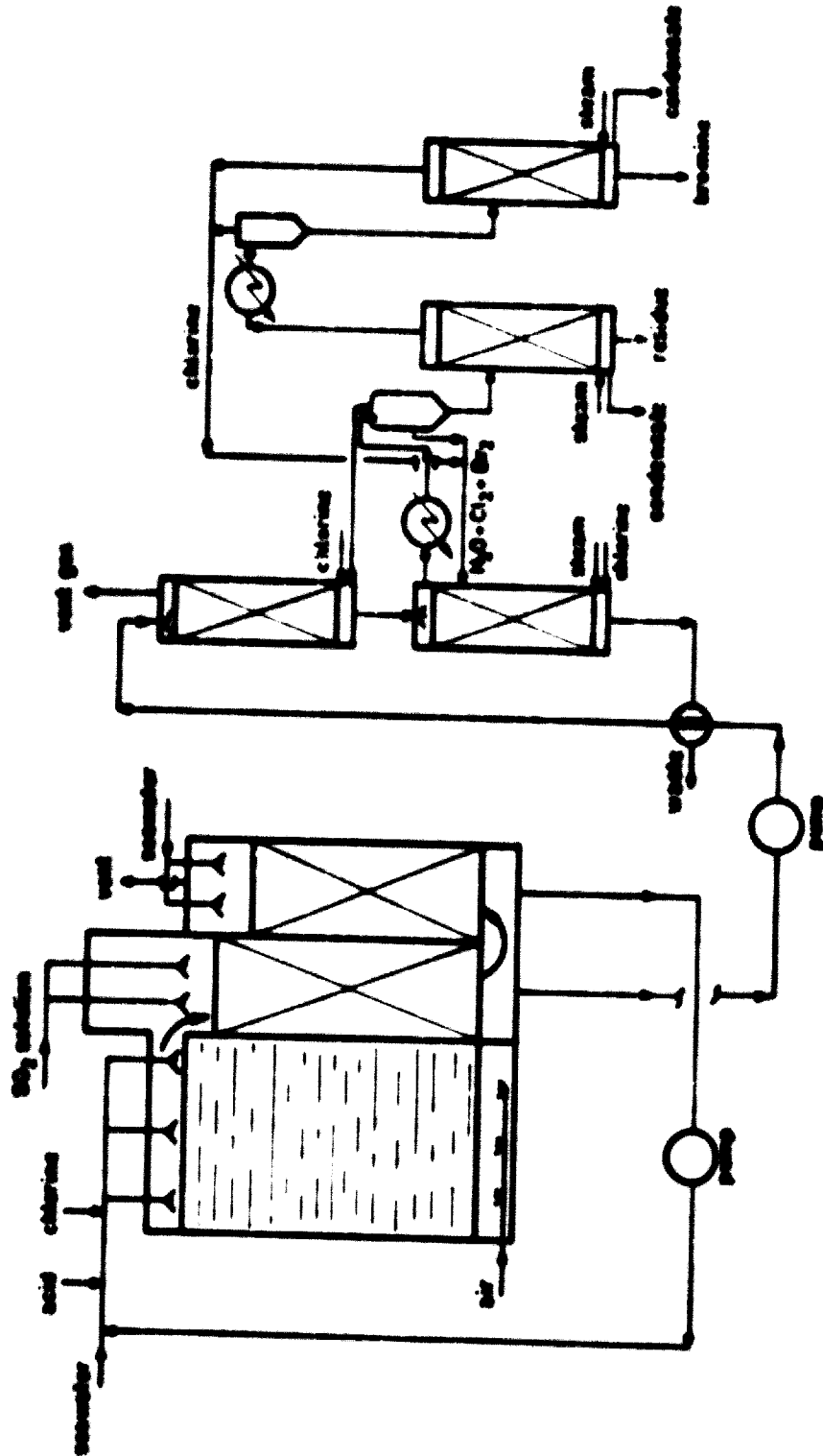


Figure 12: Production of bromine from seawater: the Kuhlmann process

Chapter 4

CHEMICALS FROM SEAWATER, INLAND BRINES AND ROCK SALT DEPOSITS: SECOND AND SUBSEQUENT GENERATIONS

SODIUM CHLORIDE

Most of the sodium chloride that is produced is used as a starting material for the chemical manufacturing industry, and particularly for the production of sodium carbonate, sodium hydroxide and chlorine.

Sodium carbonate

Sodium carbonate (Na_2CO_3) is used in the detergent, paper and textile industries and as a source of sodium iron. In the United States, production of this chemical has remained steady over the last few years, but the percentage obtained from natural sources has increased at the expense of other sources. The data for the years 1964–1968 are shown in table 16.

TABLE 16. UNITED STATES PRODUCTION OF NATURAL AND MANUFACTURED SODIUM CARBONATE, 1964–1968
(Thousand tons)

	1964	1965	1966	1967	1968
Natural	1,155	1,355	1,575	1,565	1,855
Manufactured	4,480	4,470	4,600	4,440	4,140
Total	5,635	5,825	6,175	6,005	5,995

Source: Bureau of Mines, United States Department of the Interior (1969), *Minerals Yearbook, 1968*, Government Printing Office, Washington, D. C.

The most important method of manufacturing sodium carbonate is the Solvay process, which is diagrammed in figure 13. The raw materials used in this process are sodium chloride, limestone and fuel; ammonia is used as an internal recycle stream only. The process is described below.

