

Principles and Economics of Salt Production and Processing

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ABSTRACT

About fifty million tons of sodium chloride are processed every year to chlorine and caustic. According to the salt production processes one distinguishes the product as evaporated salt, rock salt, solar salt and salt precipitated during diaphragm liquor evaporation. A major quantity of salt is produced and consumed in chlorine caustic production as brine.

These kinds of sodium chloride have different production costs and contain different amounts of impurities. Well known impurities are sulphate, calcium, magnesium. These impurities increase costs in chlorine caustic production, if, e.g. sulphate is purged from a brine circuit, which is well known practice in chlorine production by the mercury electrolysis process, salt losses and thus costs increase with increasing amount of sulphate in the raw material salt.

Environmental problems, costs of brine purification, transport costs and many other items have to be evaluated in order to answer the question which raw material: a cheap salt but with impurities or a relatively expensive salt, but without impurities gives lowest production costs.

INTRODUCTION

World chlorine-caustic industry is using four salt resources, rock salt, solar salt, evaporated salt and brine. In case two salt resources are available, choice of a specific type of salt as a raw material for a salt-consuming process is made on the basis of economic evaluations. In these evaluations, items considered are the price of salt, transportation costs and purification costs due to impurities.

The salt resource ultimately chosen is a result of these evaluations and will represent the outcome of the evaluations. Now in the USA chlorine producers use brine and rock salt, Japanese producers are using solar salt, whereas in the European Community, 32 chlorine producers use rock salt or brine and 38 are utilizing evaporated salt.

In the Scandinavian countries, 17 chlorine producers are utilizing evaporated salt. In these countries evaporated salt must be very economic. In the European Community we find 23 mercury plants operated on a basis of rock salt and 21 operated on a basis of evaporated salt. For example, in the Ruhr area and in Antwerp we find plants of which one is operated on a basis of rock salt and the other on a basis of evaporated salt just a few miles distance.

TABLE I

West European Salt Consumers
Classified to Process and Salt Resource

| | Brine | Solar Salt | Rock Salt | Evaporated Salt |
|--------------------------------|-------|------------|-----------|-----------------|
| Cl ₂ /Na OH process | | | | |
| diaphragm cells EEG 6 | 9 | 2 | — | — |
| Scandinavia | — | — | — | 2 |
| Mercury cells EEG 6 | — | 2 | 23 | 21 |
| Scandinavia | — | — | — | 15 |

These facts make clear that salt price plus transportation cost and precipitation cost must be approximately equal for evaporated salt and European rock salt. In this situation even minor cost differences are worth being discussed.

Impurities in salt. During underground leaching of salt deposits, the brine will become saturated with respect to calcium sulphate and other impurities. Consequently, brine will be impure. During mining of underground deposits the purest layers are selected. However, due to the nature of the deposits considerable differences in impurity content of salt can occur. The brine purification and evaporation processes

TABLE 2
Salt Analysis

| | Brine* | Solar Salt | Rock Salt | Evaporated Salt |
|-----------------------------------|---------|------------|------------|-----------------|
| SO ₄ ²⁻ ppm | 13000 | 1500–4000 | 1500–13000 | 200–400 |
| Ca ⁺⁺ ppm | 5000 | 400–3000 | 2500–3000 | 12 |
| Mg ⁺⁺ ppm | 40–1000 | 20–1600 | 400–1800 | 1 |

*Brine analysis recalculated to ppm or g impurity/l salt

ensure a low and constant level of impurities in the evaporated salt.

Production costs rise with increasing purity of the salt. Costs are highly dependent on scale of operation. Small-scale operations are uneconomic compared to large-scale operations.

Impurity treatment in mercury electrolysis. Since mercury electrolysis started on a commercial scale at the end of the nineteenth century, many authors discussed both influence and cost of the removal of impurities from mercury electrolysis cell feed brines. Four well known techniques of impurity treatment are 1) the precipitation of sulphate as barium sulphate by means of barium carbonate; 2) the purge of sulphate as sulphate-rich brine (~ 13 g SO₄²⁻/l); 3) the precipitation of calcium as calcium carbonate by sodium carbonate; and 4) the precipitation of magnesium as magnesium hydroxide by means of caustic.

