

## CHEMICALS FROM BRINE

### 1. Introduction

Nearly every country in the world has a source of brine containing useful minerals. Many have underground ore bodies that may be turned into brine by solution mining. Oceans and seas of the world are the largest sources of brine. Hundreds of companies extract sodium chloride, commonly called salt or halite, from the sea. Exportadora Del Sal is the largest producer of solar salt. They process over 8,000,000 tons each year at their facility in Baja California, Mexico. Many other small and large salt producing companies can be found along the coasts of Africa, India, China, Australia, South America, and coasts of the Mediterranean and the Aegean Sea. Salt is produced in the largest quantities, but there are other compounds of sodium, magnesium, potassium, and calcium made from sea brine.

A second, and significant source of brine, is found in terminal lakes. The Dead Sea in Israel and Jordan is an example of a large terminal lake with almost unlimited supplies of magnesium chloride, potassium chloride, and sodium chloride. Over two and one-half million tons of potassium chloride are extracted from the Dead Sea each year. Magnesium compounds and bromine are also extracted.

Great Salt Lake, Utah, is the largest terminal lake in the United States. From its brine, salt, elemental magnesium, magnesium chloride, sodium sulfate, and potassium sulfate are produced. Other well-known terminal lakes are Qinghai Lake in China, Tuz Golu in Turkey, the Caspian Sea and Aral'skoje in the states of the former Soviet Union, and Urmia in Iran. There are thousands of small terminal lakes spread across most countries of the world. Most of these

Table 1. Some Common Evaporite Salts

Mineral name	CAS Registry Number	Other names	Formula
anhydrite	[7778-18-9]	muriazite	$\text{CaSO}_4$
antarcticite			$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
aragonite	[14791-73-2]	calcite	$\text{CaCO}_3$
arcandite	[14293-72-2]	sulfate of potash (SOP)	$\text{K}_2\text{SO}_4$
bischofite	[13778-96-6]		$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
bloedite	[15083-77-9]	astrakanite	$\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$
borax	[1303-96-4]		$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
burkeite	[12179-88-3]		$\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$
caliche		mixture of nitrate, chloride, and sulfate salts	
carnallite	[1318-27-0]	crackel salt	$\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$
colemanite	[12291-65-5]		$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$
darapskite	[12196-75-7]		$\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
epsomite	[14457-55-7]	epsom salts, pickrite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
gaylussite			$\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5\text{H}_2\text{O}$
glaserite	[16349-83-0]	aphthitalite	$3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$
gypsum	[13397-24-5]	karstenite	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
halite	[14762-51-7]	salt	$\text{NaCl}$
hanksite	[12180-10-8]		$9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$
hexahydrate	[17830-18-1]		$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
hydrophilite			$\text{CaCl}_2$
kainite	[1318-72-5]		$4\text{KCl} \cdot 4\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$
kieserite	[14567-64-7]	wathlingenite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$
kernite	[12045-87-3]		$\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$
langbeinite	[14977-37-8]		$\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$
leonite	[15650-69-8]		$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$
loweite	[16633-52-6]		$\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2.5\text{H}_2\text{O}$
mirabilite	[14567-58-9]	Glauber's salt	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
nahcolite	[15752-47-3]		$\text{NaHCO}_3$
niter	[7757-79-1]		$\text{KNO}_3$
polyhalite	[15278-29-2]	mamanite	$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
pinsonite			$\text{NaCO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$
schoenite	[15491-86-8]	picromerite	$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
silvinite	[12174-64-0]		$\text{KCl} + \text{NaCl}$
sylvite	[14336-88-0]	muriate of potash (MOP)	$\text{KCl}$
syngenite		kaluszite	$\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$
tachydrite	[12194-70-6]	tachydrite	$\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$
thenardite	[7757-82-6]	salt cake	$\text{Na}_2\text{SO}_4$
trona	[15243-87-5]		$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
ulexite	[1319-33-1]		$\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$
vanthoffite	[15557-33-2]		$3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$

lakes contain sodium chloride, but many contain ions of magnesium, calcium, potassium, boron, lithium, sulfates, carbonates, and nitrates. Some terminal lakes have dried up leaving large expanses of salt called salars and salt flats. One such flat is in Wendover, Utah. This large expanse of salt is used as a race-way where many land speed records have been recorded. The largest salar in the world is in Uyuni, Bolivia. It is 100-km wide.

A third source of brine is found underground. Underground brines are primarily the result of ancient terminal lakes that have dried up and left brine entrained in their salt beds. These deposits may be completely underground or start at the surface. Some beds are thousands of meters thick. The salt bed at the Salar de Atacama in Chile is >300-m thick. Its bed is impregnated with brine that is being pumped to solar ponds and serves as feed stock to produce lithium chloride, potassium chloride, potassium sulfate, borax, and magnesium chloride. Searles Lake in California is a similar ancient terminal lake. Brine from its deposit has been used to recover soda ash, borax, sodium sulfate, sodium bicarbonate, potassium chloride, potassium sulfate, and lithium compounds.

A fourth source of brine is obtained through solution mining. Potash (KCl) is mined at Kane Creek, in Moab, Utah by solution mining. Much of the food grade sodium chloride in the United States, Europe, and other parts of the world is solution mined. Large beds of potassium salts in Canada and trona beds in Wyoming and California are being solution mined.

The main metals in brines throughout the world are sodium, magnesium, calcium, and potassium. Other metals are found in lesser amounts such as lithium, and boron. The nonmetals are chloride, sulfate and carbonate, with nitrate occurring in a few isolated areas. A major fraction of sodium nitrate and potassium nitrate comes from these isolated deposits. Other nonmetals produced from brine are bromine and iodine.

All of these metallic and nonmetallic ions join together in a complicated array of salts and minerals called evaporites. Several evaporites usually crystallize simultaneously in a mixture, which often makes separation into pure chemicals difficult. A list of some of the more common evaporites is shown in Table 1. This table also shows the chemical formula, and other mineral names.

## 2. Recovery Process

**2.1. Solar Evaporation.** Recovery of salts by solar evaporation is favored in hot dry climates. Solar evaporation is also used in temperate zones where evaporation exceeds rainfall and in areas where seasons of hot and dry weather occur. Other factors affecting solar pond selection are wind, humidity, cloud cover, and land terrain.

Large solar salt operations in the United States can be found along the shores of Great Salt Lake (1) and in the San Francisco Bay area (2). Salt production from solar ponds represents 14% of the total salt produced in the United States.

Total salt (NaCl) produced and consumed from all sources in the world is near 225 million tons. Large quantities of unusable salt are produced in

preconcentration ponds as an intermediate step in the production of other chemicals such as potassium chloride. For example, the Dead Sea facilities produce 50 million tons of salt each year but sell <0.5 of 1% because of the high cost of transportation to markets. Great Salt Lake Minerals Corporation also deposits >15 million tons a year of by-product salt, but can market only 1 million tons.