Ammonia is absorbed in a saturated, purified sodium chloride solution in an absorber. The solution is then reacted with CO_2 gas in the carbonators, where sodium bicarbonate is precipitated. The suspension of sodium

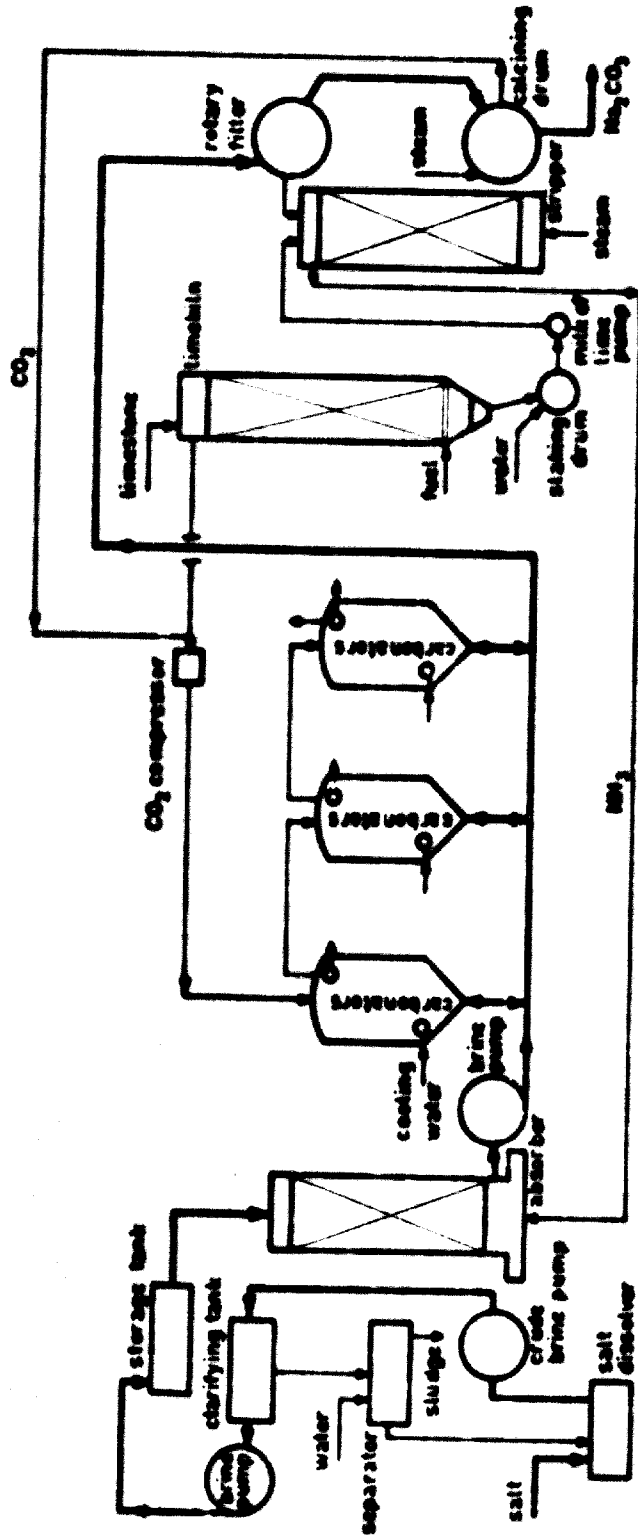


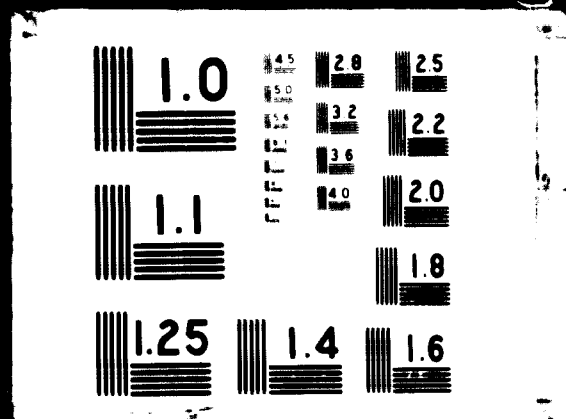
Figure 13: Production of sodium carbonate: the Solvay process



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bicarbonate is then filtered in a rotary vacuum filter, and the sodium bicarbonate is calcined in a drum to yield sodium carbonate and CO_2 gas. The CO_2 gas is recycled to the carbonators, together with make-up CO_2 from a limekiln. The filtrate is then heated with a milk-of-lime solution, and the ammonia is stripped with live steam. The ammonia generated is returned to the absorber, and the calcium chloride formed is discharged as waste.

The chemistry of the process is as follows:

- (a) Precipitation of sodium bicarbonate:
 $2\text{NaCl} + 2\text{CO}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{NaHCO}_3 + 2\text{NH}_4\text{Cl}$
- (b) Calcination:
 $2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$
- (c) Stripping:
 $2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCl}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O}$
- (d) Preparation of carbon dioxide and milk of lime:
 $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
 $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$

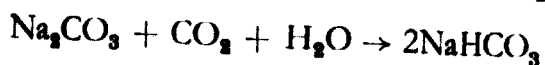
The requirements for the production of 1 ton of Na_2CO_3 are as follows:

[29]

Sodium chloride	1,600 kg
Limestone	1,450 kg
Fuel (for lime burning):	
Coke or	120 kg
Natural gas or	140 Nm^3
Fuel oil	120 kg
Ammonia	4 kg
High-pressure steam	3,800 kg
Cooling water (20°C)	175 m^3
Electric energy	400 kWh

SODIUM BICARBONATE

Sodium bicarbonate (NaHCO_3) is used extensively in the food and pharmaceutical industries and also as a fire-extinguishing material. It is produced by the reaction between Na_2CO_3 and CO_2 as follows:



Sodium carbonate (soda ash) is dissolved in water as a saturated solution and reacted with gaseous CO_2 . The precipitated sodium bicarbonate is filtered, washed and dried at approximately 70°C to minimize decomposition. The mother liquor is recycled for further dissolving of sodium carbonate.

