Production of Solid Salt From Diaphragm Cell Liquor

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ABSTRACT

The Chlor-Alkali Industry consumes approximately 16.5 million tons of sodium chloride per year. Sodium chloride brine is electrolyzed in either diaphragm or mercury cells to produce chlorine and caustic soda.

Solution mining of salt provides an economic advantage that is exploited with diaphragm cells. The cost of salt is dependent upon geographical area and method of mining. Salt in solution from wells cost \$1.00 to \$1.50 per ton. Solid salt from conventional mining or solar evaporation cost \$4.00 to \$8.00 per ton.

The mercury cell process requires solid salt. About 10% to 15% of the salt contained in the brine is decomposed electrolytically as it passes through the mercury cells. Depleted brine must be resaturated with solid salt and recycled to the cells.

The Diaphragm cell process does not require solid salt but produces high quality salt. Diaphragm cells decompose about half of the sodium chloride content of the feed brine by electrolysis and produce cell liquor containing 9% to 15% caustic soda and 12% to 18% sodium chloride. Cell liquor is evaporated in multiple effect evaporators to produce 50% caustic soda and solid salt. A 100 ton of chlorine per day diaphragm chlor-alkali plant may produce 100 to 200 tons per day of solid salt from brine. In areas or circumstances where a demand for solid salt exist a considerable credit for salt produced is realistic.

Diaphragm cells may produce the salt required by mercury cells in an integrated plant.

The Chlor-Alkali Industry.

The chlor-alkali industry includes the production of chlorine, caustic soda, caustic potash, soda ash, and sodium chlorate. The United States industry consumes more than 22.5 million tons of sodium chloride per year. This is more than half of the total sodium chloride production in the United States.

The chemical industry is built on a number of basic commodity chemicals, or heavy chemicals, that serve as raw materials for the production of many other chemicals, plastics, textiles, and various consumer products. A total of 19 million tons of chlorine and caustic are produced in the United States per year. The raw materials for the chlorine and caustic industry are power, sodium chloride, and water. About 16.5 million tons of salt are consumed per year in the production of chlorine and caustic.

The United States chlor-alkali industry produced about 8.5×10^6 tons of chlorine and 9.35×10^6 tons of caustic in 1968. The two major processes used for this production are the diaphragm cell process and the mercury cell process. In the United States, the diaphragm cell produces about 65% of these chemicals, while the mercury cell produces most of the remaining tonnage. In Europe, and the rest of the world, the mercury cell is used more extensively than the diaphragm cell, and the percentages of production by the two processes are approximately reversed. Both of these processes electrolyze brine and produce chlorine, hydrogen, and caustic in a 50% solution.

The equations involved, and 1968 capacities, for the diaphragm and mercury cell processes are as follows:

$$\underset{5.18 \times 10^6\ T/Y}{2NaCl} + 2H_2O \xrightarrow[\text{Cells}]{\text{Mercury}} \underset{2.96 \times 10^6\ T/Y}{Cl_2} + \underset{3.25 \times 10^6\ T/Y}{2NaOH} + H_2$$

$$\underset{11.2 \times 10^6\ T/Y}{4NaCl} + 2H_2O \xrightarrow[\text{Cells}]{\text{Diaphragm}} \underset{6.03 \times 10^6\ T/Y}{Cl_2} + \underset{6.6 \times 10^6\ T/Y}{2NaOH} + \underset{9.2 \times 10^6\ T/Y}{2NaCl} + H_2$$

In the case of the diaphragm cell process, the sodium chloride values are supplied as brine, and from this process purified-grade solid sodium chloride is produced. This is usually recycled to the cells as brine. The 1968 capacities show that 9.2×10^6 T/Y of pure crystal sodium chloride could have been produced as a by-product of the diaphragm cell process.

Sources of Salt.

Salt for the chlorine and caustic industry comes from three sources—solution mining, conventional mining of solid salt, and from solar evaporation of sea water. Many large diaphragm cell plants, and some mercury cell plants, have been built near underground salt deposits. These salt deposits are solution mined and the brine is piped to chlor-alkali plants as nearly saturated solutions. Solution mining can produce salt, in the form of brine, for \$1.50 per ton or less. The cost at the chlor-alkali plant site depends on the depth and thickness of the salt deposit, pipeline cost for transporting the brine from the well site to the plant, and operating expense for pumping. It is generally economical to pipe brine to diaphragm cell plants as far as 50 miles from the wells.