Brine depth in solar ponds is typically 15–50-cm deep. Ponds are usually built over flat areas where silts and clays have settled to make a tight soil base to prevent leakage through the bottom of the pond. In areas where soils are not tight, artificial liners of rubber, poly(vinyl chloride) (PVC) or high density poly ethylene (HDPE) are used.

Until the 1970s, solar ponds were constructed and operated as more of an art than a science. Since then, rising land value, environmental conscientiousness, limited space, and rising costs have forced a scientific approach to solar pond optimization, design, and operation, to make ponds more productive.

Where possible, solar salt is replacing vacuum salt because of rising energy costs. For example, at noon in July, the 162 km<sup>2</sup> (40,000 acres) of solar ponds at Great Salt Lake Minerals Corporation evaporate >907 million kg (2 billion lb) of water each day. This would require an equivalent of 100,000 tons of coal to supply the same energy each day.

Salts formed in saturated terminal lakes or in manmade solar ponds and lakes are called evaporites. A list of major evaporites is shown in Table 1.

**2.2. Seawater.** Salt extraction from seawater is done in most countries having coast lines and weather conducive to evaporation. Seawater is evaporated in a series of concentration ponds until it is saturated with sodium chloride. At this point >90% of the water has been removed along with some impurities, CaSO<sub>4</sub> and CaCO<sub>3</sub>, which crystallize at the bottom of the ponds. This brine, now saturated in NaCl, is transferred to ponds, called crystallizers, where salt precipitates on the floor of the pond as more water evaporates. Brine left over from the crystallizers is called bitterns because of its bitter taste. Bitterns is high in MgCl<sub>2</sub>, MgSO<sub>4</sub>, and KCl. In some isolated cases (India and China), magnesium and potassium compounds have been commercially extracted, but these represent only a small fraction of total world production.

Bays in San Francisco and San Diego are used to make salt from sea water. Worldwide, ~50 million tons of salt is produced from ocean water. Salt made from the seas is 97 to 98% pure (unwashed). The deposit is harvested in the fall after the weather turns cool and evaporation ceases (3). After harvesting, some of the salt may be washed to obtain salt >99% pure. Much of this salt is sold in bulk but some is rewashed and dried in rotary kilns or fluidized bed dryers to obtain salt of 99.8 and higher purity.

**2.3. The Great Salt Lake.** The Great Salt Lake, located in Northern Utah, is the largest lake in the western hemisphere that does not drain into an ocean. The level of the lake fluctuates depending on the weather and so does the mineral concentration. In 1983, annual rainfall was double the normal and runoff caused the lake to rise 5 ft. Again, in 1984, rain was above normal and the lake rose another 5 ft. causing hundreds of millions of dollars in flood damage and diluting the mineral concentration to half its pre-flood value.

In 1981, seven facilities extracted minerals from Great Salt Lake brine but flooding in 1983 and 1984 reduced the number to five. By 1992, four companies

were operating and are still in operation in 2003. All Great Salt Lake mineral extracting facilities have solar ponds as the first stage in processing minerals from brine.

The first salt to saturate and crystallize is halite. This salt is successively followed by epsomite, schoenite, kainite, carnallite, and finally bischofite. See Table 1 for the chemical composition of these minerals. In the winter, freezing temperatures cools the brine causing mirabilite (Glauber's salt) to crystallize. Solar pond end brine, called bitterns, contains 30–35% magnesium chloride. These bitterns are used as a feed stock to make magnesium metal, bischofite flake, dust suppressants, freeze prevention, fertilizer sprays, and in ion exchange resins. See Figure 1 for a multiproduct facility that uses Great Salt Lake Brine.

**2.4. Solution Mining.** Solution mining, also known as brining, is the recovery of sodium chloride (or any soluble salt) in an underground deposit by dissolving it *in situ* and forcing the resultant solution to the surface.

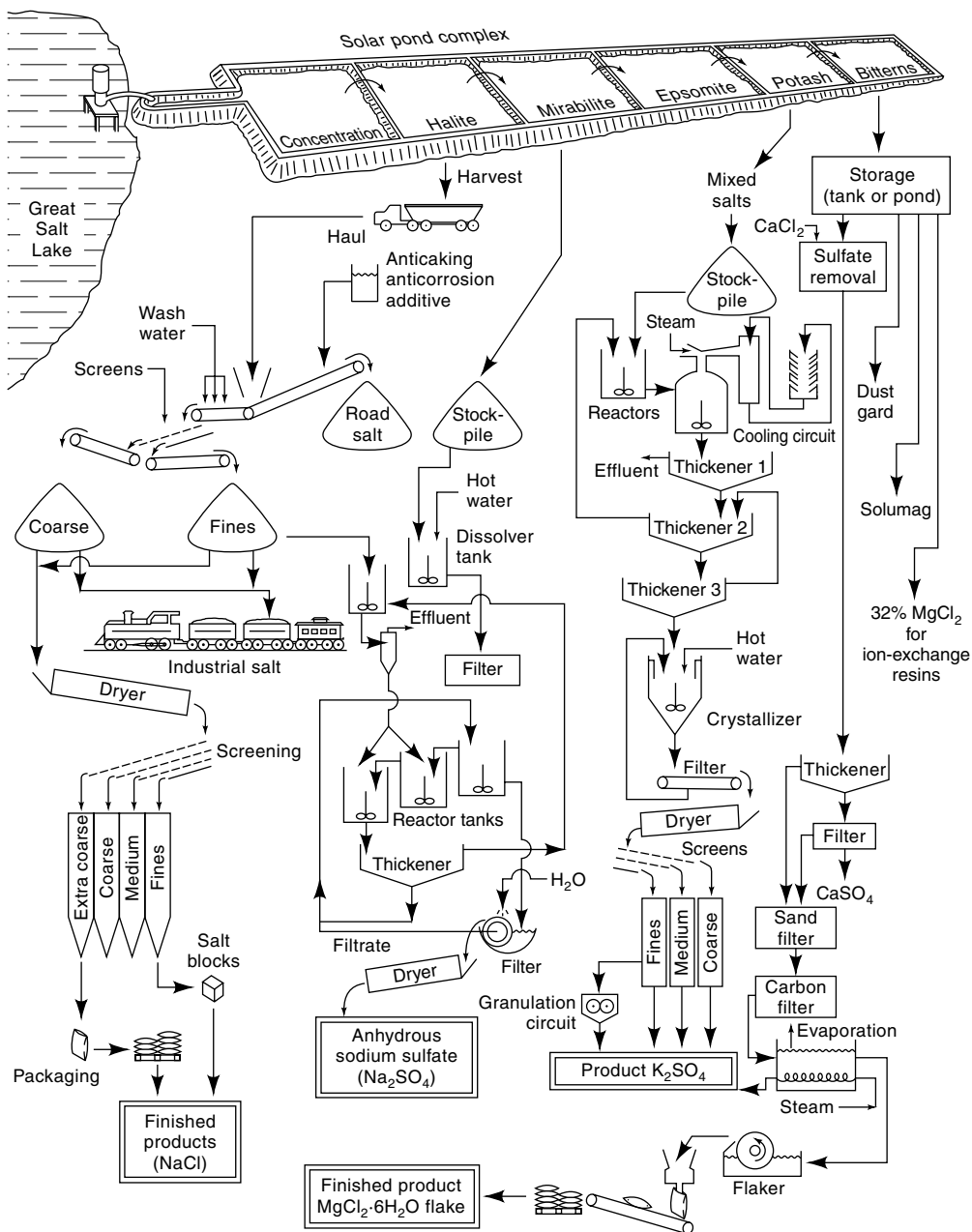
Solution mining produced nearly 20.5 million metric tons of salt in 2001 representing about one-half of the total U.S. salt production (4). Salt brine is made from bedded salt at >18 different locations and from 17 salt domes. Bedded salt of the Salina formation is the most widely and intensively exploited by solution mining. Enormous reserves of Salina salt are available. Cost of solution mining salt is usually less than the cost of salt produced by dry mining. The method is particularly good where salt deposits are deep and dry mining would not be feasible.