The requirements for the production of 1 ton of NaHCO_3 are as follows: [29]

Light soda ash	670 kg
Fuel:	
Gas or	235 Nm^3
Fuel oil	202 kg
Electric energy	175 kWh

SODIUM SULPHATE

The demand for sodium sulphate (salt cake — Na_2SO_4) far exceeds the amount recovered from natural sources, as shown in table 17, which gives data for United States production of this material during the five years 1964 through 1968.

TABLE 17. UNITED STATES PRODUCTION OF SODIUM SULPHATE, 1964—1968
(Thousand tons)

	1964	1965	1966	1967	1968
Natural	522	544	581	577	635
From salt cake, crude, manufactured and natural	840	885	917	857	965
Total ...	1,362	1,429	1,498	1,434	1,600

Source: Bureau of Mines, United States Department of the Interior (1969), *Minerals Yearbook, 1968*, Government Printing Office, Washington, D. C.

On a global basis 48 per cent of the sodium sulphate was produced from natural sources. It is used for the production of kraft paper (major use), glass, ceramic glazes, detergents, dyes, medicines and textiles.

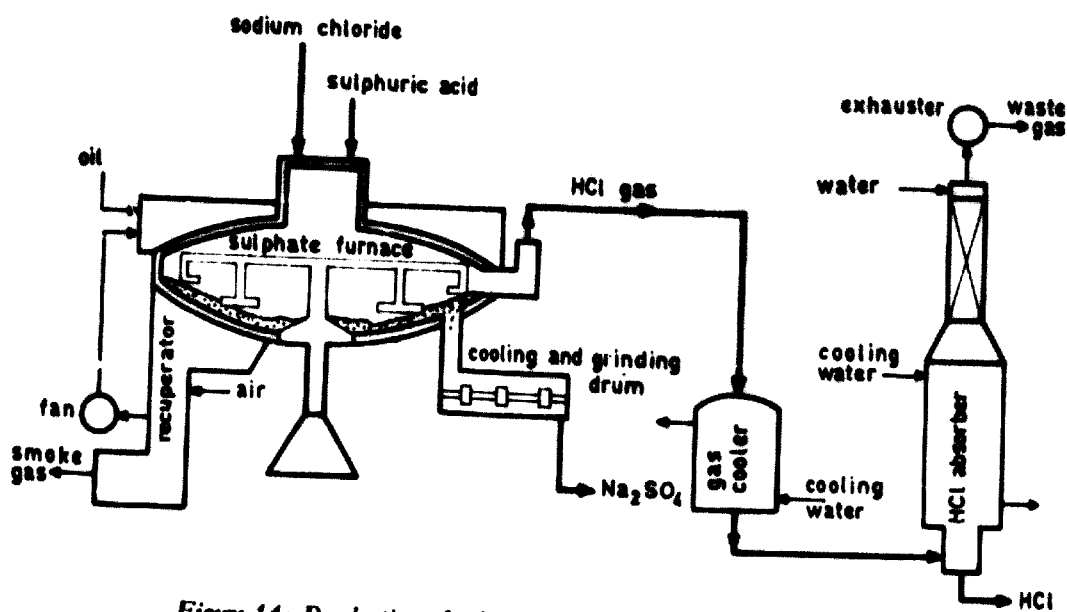
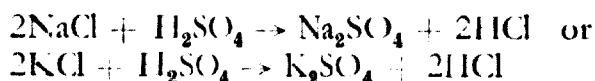


Figure 14: Production of sodium sulphate: the Mannheim process

Manufactured sodium sulphate is produced primarily by the salt cake process and as a by-product in the manufacture of viscose rayon. Until fairly recently, the most important salt cake process was the so-called Mannheim process, in which sodium chloride and sulphuric acid are reacted together and heated to a high temperature in a Mannheim furnace, which is a brick-lined furnace, oil- or gas-fired, fitted with a mechanical agitator to move the mixture and assist decomposition. The process is shown schematically in figure 14. The method of operation is as follows: [29] Sodium chloride and sulphuric acid are continuously fed from the top into the centre of a completely closed muffle furnace and are uniformly distributed around the centre of the muffle by an agitator, which moves the mixture slowly towards the outside and the discharge opening. The speed of the agitator is adjusted so that complete conversion of the sodium chloride to sodium sulphate is assured. The hot sodium sulphate discharged from the furnace falls into a cooling and grinding drum, which has a gastight connexion to the muffle. The muffle is heated indirectly by gas or fuel oil. The waste heat of the furnace is utilized to preheat the combustion air by means of a recuperator in the flue. The HCl gases leave the muffle through a pipe that enters its side wall and then go to the absorption plant via a gas cooler.

The reaction is as follows:



Hydrochloric acid (up to 32 per cent HCl) is obtained as a by-product.

This method of production is now being superseded by the fluidized-bed reactor, which is shown schematically in figure 15. The process is described below. [29]

The salt is delivered to the bin (1) and from there to the mill (2), which grinds it to the required size. The ground salt, in metered quantities, is fed into a current of hot air and combustion gases, where it is heated to the required reaction temperature before entering the reactor (10). Sulphuric acid from the storage tank (7) is pumped by the metering pump (8) in controlled quantities to the evaporator (9), the flow of acid being controlled by the flow of the salt in stoichiometric proportions. Two compressors (3 and 5) supply the air necessary to maintain the fluidized bed as well as to transmit the reaction heat. The air required for heating and conveying the salt is brought to the required temperature in the heater (4), and the heater-evaporator (6) supplies hot air for the evaporation of the acid. The conversion of the salt and sulphuric acid into sodium sulphate and HCl takes place in the reactor (10). The sodium sulphate is continuously discharged from the bottom of the reactor and crushed to the required size in the mill (11). Fine sodium sulphate particles carried over in the gas stream are recovered in the cyclone separator (12). A fan (14) conveys the sodium sulphate pneumatically via the separator (13) to the storage bin (15), during which time the sodium sulphate is cooled. The waste gas containing HCl