Less than 30% of the salt consumed in the United States is produced from conventional underground mining of solid salt. The cost of this salt is higher than that obtained by solution mining, due to the higher capital investment required and the high labor cost in mining and handling operations. Mined salt is sold at prices ranging from \$3 to \$5 per ton. In the United States, mined salt is usually shipped into areas where there are no salt deposits. Shipping distances may be as great as 500 miles or more.

Solar evaporated salt is used in United States chlor-alkali plants on both the East and West coasts. A review of the chlorine capacity in the United States indicates that 8% to 10% of the production may be from solar salt. In other parts of the world, especially in arid, hot climates, solar evaporation of sea water is the conventional method of supplying salt to the chlor-alkali industry. In some cases, solar salt is shipped by ocean freighter for great distances.

All three of these sources of salt can produce brine of adequate quality. Impurities such as sulfates, calcium, and magnesium, are detrimental to the diaphragm cell process. These same impurities are undesirable to the mercury cell process which, in addition, is sensitive to heavy metal impurities.

The Mercury Cell Process.

A block diagram of the mercury cell process is shown in Figure 1. Because of the water balance in the process, the mercury cell requires solid salt.

There are some mercury cell plants operating on solution mined brine. This is usually at the expense of wasting a considerable portion of the brine. Stricter antipollution laws, plus unfavorable economics, will probably decrease the volume of this operation. The major point is that mercury cell plants are normally solid salt consumers.

The Diaphragm Cell Process.

The diaphragm cell process is shown in the block diagram of Figure 2. One of the significant aspects of this process is that it does not require solid salt. The products of this process are chlorine, caustic, hydrogen, and solid salt.

Nearly saturated brine is fed to the diaphragm cell. This brine flows through the diaphragm in the cell where approximately one half of the salt is converted to sodium chloride. Thus the solution effluent, commonly called cell liquor, contains approximately 11% caustic, 16% sodium chloride, sulfate impurity, and the rest water. Salt is produced at a ratio of 1.4 to 1.5 pounds of sodium chloride per pound of sodium hydroxide. This cell liquor, or caustic solution, is evaporated in multiple-effect evaporators to produce a 50% sodium hydroxide solution. During the water removal process the salt in the solution precipitates and is separated from the caustic solution as solid salt.

The solubility of sodium chloride in sodium hydroxide at various concentrations and temperatures is shown in Figure 3.

Figure 4 shows a diagram of a triple-effect caustic evaporation system. Cell liquor is fed into the