The essentials of solution mining a salt dome have not changed over the years. The method is shown in Figure 2. Production rate of any given mine is limited to the dissolving rate of the salt to bring it close to saturation. The flow rates of the injected water controls the rate of out flowing brine. Adjustment of this injected brine therefore controls the degree of saturation of recovered brine. Since energy must be used to remove all the water to recover sodium chloride, it is important to keep brine near saturation. Frequently, in thin bed salt strata, two wells (5) are used. The wells communicate through hydraulically formed fracture channels.

An environmental risk in solution mining is surface subsidence. This risk is greatest with embedded salt. No cases of salt subsidence have been reported in mining domes that have been mined according to standard industry approved practice in the United States, but some has been seen in other countries. One side benefit of dome solution mining is use of the cavities later for storage of industrial fluids, chiefly petroleum and natural gas.

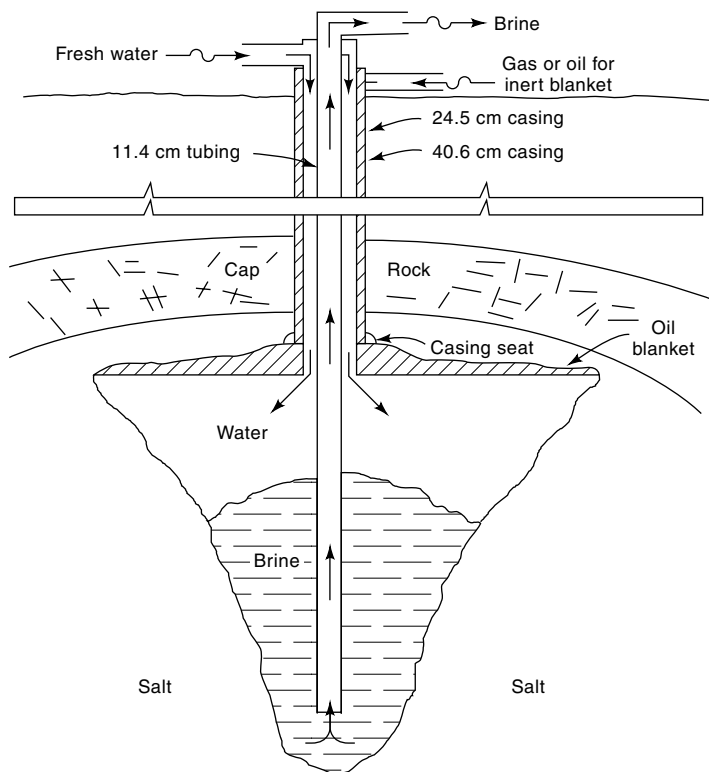
Solution mining for sodium chloride is extensively used in Europe and the states of the former Soviet Union.

**2.5. General Economics and Uses.** Demands and prices have a wide swing for some evaporites. New technology and development of brine reserves are increasing each year in the United States and abroad. This affects the uses and price of brine chemicals. Development of the Salar de Atacama in Chile in the 1980s as the largest producer of brine lithium in the world has affected lithium production and prices world wide. Figure 3 illustrates some major brine evaporites and their derivative products. Some of these chemicals find application in thousands of household objects. Sodium chloride alone is reported



**Fig. 1.** Abbreviated flow sheet of the multiproducts of Great Salt Lake Minerals Corporation.

to have over 14,000 different uses (6). The United States Geological Survey, USGS, has a web site (7) and a list of most evaporites showing pricing and production rates in the United States and abroad. Much information may be obtained about these chemicals from this web site.