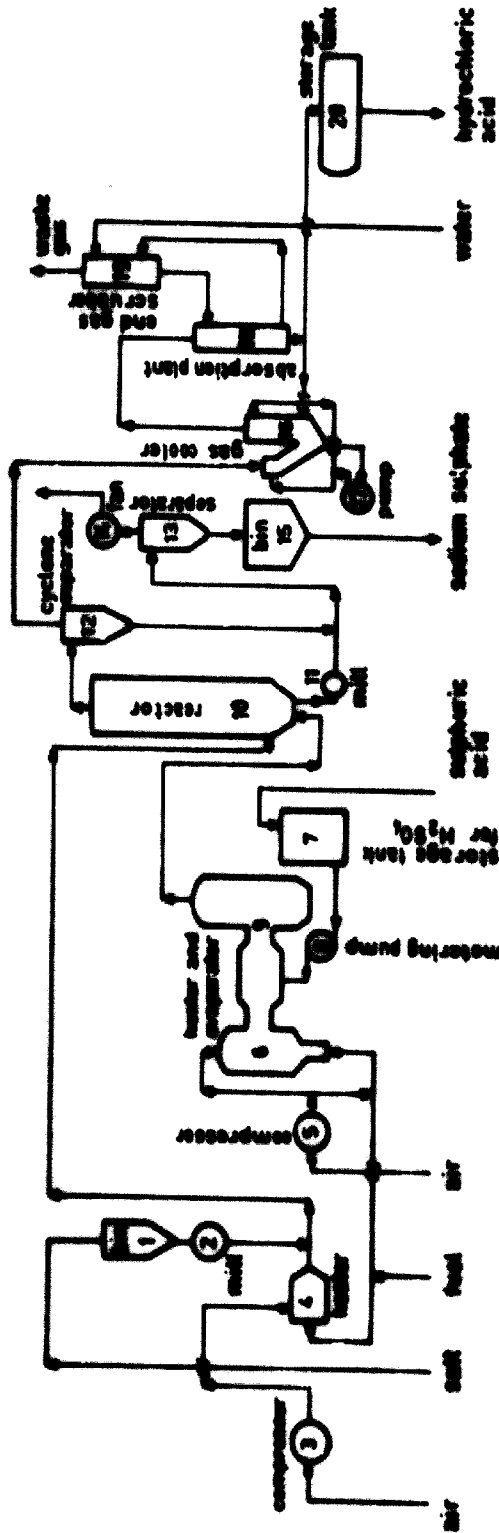


Figure 15: Production of sodium sulphate: fluidized-bed reactor

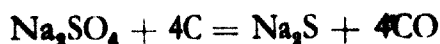
from the reactor is cooled in the gas cooler (16), and the cooled gases are fed to the absorption plant (18), where HCl is absorbed to give 32 per cent HCl solution. Waste gases are then scrubbed (19), and the HCl-free waste gases are discharged to atmosphere.

The requirements for the production of 1 ton of Na_2SO_4 are as follows:

Sodium chloride	840 kg
Sulphuric acid (100%)	715 kg
Fuel oil	
(C. V. = 10,000 kcal/kg)	75 kg
Power	150 kWh
Cooling water (once through)	54 m ³
Absorption water	1—1.4 m ³
Labour	0.16 man-hours

In addition, 1.5 tons of 30–32 per cent HCl are produced as a by-product.

In addition to other uses, sodium sulphate is a starting material for the production of sodium sulphide, which is used in making sulphur dyes, in tanneries for depilating hides, and in rayon factories for the desulphurization of viscous filaments. The process consists of reducing sodium sulphate with carbon at temperatures of approximately 1,100°C, according to the equation:



The requirements per 1,000 kg of sodium sulphide, 60 to 62 per cent pure, are as follows:

	<i>Kilograms</i>
Na_2SO_4 (96–97%)	1,350
Coal for reduction	400
Fuel oil	
(C. V. = 10,000 kcal/kg)	300–330

CAUSTIC SODA AND CHLORINE

Caustic soda (NaOH) and chlorine (Cl_2) are produced concurrently by the electrolysis of an aqueous solution of sodium chloride. The passage of a direct electric current (DC) through an aqueous solution of sodium chloride will produce a concentration of NaOH and H_2 at the cathode and of chlorine at the anode. Unless precautions are taken to keep the products apart, they will recombine. Two main types of electrolytic cells, diaphragm cells and mercury cells, are used for this purpose.

Diaphragm cells

A diaphragm cell consists of a bath containing sodium chloride solution in which a porous diaphragm, usually of asbestos, is fitted. On one side of the diaphragm is the anode, normally made of graphite but now increas-

ingly being made of titanium alloys, and on the other side the cathode, made of steel. When a direct current is passed through the electrolyte, ions of chlorine and sodium migrate to the anode and cathode, respectively, where they give up their electric charges, the sodium reacting with the water to yield NaOH and H₂. The cell must be so designed as to minimize the recombination of the chlorine and caustic soda, which would yield sodium hypochlorite (NaOCl). The chlorine gas is piped away from the system, dried, compressed and liquefied. The cell is continuously fed with fresh 20 to 25 per cent NaCl solution; the liquor, after electrolysis, contains approximately 10 to 12 per cent NaOH, the balance being NaCl. This liquor is removed from the cell and concentrated to 50 per cent NaOH by evaporation. The NaCl that is salted out during concentration is recycled to the process. The 50 per cent NaOH produced is liquid and can be sold as such, or it can be further concentrated to a solid by evaporation in direct-fired or Dowtherm-heated concentrators. The molten caustic soda is then cooled and solidified.