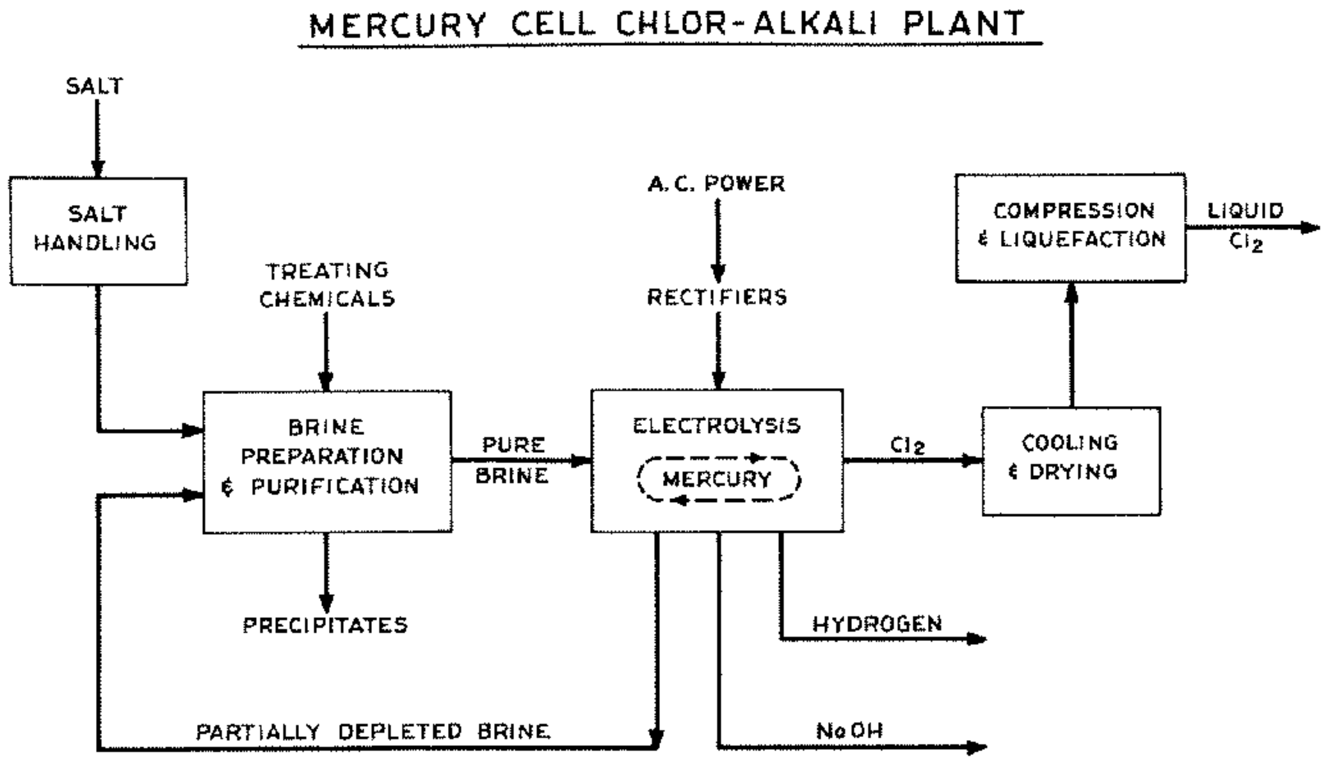

Figure 1.

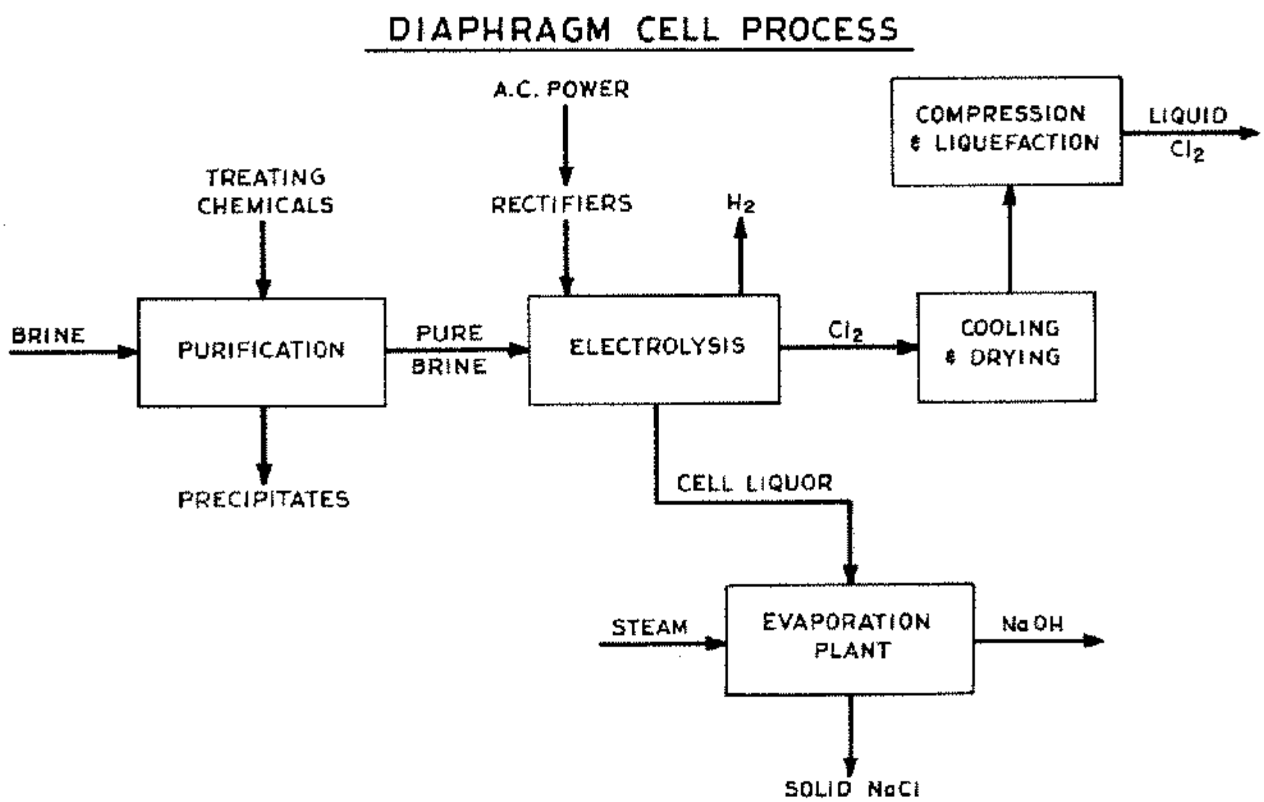

Figure 2.