**Fig. 2.** Typical solution mining operation in a salt dome (9).

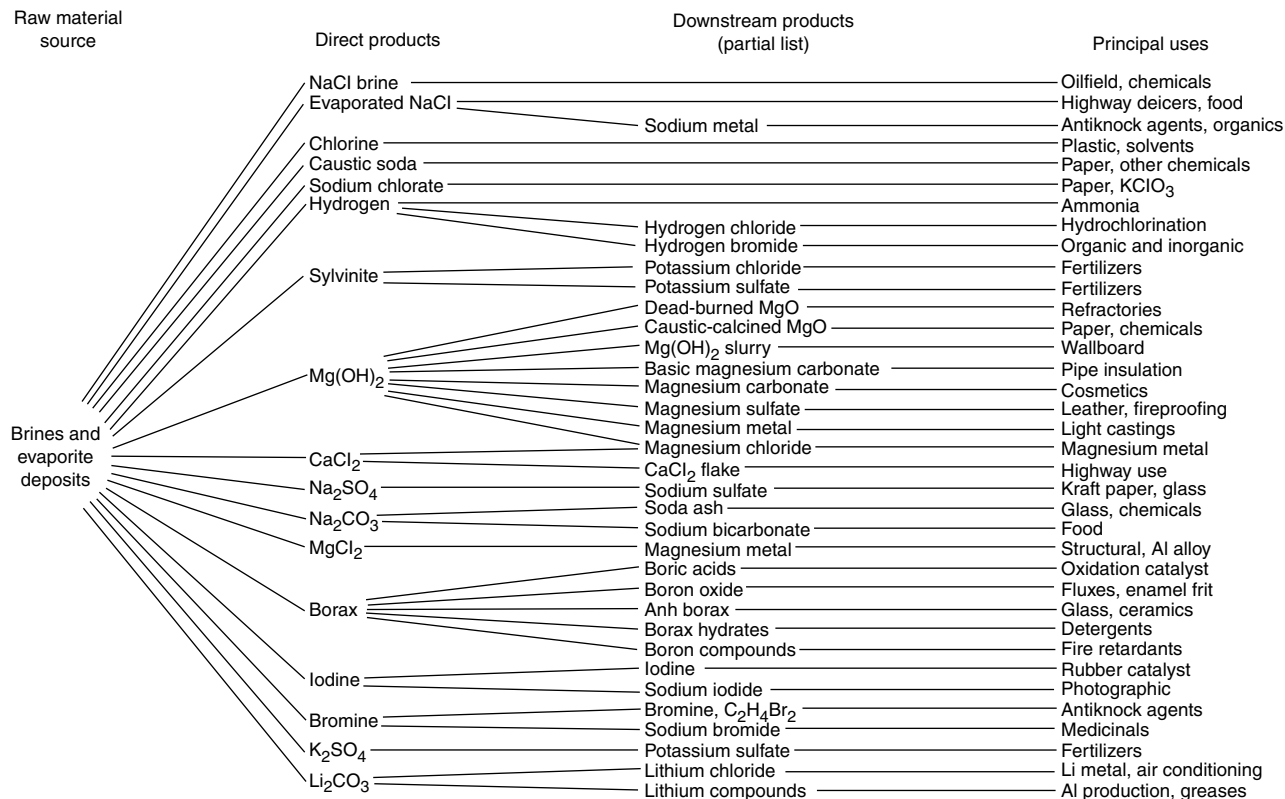
There has been much interest in making chemicals from brine because of the low expense as compared to alternative methods. Lithium, eg, had been mostly produced from spodumene ore in the 1970s but is now produced from brine. Similarly, solar salt has cost advantages over mined rock salt. Potassium chloride produced from brine has more than doubled from 1980 to 2000.

### 3. Minerals from Brine

A list of common minerals and their use is shown in Figure 3. This is only a small fraction of the tens of thousands of uses of these minerals extracted from brine.

**3.1. Boron Compounds. Occurrence.** Brine found in Searles Lake, California is the only major brine source where boron from brine is produced commercially in the United States. Brines at the Salar De Atacama in Chile also contain boron and extraction began in the 1990s.

Boron is found in two underground ores, ulexite, and colemanite. Research and pilot plant studies were completed in the last decade to solution mine these ores with water. Yield with water was low and replaced with a dilute solution of sulfuric acid that gave much higher yields. Boron is found in over 200 minerals but only four are of major importance. Borax, kernite, colemanite, and ulixite. These mineral are extracted mostly in California, and Turkey. To a lesser extent



**Fig. 3.** The brine chemical industry and some of its products.



Argentina, Bolivia, Chile, China, and Peru also produce boron compounds from these minerals.

**Recovery Process.** Boron values are recovered from brine of Searles Lake by North American Chemicals Corp. In one process, the brine is heated to remove some water and burkeite. The remaining brine is cooled to remove potassium chloride. This cooled brine is then transferred to another crystallizer where borax pentahydrate,  $\text{NaB}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ , precipitates. In a separate process, boron is removed by liquid-liquid extraction, followed by stripping with dilute sulfuric acid. Evaporator-crystallizers are used to recover boric acid. In a third process, borax is recovered by refrigerating carbonated brine. The most recent production is by Fort Cady Minerals Corp near Hectar, California. A solution of dilute sulfuric acid is used to solution mine a bed of borate ore 427 m underground. The boron enriched solution is then reacted with lime to precipitate a pure calcium borate product (8).

**Economics and Uses.** The principal producers in the United States are U.S. Borax and Chemical Corporation, North American Chemical, American Borate Corporation, and recently, Fort Cady.

**Minerals.** Their combined annual capacity in 2001 was reported to be 536,000 metric ton of equivalent  $\text{B}_2\text{O}_3$ . Of this tonnage, about one-half is exported. About 41% of boron compounds are used in glass fiber insulation, and heat resistant glass. Another 13% is used in enamel frits and glazes. Soaps and personal care products take 12%; Agriculture uses another 6% and the remaining 28% is consumed in all other uses. The United States is the largest producer of boron compounds in 2002.

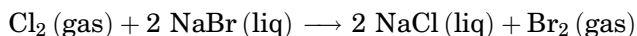
**3.2. Bromine. Occurrence.** Bromine is found in sea water and in underground brine deposits of marine origin (9). Bromine is also found in Dead Sea brine and is currently being produced there by the Dead Sea Works and the Jordan Bromine Co.

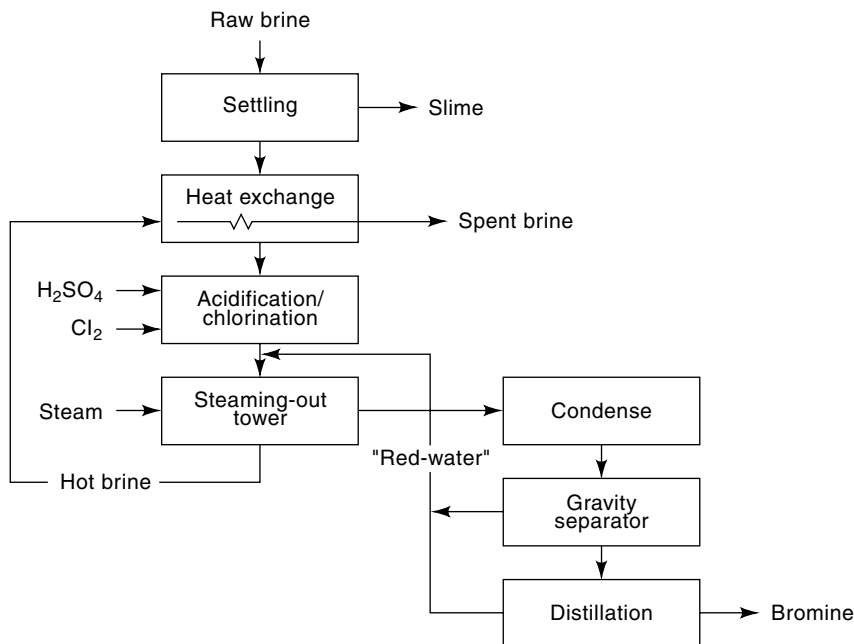
The earliest commercial production of Bromine in the United States, in the mid-1800s, made use of a brine well in Freeport, Pennsylvania. Later, recovery of bromine from brine wells in Midland County, Michigan was developed. Production from brines in Michigan, Ohio, and West Virginia supplied the major portion of production in the United States until 1935. Michigan brines are still a source of bromine today. A major source of bromine comes from wells in Arkansas. Albermarle Corp opened up new wells in Union county, Arkansas July 2000. They now have a total of 31 wells.