Mercury cells

The mercury cell consists of a rectangular body, with a slight slope down which a film of mercury flows. Fitted into the base of the cell are steel connexions that allow current to be applied to the mercury film. Flowing countercurrent to the mercury is a 25 per cent brine solution into which are fitted graphite or titanium alloy anodes. The cell is fabricated in steel and is lined to isolate the anode and cathode electrically. Application of a direct current to the anode and cathode causes migration of ions as above. The chlorine ions discharge at the anode, and the chlorine gas liberated is piped from the roof of the cell, dried, compressed and liquefied, as above. The sodium ions give up their charges at the mercury cathode and react with the mercury to form a sodium amalgam. Fresh mercury is introduced to the high end of the cell, and the sodium amalgam flows out at the lower end, where it then enters a decomposer to which demineralized water is added. This decomposes the amalgam into NaOH, hydrogen and mercury, the mercury being recycled back to the cell. The concentration of NaOH formed is 40 to 50 per cent, which is considerably stronger than that from diaphragm cells.

Diaphragm versus mercury cells

The choice of the type of cell to be employed can be made only after thorough assessment of all the relevant facts, such as the capacity required, the location of the plant, the market for caustic soda and chlorine, the forms of caustic soda and chlorine to be produced, and whether the products will be used on or off the site. For small-capacity plants, where the products are mainly used on site for further processing, the advantage would probably be with diaphragm cells.

Utilization of end products

The production of NaOH and chlorine in turn permits the creation of an almost unlimited number of chemical industries and the consumption of these chemicals is widespread. Figure 1 indicates some of the many outlets for these salt-based chemicals.

The hydrogen produced as a by-product in the manufacture of caustic soda and chlorine can be used for the production of HCl by combining with the chlorine, for hardening fats for human consumption, and for the production of NH_3 and of urea by reacting the NH_3 with CO_2 . The HCl produced by this method can be used for a variety of purposes, including the digestion of phosphate rock in sulphur-deficient countries and the production of phosphoric acid, which in turn can be used for the production of dicalcium phosphate as a mineral feed supplement for animals.

MAGNESIUM

The production of MgO and MgCl_2 from aqueous sources, such as seawater and inland brines, establishes a first-generation type of industry whose products find application in the refractory and ceramic industries (MgO) as well as the wood-pulp industry ($\text{Mg}(\text{OH})_2$), animal feedstuff supplements, the extraction of uranium and elsewhere in the chemical and processing industries. Also, they are used as starting materials for second-generation plants and products, such as those considered below.

Magnesium carbonate (MgCO_3). Magnesium carbonate is made by carbonating $\text{Mg}(\text{OH})_2$ with CO_2 obtained from lime burning. The CaCO_3 precipitated in the initial stages of solar salt production would, after drying, be a suitable source of the carbonate, and hence of the CO_2 . Various grades consisting of different proportions of magnesium carbonate and magnesium hydroxide can be produced to meet specifications for use in paint, varnish, fillers etc.

Magnesium sulphate (MgSO_4). Where magnesium sulphate does not occur naturally as Epsom salts, it can be made by the reaction of $\text{Mg}(\text{OH})_2$ or MgCl_2 with H_2SO_4 . It finds uses as sizing and as a fireproofing agent.

Magnesium chloride (MgCl_2). If magnesium chloride is not produced as a primary product from solar evaporation of seawater, it can be obtained by the action of HCl on $\text{Mg}(\text{OH})_2$; and if the magnesium chloride is to be used for the production of magnesium metal, the by-product, chlorine, from the electrolysis of the magnesium chloride can be used for the production of HCl.

Magnesium metal. Magnesium metal is widely used as in the production of magnesium alloys and of the alloy of aluminium. It is most commonly produced by the electrolysis of magnesium chloride, which can be obtained either directly from the salines or, as noted above, by the reaction between $\text{Mg}(\text{OH})_2$ and HCl to give an aqueous solution of MgCl_2 . This solution is dried by evaporation, and the solid chloride is mixed with NaCl to form

a eutectic and thus reduce the melting point of the mixture in the cell. [30] The cell consists of a ceramic-covered steel vessel through the roof of which pass graphite anodes, the vessel itself acting as a cathode. The contents of the cell are maintained in a molten state at approximately 710°C by the resistance of the current passing through the molten salt and by supplementary firing of the vessel. The cell operates at 6 V and 80,000 to 100,000 A, with current efficiency of 80 per cent, and requires 17.8 kWh/kg Mg. The molten magnesium metal liberated at the cathode overflows a weir into a metal sump and is periodically removed as 99.5 per cent magnesia. The chlorine liberated at the anodes is piped off and can be reused for the production of the magnesium chloride feedstock or can be cooled, compressed, liquefied and sold.

POTASSIUM

The second-generation potassium salts follow a pattern similar to that of the sodium salts, and the methods of manufacture are fundamentally the same.

Potassium sulphate (K_2SO_4). Potassium sulphate can be made from potassium chloride and sulphuric acid in the same manner and with the same equipment as described above for sodium sulphate. Like potassium chloride, potassium sulphate is used mainly as a fertilizer, particularly for tobacco and citrus fruits. Where sodium sulphate occurs naturally, it can be used to produce potassium sulphate by reaction with potassium chloride.

Potassium hydroxide (caustic potash—KOH). Potassium hydroxide is produced by electrolysis of potassium chloride solutions and is used in the production of soaps, detergents and dyes, in the textile industry for bleaching and mercerizing.

Potassium nitrate (saltpetre— KNO_3). Potassium nitrate is used in place of potassium chloride in NPK fertilizer formulations to maintain high concentrations of potassium and nitrogen. It is also used in the preservation of meat.