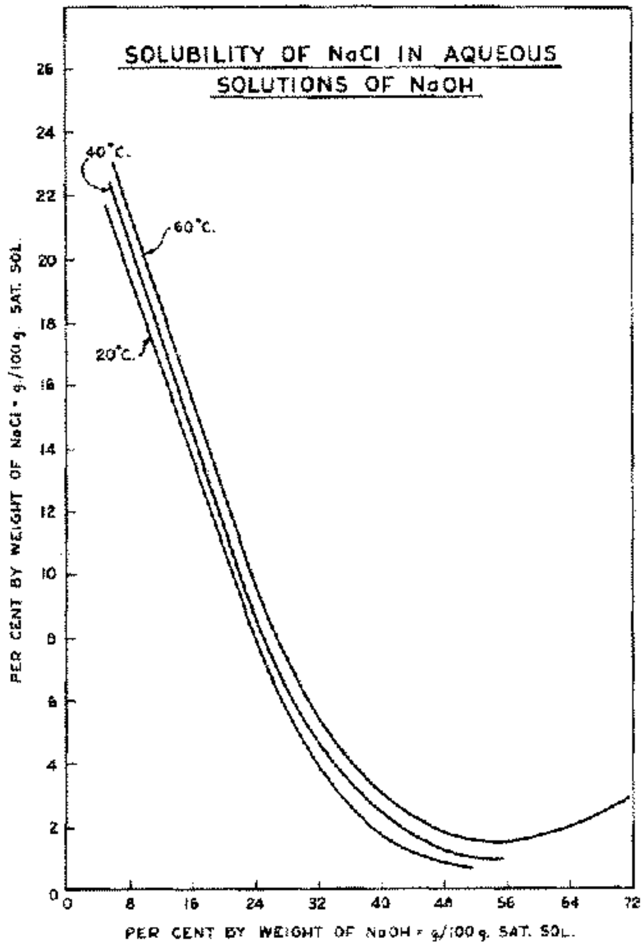

Figure 3.

third steam effect and emerges from the flash tank as 50% sodium hydroxide. Salt is removed as a heavy slurry. The analysis of the salt, taken from a typical caustic evaporator, before and after washing and drying is as follows:

	Wet	Dry
NaCl	85% - 95%	99.5 % - 99.8 %
Na_2SO_4	0.40%	0.1 % - 0.4 %
NaOH	0.10%	0.05% - 0.06%
Ca	10 ppm	10 ppm
Mg	50 ppm	50 ppm

The crystal size varies greatly depending upon the equipment used. Where the solid salt is recycled to the brine feed system, crystal size has little practical significance, except that the separation of the salt from the caustic solution is more difficult when the crystal size is small. Many caustic plants produce salt that is retained on a 120 mesh screen and passes a 60 mesh screen. Larger crystals can be produced, if required, but this would necessitate equipment changes.

The solid salt produced can be utilized in many ways. In most cases it is recycled to the cells as brine. A number of companies ship purified solid salt to other chlor-alkali plant locations. At these locations, brine treating facilities are not necessary because of the purity of the recovered salt. Some companies ship or sell recovered salt which is used to produce chemicals other than chlorine and caustic. For example, there are a number of chlorate plants operating on salt recovered from caustic evaporators. Another example is the use of this salt to produce chlorine dioxide for pulp bleaching. In these cases, capital investments and operating costs are reduced by the use of pure recovered salt.

Combined Diaphragm and Mercury Cell Plant.

The mercury cell plant, as we know it today, is a net solid salt consumer. The diaphragm cell plant produces a high-quality solid salt. It became apparent to the chlorine producers that, by combining diaphragm and mercury cell plants, certain advantages could be achieved. Low-cost brine can supply the sodium chloride values for both plants. It becomes economical to transport the brine considerable distances from the brine well to the plant site. Thus, the diaphragm cell process not only produces the chlor-alkali products, but also produces sufficient solid salt to supply the needs of the mercury cell process. Material balances on the conventional systems used today indicate that 60 tons per day capacity in diaphragm cells can easily supply the solid salt for 40 tons per day of mercury cell capacity.

Conclusion.

The technology involved in producing solid salt from the diaphragm cell process has been reviewed briefly. The diaphragm cell process can produce solid salt, in addition to its normal chlorine, caustic, and hydrogen products. The solid salt produced is an asset and, in many cases, is utilized to generate additional sales or credits, which are applied to the diaphragm cell process economics.