Bromine is found in Searles Lake brine and was produced there at one time, but commercial extraction has been discontinued. The United States produces 40% of the world bromine production.

**Recovery Process.** Commercial processes depend on the oxidation of bromide to bromine. Most of the liberated bromine remains dissolved in the brine. The brine is then stripped of bromine, followed by recovery of bromine from the stripping agent. Subsequent purification by distillation is often a final step.

Direct electrolysis was used at one time for the oxidation step. Manganese dioxide has also been used as an oxidant. Most present day processes use chlorine:





**Fig. 4.** Steaming-out process for recovery of bromine from high bromide brines.

Steam stripping or steaming-out (Fig. 4), is a method used in the United States to remove elemental bromine from the brine. This method is economical for brines containing bromine  $>1000$  ppm (10).

Older methods of stripping used with concentrations below 1000 ppm utilize a stream of air flowing counter current to the brine stream. The bromine is then recovered from the air with wet scrap iron, ammonia, sodium carbonate, or sulfur dioxide (11,12).

**Economics and Uses.** The United States produces  $\sim 225,000$  tons of bromine per year at an estimated value of 200 million dollars. All bromine is extracted from brine wells. Abermarle Corp. reported in 2000 that 31% of bromine production was used for flame retardants; pharmaceuticals and agriculture, 18%; catalysts and additives, 21%; and performance chemicals, 30%.

Ethylene dibromide is used in gasoline. It is also used as a soil fumigant (methyl bromide). Other commercial forms are alkali metal bromides, ammonium bromide, and hydrobromic acid. About 100 kg of plastic is used per car. These plastics use bromine flame retardant (BFR). The BFRs are used in oil filters, battery cases, bumper fascias, carpeting, connectors, corrugated wire conduits, dash board covers, electric insulation, and many more automotive parts.

## 4. Calcium Chloride

**4.1. Occurrence.** Brines are the main commercial source of calcium chloride. Some brines of Michigan, Ohio, West Virginia, Utah, and California

contain >4% calcium. Michigan is the leading state in natural calcium chloride production with California a distant second.

A former commercially important source of calcium chloride was a by-product of the Solvay Process used to produce soda ash. Because of environmental concerns and high energy costs, the Solvay Process has been discontinued in the United States, but it is still used extensively elsewhere in the world.

**4.2. Recovery Process.** Because of its high solubility compared to that of other brine constituents, calcium chloride is the final constituent recovered in a multiproduct brine processing operation. Magnesium chloride is another highly soluble component that may occur with the calcium chloride. Separation of magnesium ions may be accomplished by precipitating magnesium hydroxide, or by crystallizing tachyhydrite,  $\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$  or  $2\text{CaCl}_2 \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ . Both yield additional calcium chloride liquor. Calcium chloride flake is made similar to magnesium chloride flake (see Fig. 5).

**4.3. Economics and Uses.** Most production of calcium chloride is from Michigan brines. The principle use of calcium chloride is to melt snow and ice from roads. It is also used in dust control, concrete setting control, waste water treatment, and various industrial uses. As a dust suppressant, it is simply

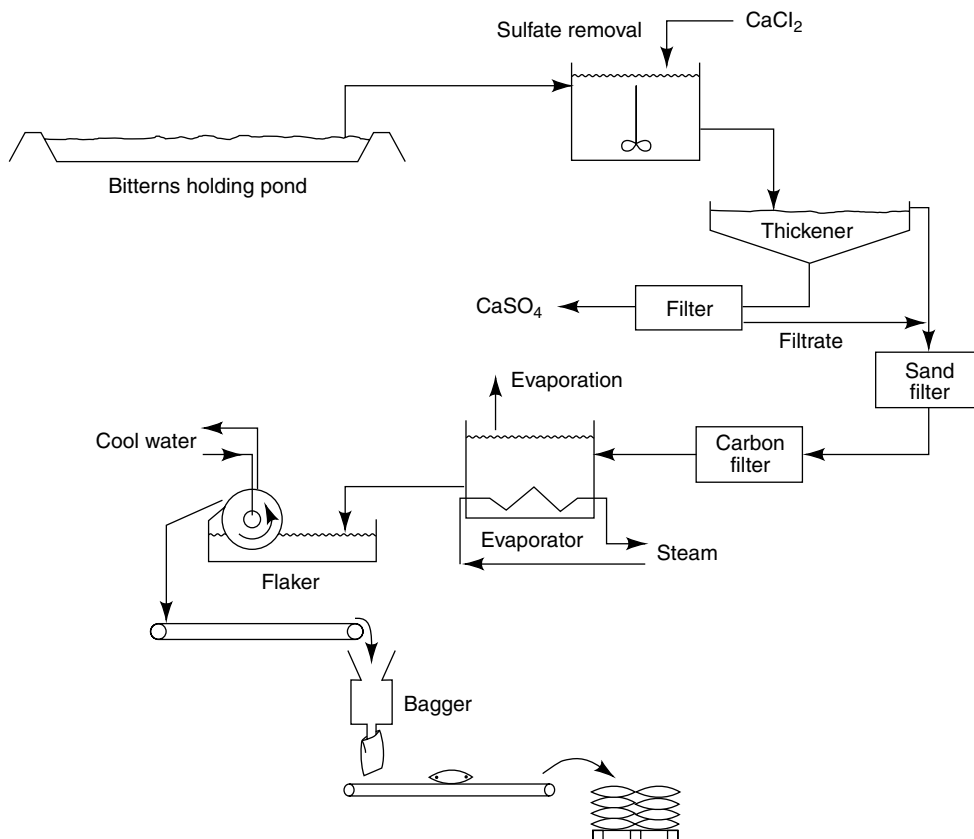


Fig. 5. Magnesium chloride flaking circuit  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

sprayed over dusty areas or on unpaved roads where its dust wetting and binding properties can last for months in dry arid regions.

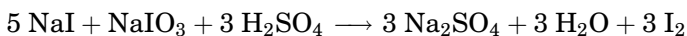
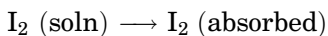
## 5. Iodine

**5.1. Occurrence.** Iodine is widely distributed in the lithosphere at low concentrations ( $\sim 0.3$  ppm). It is present in sea water at a concentration of 0.05 ppm. Three companies in Oklahoma accounted for all of the Iodine made in the United States in 2002. Certain marine plants concentrate iodine to higher levels than occur in the sea brine and these plants have been used for their iodine content. A major source of iodine is caliche deposits of the Atacama Desert, Chile. About 32% of the world's iodine is produced in Japan from natural gas wells. This is down from 40% over the last 10 years because of lower production costs from Atacama Desert caliche. By 1992, Chile was the major world producer and by 2002, Chile was producing 55% of the world's Iodine. In the United States, underground brine is the sole commercial source of Iodine. Such brine can be found in the northern Oklahoma oil fields originating in the Mississippian Geological System.