BROMINE

The largest demand for bromine is in the production of ethylene dibromide, which accounts for more than 75 per cent of the total world bromine production. Other uses include: pharmaceuticals, photographic chemicals, fire-extinguisher fluids, fire retardants, hydraulic and gauge fluids, agricultural chemicals, dyes, intermediates for other chemical processes and sanitary and water-treatment chemicals.

Ethylene dibromide ($BrCH_2CH_2Br$) is made by the direct reaction of ethylene and bromine. It is used almost exclusively in the formulation of TEL and TML fuel blends and accounts for 18 per cent of the TEL blend

used for automobile fuels and 36 per cent of the TEL blend in aviation fuels.

Growing air pollution, especially in areas of high densities of both people and automobiles, has led to intensive efforts to determine the causes of the pollution, particularly smog, and to devise methods for its reduction and/or elimination. Research to date indicates that the most likely contribution to smog formation is the presence in the air of hydrocarbons and unsaturated hydrocarbon compounds, carbon monoxide and oxides of nitrogen, which, under conditions of strong sunlight and temperature inversion, undergo a photochemical reaction. The United States Department of Health estimates that 130 million tons of pollutants enter the air each year, of which 62 million tons are from automobile exhausts. [31] Regulations have now been introduced, at both the federal and local levels, to limit the concentrations of hydrocarbons, CO and NO that can be emitted in automobile exhaust. These limits are to be reduced progressively over the years.

A number of mechanical attachments to automobile engines have been devised to reduce the level of pollutants, but to achieve the specified levels the only practical device thus far developed has been the catalytic afterburner, which oxidizes the hydrocarbons, CO and NO to H_2O , CO_2 and NO_2 , respectively, in the final exhaust emission. However, this device is susceptible to accumulation of lead and consequent loss of effectiveness. It is thus essential to ensure that the fuel contain no lead if such devices are to work effectively over extended periods.

In addition, it is asserted that lead in the form of particulate matter in the air is harmful when inhaled, but differences of opinion exist on this point. Work carried out in Frankfurt, Federal Republic of Germany, by the Erlangen University's Institute for Industrial Medicine is claimed to have established that men constantly exposed to exhaust fumes have in their bloodstreams alarmingly high levels of lead, which restricts the production of important enzymes and red corpuscles. It is also claimed that tests have established a significant increase in the lead content of the dust from the roads. However, the British Medical Council Air Pollution Research Unit in London has reported maximum concentrations in the air of $1.7 \mu\text{g}/\text{m}^3$ in the centre of London. This level is less than one hundredth of the MAC (maximum allowable concentration) of $200 \mu\text{g}/\text{m}^3$ in plants that process lead, i. e. battery manufacture.

The effect of the imposition of emission standards on automobile exhausts in the United States, with decreasing upper limits for cars produced up to 1974, has been for the automobile industry to design automobile engines capable of operating with lead-free fuels, that is, with lower compression ratios, and for the petroleum industry to market fuels either entirely lead free or with reduced TEL and TML content.

If, as appears probable, all cars produced in the United States in the near future will be designed for operation on lead-free fuel and if all the major United States petroleum producers are to produce lead-free motor

fuels, a decline in the demand for ethylene dibromide may be expected. The bromine industry appears to be reasonably confident, however, that other uses for ethylene dibromide, such as in agricultural formulations, are growing so rapidly that increased production facilities will be required, irrespective of the trend in the automobile industry. [32]

The producers of lead appear less optimistic; they anticipate that new markets for the 235,000 tons of lead consumed in the production of TEL and TMJ in 1968 will have to be found in the immediate future. [33] On balance, it would appear prudent that, unless there is a guaranteed captive market for bromine and its compounds, their manufacture should not be contemplated until the situation with respect to their use in automobile fuels has been clarified.

Chapter 5

SUMMARY AND CONCLUSIONS

Reference to the block diagram of the products from seawater, rock salt deposits and inland brines (figure 1) shows that, although the number of chemical species actually recovered from these sources is small, [14] they are such as to be of considerable value to any economy, and the various combinations of these species provide a reasonably viable chemical industry capable of supplying several of the basic needs of any country.

Extension of the scope of such an industry to include second-generation products increases the number of products by at least fifteen, and, apart from one feedstock (ethylene) all the products could be produced from indigenous sources. Thus, a chemical industry of thirty or so products could be set up, based entirely on what could be considered normal indigenous resources, namely, seawater, rock salt deposits and/or brine, coal and sand.

Extension of this hypothetical chemical complex to third-generation products with the addition of phosphate rock, which is fairly widespread throughout the world, increases the scope and extent of the complex considerably. It can thus be shown that an array of basic products can be manufactured from predominantly local sources. These products are not interlocked, in the sense that the production of any one necessarily involves the production of others that may or may not have economic outlets. Therefore, the establishment of a magnesium or bromine production unit could be carried out in isolation (as, in fact, it often is) and could be added to or combined with others at some future date as a first stage of expansion, as, for example, the production of sodium chloride and/or potassium chloride or the addition of bromine production to an existing magnesia plant, or vice versa. It can also be seen from figure 1 that there is often more than one route to certain end products, so that some degree of freedom exists in the selection of routes and associated secondary products.

It should be noted, however, that figure 1 shows only a few of the more common products capable of being produced by the given raw materials, and that, at each generation of products, the range and variety of products that can be produced increases nonlinearly, so that third- and fourth-generation products provide a range of products which would, in fact, be multiples of those actually shown. The purpose of the figure is

merely to indicate the range and type of the products capable of being produced from the three main sources and not to give an exhaustive list. Also, the routes indicated are not necessarily the most economic ones; for example, the production of H_2SO_4 is shown from $CaSO_4$ precipitated from seawater, but other routes to H_2SO_4 from elemental sulphur, by-product H_2S and mined anhydrite are possible. Similarly, HCl production is shown as a by-product from the production of Na_2SO_4 and K_2SO_4 . It is also shown as the main product by the direct combination of H_2 and Cl_2 . Other routes exist, such as by-product HCl from the chlorination of hydrocarbons (not shown). The route best suited to the actual site conditions can be selected only after proper consideration of the relevant economic and technical problems.