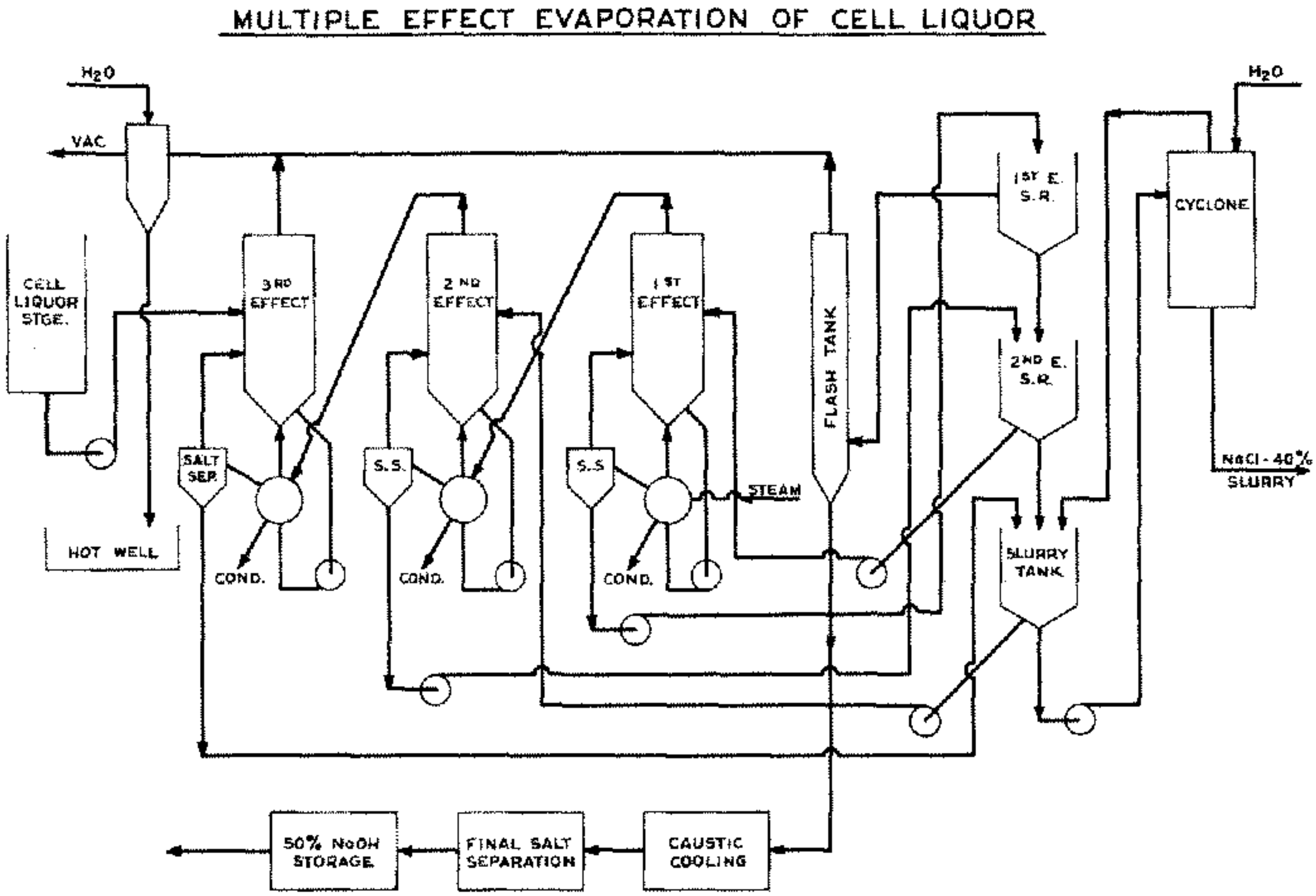
MULTIPLE EFFECT EVAPORATION OF CELL LIQUOR
H2O
VAC
CELL LIQUOR STGE.
HOT WELL
3RD EFFECT
2ND EFFECT
1ST EFFECT
SALT SEP.
S.S.
S.S.
COND.
COND.
COND.
STEAM
FLASH TANK
1ST E. S.R.
2ND E. S.R.
SLURRY TANK
H2O
CYCLONE
NaCl - 40% SLURRY
50% NaOH STORAGE
FINAL SALT SEPARATION
CAUSTIC COOLING

Figure 4.