**5.2. Recovery Process.** Prior to 1966, iodine was recovered at Long Beach, California from oil field brine and from natural brines near Shreveport, Louisiana. The silver process was used. Silver nitrate was reacted with sodium iodide to precipitate silver iodide. Iron was then added to form ferrous iodide and free silver. The ferrous iodide was then reacted with chlorine gas to release free iodine. After 1966, the silver process was replaced with the "blowing out" process similar to the bromine process.

Later, more concentrated brines of the Midland, Michigan producers displaced the California producers. In 1976, Houston Chemicals began recovery using the blowing out process from underground brines of the Anadarko Basin in northwestern Oklahoma. Annual capacity was 900 metric tons. By 2003, all of the iodine produced was made from Oklahoma brines by a blowing out process.

Japan was the leading producer of iodine in the 1980s, producing nearly 7000 metric tons/year. Production in 2002 was 6,100 tons. Elemental iodine is released into brine by treatment with sodium nitrate or chlorine. The free iodine is then absorbed on activated carbon, and stripped from the carbon with sodium hydroxide followed by acidification to form a slurry of elemental iodine:



A large reserve of caliche ore-bearing iodine is being processed in the Atacama Desert. About 55% of the world supply of iodine is made from these Chilean deposits. The process consists of leaching the caliche with water. Brine is stripped of iodine using an organic solvent. The iodine is then removed from the solvent to form a slurry. Solid-phase iodine is separated from the slurry

in conventional flotation cells, dried and packaged. Details of the process are proprietary.

**5.3. Economics and Uses.** Most of the iodine used in the United States comes from Japan and Chile. The United States produces 7% of the world supply but consumes 28%. Iodine is produced in Woodward, and Vici Oklahoma. These two locations produced 1290 tons in 2001, and an estimated 1700 tons in 2002. Total world consumption is approximately 19,000 tons. Price per kilogram in 2002 was ~\$13.

In 2001, estimated uses for Iodine were as follows: sanitation 45%; animal feed, 27%; pharmaceuticals, 10%; catalysts, 8%; heat stabilizers, 5%; and other, 5%. These other uses include inks and colorants, photographic chemicals, laboratory reagents, batteries, motor fuels, and lubricants (13).

## 6. Lithium

**6.1. Occurrence.** Numerous brines contain lithium in minor concentrations. Commercially valuable natural brines are located at Silver Peak, Nevada (300 ppm), and at Searles Lake, California (50 ppm). Great Salt Lake brine contains 40 ppm and is a source not yet exploited. Sea Water contains <0.2 ppm. Lithium production started at Silver Peak in the 1970s, but concentrations of lithium in the brine have diminished by 25% and now major production occurs from brine in the Salar de Atacama, Chile. Lithium brines with commercial potential are found in the Altiplano of Bolivia and Argentina, in salt beds of Chile, and in several salt beds in central and western China. Lithium is presently being extracted from the Salar de Hombre Muerto in Argentina.

**6.2. Recovery Process.** Lithium is extracted from brine at Silver Peak Marsh, Nevada, and at the Salar De Atacama, Chile. Both processes were developed by Foote Mineral Corporation. The process at Silver Peak consists of pumping shallow underground wells to solar ponds where brines are concentrated to 6000 ppm. Lithium is then removed by precipitation with soda ash to form lithium carbonate [554-13-2]. At the Atacama, virgin brine with nearly 3000 ppm lithium is concentrated to near saturation in lithium chloride. This brine is then shipped to Antofagasta, Chile, where it is combined with soda ash to form lithium carbonate.

**6.3. Economics and Uses.** In 1976, one-third of the lithium produced in the United States was extracted from brines of Searles Lake and Silver Peak. Since then, Lithium production at Searles Lake has been discontinued and the lithium concentration at Silver Peak is decreasing. During the 1980s lithium extraction was started at the Salar De Atacama, Chile, and expanded in the 1990s. The Chilean operation is the largest lithium production in the world. Prior to 1980 most of the lithium was produced from Spodumene ore. It still is in some countries, but now nearly all lithium is produced from brine.

The United States produces and consumes about one-half of all the world production. Imports of brine based lithium carbonate are increasing. FMC, Lithium Division, now has long term contracts with Producers of lithium carbonate in Chile (14).

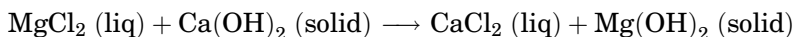
Over one-half of the lithium production is used as a cell-bath additive in aluminum production and in ceramics and glass. Almost all major battery manufacturers produce some types of lithium batteries. Other uses are in lubricants, synthetic rubber, plastics, and pharmaceuticals. Since lithium is a light, strong metal, it finds applications in aerospace metals and alloys where a light metal is needed.

Lithium carbonate prices are steady at \$4.47/kg from 1990 to 2000, but pricing for 2001 and 2002 is not available (15).

## 7. Magnesium Compounds

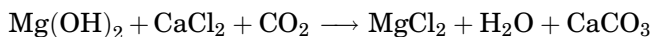
**7.1. Occurrence.** Magnesium hydroxide and magnesium chloride are two commercially important magnesium compounds recovered directly from natural brines. From these compounds many other compounds of magnesium are made such as elemental magnesium and magnesia. Other important compounds containing magnesium are epsomite, schoenite, kainite, and carnallite (see Table 1). Major magnesium sources are sea water (1300 ppm Mg), Great Salt Lake (1.1% Mg), underground brines near the surface east of Wendover, Utah (1%), subterranean brines in Michigan (0.7–2.5%), and brine from the Yates formation in the Midland Basin of West Texas (3%). Besides the oceans, there are vast reserves of magnesium chloride in the Dead Sea, Qaidam Basin, China, and many salars of South America.

**7.2. Recovery Process.** Magnesium hydroxide [1309 42-8] can be recovered in relatively pure form either from the brine or from an intermediate plant liquor by increasing alkalinity. For example:



Better recoveries can be made by replacing lime with dolomite [39445-23-3] that has been calcined. Sometimes NaOH is used when low calcium in the product is required.