The interrelation between such a chemical complex and desalination plants provides considerable scope for the reduction in operating costs of both and merits serious consideration. One such plant already exists in Kuwait, and increases in output to 45 tons/day of purified salt, 12 tons/day of chlorine and 14 tons/day of caustic soda have been announced. [34]

Some basic points must be determined before such chemical plants can be established. These are:

Economic:

The country's present and future need for the proposed product(s);

Present sources (if any), i. e. local production or imports;

Export potential;

Value of production for import-substitution purposes, i. e. whether the indigenous cost of production is likely to exceed world market prices and, if so, the advantage (if any) of local production as compared with imports, e. g. in the saving of foreign exchange or stimulation of secondary or associated industries.

Technical:

Sources of raw materials, i. e. seawater, rock salt deposits or inland brines with availability and quality;

Possibility of integrating production with that of desalination plants;

Selection of locations suitable as regards both the sources of the raw material and the market;

Selection of the process best suited to the raw material and to the type of final product(s) required.

The location of a plant using seawater as the feedstock should be selected to ensure:

The maximum possible concentration of the salts;

Consistent concentration throughout the year, not subject to dilution during rainy seasons or for similar reasons;

Method of disposal of the plant effluent that avoids contamination or dilution of the incoming feedstock;

Soil structure suitable to minimize seepage of brine from the evaporating pans.

The absence of any centralized source of data on deposits, wells, lakes etc. that could be considered sources of chemicals, presents a problem when the establishment of such a chemical-processing facility is contemplated. The collection of all known sources in a given country, together with analysis of each individual source, is of fundamental importance in deciding on the location and scope of the proposed facility.

Apart from the production of urea, ammonia and the hydrogenation of fats, all of which require high pressures and sophisticated and complex equipment, most of the processes shown in figure 1 are capable of being maintained and serviced by average engineering facilities.

Annex

POSSIBLE SOURCES OF ASSISTANCE TO DEVELOPING COUNTRIES FROM PRIVATE INDUSTRY IN CREATING OR EXPANDING FACILITIES FOR THE PRODUCTION OF CHEMICALS FROM SEAWATER AND OTHER NATURAL SOURCES OF SALTS

The firms listed below have indicated their willingness, in principle, to supply to countries that wish to establish or expand facilities for the production of industrial chemicals from seawater and other natural sources, assistance of one or more of the following kinds:

- Licensing of process know-how;
- Design, construction and commissioning of plants;
- Financial and/or technical participation in certain projects.

The Steetley Company Limited P.O. Box No. 8 Hartlepool, County Durham England	For magnesia from seawater plants through a nominated contractor
Società Lavorazioni Organiche Inorganiche Via Calzolerie 1 Bologna Italy	Bromine from seawater
Rust Engineering Company Limited Carolyn House Croydon, Surrey England	Sodium and potassium sulphates with by-product HCl, both fixed and fluidized beds Solvay process for soda ash Sodium sulphate by reduction of sodium sulphate
Dead Sea Works Limited Potash House P.O. B. 75 Beersheba Israel	Chemicals from brines etc.

In addition, the following processes have been reported as being available under licence:¹

- Ammonium sulphate from calcium sulphate;
- Tropical bleach from chlorine and calcium oxide;
- Salicylic acid from carbon dioxide, caustic soda and phenol;
- Sodium bicarbonate from sodium carbonate and carbon dioxide;
- Hydrogen chloride from chlorine and hydrogen;
- Cement and sulphuric acid from calcium sulphate;
- Wallboard from calcium sulphate;
- Chlorine, caustic soda and hydrogen by electrolysis of sodium chloride;
- Chlorine dioxide from sodium chlorate and hydrochloric acid;
- Chlorine from hydrogen chloride;
- Sodium carbonate from sodium chloride and calcium carbonate;
- Refined salt from raw brine;
- Chlorine, potassium hydroxide and hydrogen from potash;
- Sodium chlorate by electrolysis of salt.

¹ R. L. Miller, Jr., D. B. Smith and D. M. Young (1970) "Process technology for licence or sale", *Chemical Engineering*, Vol. 77, No. 8, 114—144.

REFERENCES

1. TRESSLER, D. K. (1951) *Marine Products of Commerce*, Reinhold, New York.
2. NATIONAL SECURITY INDUSTRIAL ASSOCIATION (1966) *Ocean Engineering*, Vol. IV, Western Periodicals, North Hollywood, Calif.
3. UNITED STATES, DEPARTMENT OF THE INTERIOR, BUREAU OF MINES (1969) *Mineral Yearbook, 1968*, Government Printing Office, Washington, D. C.
4. RILEY, J. P. and G. SKIRROW (1965) *Chemical Oceanography*, Academic Press, London.
5. HORNE, R. A. (1969) *Marine Chemistry*, Wiley-Interscience, New York.
6. UNITED NATIONS ECONOMIC AND SOCIAL COUNCIL (1964) *Water Desalination in Developing Countries* (Sales No.: 64. II. B. 5.), pp. 65, 178 and 181.
7. MCILHENNY, W. F. and M. A. ZEITOUN (1969) "A chemical engineer's guide to seawater", *Chemical Engineering*, Vol. 76, No. 25, pp. 251—256.
8. CLARKE, F. W. (1924) "Data on geochemistry", *United States Geological Survey*, Bulletin No. 770, 5th ed., Government Printing Office, Washington, D. C.
9. MEGLIS, A., Comp. (1961) "Bibliography on limnology", *Meteorological and Geostrophysical Abstracts*, Vol. 22, pp. 555—619.
10. SPEIGLER, K. S. (1962) *Salt Water Purification*, Wiley, New York.
11. OTHMER, D. F. (1964) "Technology of water desalination" in UNITED NATIONS ECONOMIC AND SOCIAL COUNCIL, *Water Desalination in Developing Countries*, Annex A (Sales No.: 64. II. B. 5).
12. "Chementator", *Chemical Engineering*, Vol. 77, No. 12, 1970, p. 66.
13. PECHENICK, W. and C. E. ENNIS (of Catalytic Inc., Philadelphia) (1968) "Desalination plants using higher steam pressures", paper presented to International Atomic Energy Agency Symposium on Nuclear Desalination, Madrid, 21 November 1968, Elsevier, Amsterdam.
14. SALUTSKY, M. L. and M. G. DUNSETH (of Washington Research Centre, W. R. Grace and Co.) (1963) "Recovery of minerals from sea water by phosphatic precipitation", *Saline Water Conversion*, Vol. II, Advances in Chemistry Series 38, Section 2, American Chemical Society, Washington, D. C.