Recovery of magnesium chloride [7786-30-3] as a direct product is usually economically feasible only as a by-product. Like calcium chloride, magnesium chloride is highly soluble and is extracted at the end of a series of processes that first removes the less soluble products as the magnesium ion concentrates. In Michigan brines, NaCl, Br<sub>2</sub>, I<sub>2</sub>, CaCl<sub>2</sub>, Mg(OH)<sub>2</sub>, and KCl are coproducts. At Great Salt Lake, NaCl, Na<sub>2</sub>SO<sub>4</sub>, and K<sub>2</sub>SO<sub>4</sub> are coproducts and MgCl<sub>2</sub> is the last to be recovered. In a current process for Michigan Basin brines, pure MgCl<sub>2</sub> liquor is formed by reacting previously precipitated Mg(OH)<sub>2</sub> with stack gas and concentrated brine:



End brines at Wendover Utah and the Great Salt Lake have concentrations up to 36% MgCl<sub>2</sub>. At Great Salt Lake Minerals Corporation, this highly concentrated brine is artificially evaporated to remove 15% of the water. The hot solution is then cooled to form bischofite (MgCl<sub>2</sub>·6H<sub>2</sub>O). Figure 5 shows the process.

Magnesium metal is produced by the electrolysis of molten  $\text{MgCl}_2$  by two different processes. In the old Dow sea water process,  $\text{MgCl}_2$  liquor is formed by reacting lime or dolomite with sea water to form  $\text{Mg}(\text{OH})_2$  and then neutralized with  $\text{HCl}$  to form  $\text{MgCl}_2$ . The slurry is dried to a hydrous cell feed containing  $\sim 70\%$   $\text{MgCl}_2$ . This process was ended in 2001 when Alcoa Inc. stopped production of its 43,000 tons/year facility. The other process used by MagCorp with Great Salt Lake brines, recovers anhydrous  $\text{MgCl}_2$  directly from concentrated brine by spray drying. In both cases, elemental magnesium and chlorine gas are formed in the cells. MagCorp's facility is the only major producer of magnesium, metal in 2003. They produce  $\sim 45,000$  t/yr magnesium from brine.

The Dead Sea has an unlimited reserve of  $\text{MgCl}_2$ . The Dead Sea Works, produces about 30,000 tons/year of  $\text{MgO}$  equivalent from some of their concentrated brines. The Arab Potash Company is also beginning to produce  $\text{MgO}$  at its new bromine plant.

$\text{MgO}$  has also been produced from concentrated ocean brines that have first been used to make sodium chloride in solar ponds. The process is basically to form  $\text{Mg}(\text{OH})_2$  by adding dolomite or lime to the brine and then to burn  $\text{Mg}(\text{OH})_2$  to  $\text{MgO}$ .

**7.3. Economics and Uses.** Magnesium is removed from brines of the Great Salt Lake in the form of magnesium chloride. This is then used to make elemental magnesium, dust suppressants, and bischofite flake. Magnesium chloride is also used in drilling mud, ion exchange resins, oxy-chloral cements, fertilizers, and miscellaneous industrial uses. Magnesium hydroxide and magnesium chloride are used as a basic feed stock to make elemental magnesium, refractories ( $\text{MgO}$ ), and reactive chemicals. Over 1,000,000 tons of magnesium and magnesium compounds were made in the United States in 2001 (16). Twelve million tons were made world wide. Prices vary widely depending on the product.  $\text{MgO}$  (dead burnt) sold for \$363/ton in march of 2003. Hydrous magnesium chloride sold for \$0.145/lb (17). The metal price is  $\sim 1.2$ /lb (18).

## 8. Potassium Compounds

**8.1. Occurrence.** There are two forms potassium compounds in brines of the world. Muriate of potash ( $\text{KCl}$ ) and sulfate of potash ( $\text{K}_2\text{SO}_4$ ). These brine potash operations are located in Utah (Moab, Ogden, Wendover) and one in California (Searles Lake). Operations in Searles Lake have produced both muriate and sulfate of potash. The Ogden operation produces sulfate of potash. The others produce muriate.

**8.2. Recovery Process.** Moab Salt, LLD, Cane Creek potash operation of Moab, Utah, produces  $\text{KCl}$  by solution mining. Brine is pumped from underground to 400 acres of solar ponds where a mixture of  $\text{KCl}$  and  $\text{NaCl}$  is crystallized in a salt mass called sylvinite. Sylvinite is removed from the ponds with scraper-loaders and hauled to a central pit. The salts are then transported to the refinery in a slurry line.  $\text{KCl}$  is separated from the  $\text{NaCl}$  by flotation. The flotation process is standard throughout the industry and is the same process used to separate  $\text{KCl}$  from impurities in a carnallite decomposition process explained later. An amine collector is used as one of the flotation reagents.

Production of KCl at the Wendover, Utah operation employs a large 7000-acre complex of solar ponds. Both shallow brine wells and deeper wells are used to pump brine into the pond complex. Surface canals 7-m deep have also been dug out into the ore body. These canals fill with brine which is pumped to nearby ponds. In the preconcentration ponds, water is evaporated and sodium chloride is crystallized. Later the brine is transferred to production ponds where sylvinite is deposited. Brine is then transferred to other ponds where carnallite is crystallized. Sylvinite is removed from drained ponds with self-loading scrapers and taken to the plant where KCl is separated by flotation with an amine oil collector. The carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) is decomposed by leaching with water. The water dissolves  $\text{MgCl}_2$  and leaves KCl and impurities, mainly NaCl. KCl is then separated from impurities by conventional flotation.

Great Salt Lake Minerals Corporation (GSL) near Ogden, Utah, produces potassium sulfate and several other products from Great Salt Lake brines. Presently 35,000 acres is divided into 85 solar ponds. Two years are required to process brine through the ponds. During the 2 years, salts crystallize in the following sequence: NaCl,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot \text{KCl} \cdot 2.75\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ , and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . In the winter  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  crystallizes. All the salts containing potassium are harvested from the ponds and hauled into the refinery where impurities are leached out and remaining potassium is converted to  $\text{K}_2\text{SO}_4$ . In addition to potassium, three other major products are made as shown in the flow of Figure 1.

**8.3. Economics and Uses.** Total world production of potassium products is 27,000,000 ton/year (19). Potassium chloride is removed from brine at Moab; Wendover, Utah; and at Searles Lake, California. Potassium sulfate is made from Great Salt Lake brine by Great Salt Lake Minerals Corporation who is the largest producer of solar potassium sulfate in the world. Combined, these U.S. facilities still produce a relatively small percentage of potash fertilizers in the world. Production from the Dead Sea, eg, is 10 times greater than production of potassium from brines in the United States. More than 95% of all the potassium produced is used in fertilizer blends. The remainder is converted to other potassium chemicals for industrial use.

Domestic potash production supplies one-third of the U.S. consumption. Price of both KCl and  $\text{K}_2\text{SO}_4$  fluctuates. KCl ranges between 105 and 125 dollars a ton. Sulfate of potash sells for \$190–200/ ton (20).

## 9. Sodium Carbonate

**9.1. Occurrence.** The brines of Searles Lake, California are the sole brine source of sodium carbonate (soda ash) production in the United States. There is a large underground deposit of sodium carbonate brine in the Sua Pan area of Botswana, Africa where 270,000 tons were produced in 2001. Another potential source is Owens Lake, California. Owens Lake brines were used to produce soda ash but discontinued in 1967. There are many other deposits in the world where there are deposits of trona and nahcolite (21).

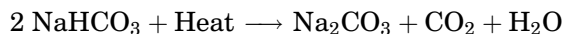
**9.2. Recovery Process.** Presently North American Chemicals Co. at Searles Lake is the only significant producer in the United States of sodium



carbonate from brine (abt. 1,000,000 tpy). The process is based on converting all sodium carbonate in the brine to sodium bicarbonate by adding  $\text{CO}_2$ :



Impurities remain in the brine solution and the sodium bicarbonate crystallizes and is filtered from the liquor. The bicarbonate is then converted to carbonate by heating:



carbondioxide is recycled back again to the carbonation vessels.

In 1976, >3,000,000 ton of soda ash was produced in the United States using a procedure called the Solvay Process. This process has been discontinued in the United States because of pollution problems and high processing costs. It is still an important process in other countries.

**9.3. Economics and Uses.** North American Chemical Company at Searles Lake is now the only producer of soda ash from naturally occurring brine in the United States. Production from brine represents ~10% of U.S. production. Total 2001 production in the United States was 10 million tons. Total world production was 35 million. Price in 2003 was \$120/ ton bulk.

One-half of all sodium carbonate is used in glass production. Production of other chemicals use another 25%. Soap and detergents use 11% and Flue gas desulfurization, pulp and paper, water treatment consume what is left.

## 10. Sodium Chloride

**10.1. Occurrence.** About one-half of all the sodium chloride produced in the world is from brine. Approximately 100 million tons a year are produced from brines of the ocean, terminal lakes, subterranean aquifers and solution mining. Sodium is found in large quantities in most areas of the world. Its quantity is so large that prices in some locations are only \$25 a ton. Many areas have millions of tons but prices are so low that it is not economical to mine or process the salt. The largest exposed sodium chloride bed is at the Salar de Uyuni, Bolivia, but Bolivia is land locked and very little of the salt can be processed and sold at a profit.

**10.2. Recovery Process.** Figure 1 shows a typical process for producing sodium chloride (halite). There are two main processes. One is to flood solar ponds with brine and evaporate the water leaving sodium chloride crystallized on the pond floor. The other is to artificially evaporate the brine in evaporator-crystallizers. Industrial salt is made from solar ponds where food grade salt made for human consumption is mostly made in the evaporator-crystallizers.

**10.3. Economics and Uses.** The United States is the largest producer of salt in the world. In 2001. Some 45 million tons was produced compared to 180 million tons made in the rest of the world. Salt continues to be one of the most heavily traded chemical ores in the world representing >50% of all seaborne mineral trade. World consumption is >200 million tons/year. Most of this salt

is made from brines. Salt is used directly or indirectly in 14,000 different products (22).

Salt has had a major impact on the economies of some countries and in some places it still does. Salt was the first chemical recognized and used in ancient times (23). It was first used in food for taste enhancement and as a preservative.

Today most salt is used to make caustic soda and chlorine. These chemicals are used in thousands of household products. The next biggest use is for highway deicing. Other uses are for water softening, livestock feeds, meat packing and foodstuffs. Chemical use in 2001 was 41%; ice control, 34%; retail distribution, 8%; general industrial, 6%; agricultural, 4%; food processing, 4%; all other, 5%. Price of salt ranges from \$20/ton raw bulk, to \$122 processed and packaged.

## 11. Sodium Sulfate

**11.1. Occurrence.** In the United States, natural sodium sulfate brines are found in California at Searles Lake, at the shallow Castile formation underlying Terry and Gains counties, Texas, and at the Great Salt Lake, Utah.

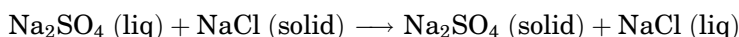
Other natural sodium sulfate brines of commercial importance are found in dry lake beds of southwestern Saskatchewan, Canada; Laguna Del Ray in Coahuila, Mexico; the Gulf of Kara-bogaz, Russia, and in western China. Some lagoons and salars around the world have brines rich in sulfates such as the Huyamampa Lagoon in Santiago, Argentina and Aguas Blancas, Chile.

**11.2. Recovery Process.** The process for making sodium sulfate is different at each facility where it is produced. One step common to all facilities is a cooling step to form Glauber's salt followed by a purification and recrystallization step to form anhydrous sodium sulfate.

In Texas, brine is pumped from underground deposits. Sodium chloride is added to bring the brine near saturation. This solution is then chilled to  $-8^{\circ}\text{C}$  to crystallize Glauber's Salt (24). Anhydrous  $\text{Na}_2\text{SO}_4$  [7757-82-6] is recovered by artificially evaporating the liquor formed after re-melting the Glauber's salt.

At Searles Lake, sodium sulfate is recovered as one of three coproducts in a series of complex operations where soda ash and borax are also recovered from the brine. Anhydrous sodium sulfate is recovered by artificially evaporating the water from melted Glauber's Salt.

In processing Great Salt Lake brine, Glauber's salt is crystallized in solar ponds by cooling during the winter. This salt is harvested and stockpiled when ambient temperatures are still cold. Once the stockpile has drained, the Glauber's salt is stable in the solid phase throughout the year and can be reclaimed at any time. Reclaimed Glauber's salt is dissolved in hot water at the refining plant. The resulting liquor is filtered to remove insolubles and then reacted with sodium chloride to form anhydrous sodium sulfate according to the reaction below. The process is shown in Figure 1.



**11.3. Economics and Uses.** About one-half of all sodium sulfate produced in the United States is from brine. In 2002, 500,000 ton was produced.

All of the production is from North American Chemicals (Searles Lake) and Ozark-Mahoning at Brownfield and Seagraves, Texas. Great Salt Lake Mineral Corp has discontinued production.

Of the sodium sulfate produced in the United States, the paper industry consumes 13%; detergents and soap, 46%; glass, 11%; textiles, 12%; carpet fresheners, 7%; and miscellaneous, 11% (25). Powdered detergents are on the decline in favor of liquids that do not use sodium sulfate. Since, the pulp and paper industry is also using less, the price of sodium sulfate has been declining.

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