15. REIS, M. T. (1966) "La désalination de l'eau de mer", paper presented to conference of Association Française des Techniciens du Pétrole, Siège, France, 19 December 1966.
16. WEINBERGER, A. J. and D. F. DE LAPP (1965) "Saline water conversion and its by products", *Chemical Engineering Progress*, Vol. 60, No. 11, pp. 56—59.
17. D'ARCY, R. G. and J. M. RILEY (assigned to Secretary of the Interior, United States Government) "Sulphate removal from brines", U. S. Patent No. 3, 378, 336, dated 16 April 1968.
18. ENNIS, C. E. (of Catalytic Construction Co.) and E. N. SIEDER (of Office of Saline Water, Washington) (1969) "Desulphating — a pre-treatment for desalting plant feedwater", paper presented to United States Exhibition and International Conference on Water Purification and Desalination, Rome, 17 February 1969.
19. OFFICE OF SALINE WATER, *Report No. 289*, Wrightsville Beach, North Carolina.
20. BLOCH, M. R., L. FARKAS and K. S. SPIEGLER (1951) "Solar evaporation of salt brines", *Industrial and Engineering Chemistry*, Vol. 43, No. 7, pp. 1544—1553.
21. HESTER, A. S. and H. W. DIAMOND (1955) "Salt manufacture", *Industrial Engineering Chemistry*, Vol. 47, No. 4, pp. 672—683.
22. "C. E. new feature: All systems are go for Great Salt Lake projects", *Chemical Engineering*, Vol. 75, No. 13, 1968, p. 106.
23. GEORGE, D. R., J. M. RILEY and J. R. ROSS (of Bureau of Mines, Salt Lake City) (1968) "Potassium recovery by chemical precipitation and ion exchange", *Chemical Engineering Progress*, Vol. 64, No. 5, pp. 96—99.
24. FOUTE (1969) "World survey of deadburnt and caustic magnesia producers' plant capacity", *Taikabutsu Kogyo*, Vol. 21, No. 11, pp. 549—550.
25. "Comment—swing to sea water magnesia", *Industrial Minerals* (London), Nos. 7, 27 and 40, 1969.
26. Technical data brochures published by The Steetley Co. Ltd., Hartlepool, United Kingdom.
27. BUTT, TALMADGE and SAVAGE (1964) "Recovering potassium from sea water", *Chemical Engineering Progress*, Vol. 60, No. 11, pp. 50—55.
28. SOCIETA LAVORAZIONI ORGANICHE E INORGANICHE (Bologna, Italy), Private communication, 27 July 1970.
29. Technical data brochures published by Rust Engineering Co. Ltd., Croydon, Surrey, United Kingdom.
30. SHREVE, R. N. (1967) *Chemical Process Industries*, McGraw-Hill, New York.
31. LOGAN, J. O. (1970) "UOP sees TEL as key to auto pollution", *Petro|chem Engineer*, Vol. 42, No. 3, p. 14.

32. ZAHORI (1970) "Private view", *Chemical Age*, Vol. 100, No. 2654, p. 12.
33. "News feature - lead is looking afield", *Chemical Engineering*, Vol. 77, No. 7, 1970, P.64.
34. BOARD OF TRADE, BRITISH EXPORT INTELLIGENCE SERVICE, *Kuwait, Purified Salt Plant*, 28 August 1970 (Ref. No. 8010/70).



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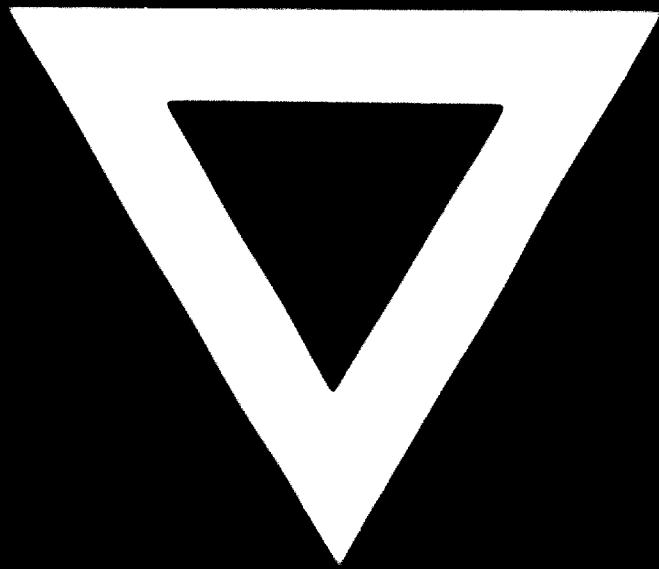
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