Moreover, there are quite advanced systems which prevent impurities from dissolving in depleted brine, together with salt. Developments of the last ten years are a consequence of the increasing strength of mercury pollution restricting measures.

Demercurization of sludges and brine purge. Impurities leave the mercury electrolysis plant as sludges and

as brine purge. Both streams contain mercury and have to be treated in some way or another. Procedures for brine demercurization are the precipitation of mercury with sodium sulphide, reduction of mercury ions and subsequent adsorption of mercury with the help of hydrazine and active carbon and ion exchange of ionic mercury on ion exchangers.

Sludges are treated with chlorinated brine and deposited in restricted depositing areas, or are stored in concrete or have to be distilled. The great advantage of evaporated salt is its low impurity content and thus only minor amounts of sludges and brine purge.

CALCULATION OF COSTS DUE TO IMPURITIES FROM SALT

There is a tremendous variety in salt quality available to chlorine producers, and consequently each plant shows its typical layout of the brine purification area. Thus, one has to delineate the examples. First of all three types of salt are considered, evaporated salt, a relatively pure rock salt (rock salt I) and an impure rock salt (rock salt II).

Moreover, brine purification systems are grouped into two kinds. In case A, total precipitation of impurities is assumed, thus sulphate is precipitated as barium sulphate, calcium as calcium carbonate and magnesium as magnesium hydroxide. In case B, purge of sulphate by means of sulphate-rich brine is assumed. Thus as brine purge increases compared to case A, calcium is partly removed by brine purge, the major part is precipitated as calcium carbonate, magnesium is precipitated as magnesium hydroxide. Insolubles and these precipitates are collected as sludges.

Cost calculations are presented in Table 4.

Influence of antimercury pollution measures. In different countries, treatment costs for mercury in sludges dif-

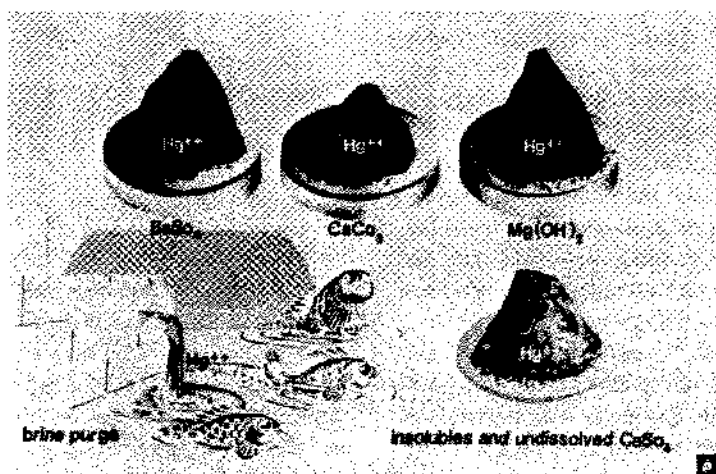


Figure 1. Mercury contamination of brine purge and sludges from chlorine-caustic production by the mercury electrolysis process.

TABLE 3
Impurities in Salt and Amounts of Sludges and Brine Purge

| Salt | Evaporated Salt | Rock Salt (1) | Rock Salt (2) |
|-------------------------------|-----------------------------|----------------------------|--------------------------|
| Insolubles | — | 1% | 2% |
| SO ₄ ²⁻ | 400 ppm | 2,500 ppm | 13,000 ppm |
| Ca ⁺⁺ | 12 | 2,500 | 3,000 |
| Mg ⁺⁺ | 1 | 100 | 400 |
| Case (A). | | | |
| Total — Precipitation | | | |
| Amount of Sludges | 1 kg/t salt | 22 kg/t salt | 58 kg/t salt |
| Amount of Brine Purge | — | — | — |
| Case (B) | | | |
| Brine Purge and Precipitation | | | |
| Amount of Sludges | 0,1 kg/t salt | 16 kg/t salt | 26 kg/t salt |
| Amount of Brine Purge | 0,03 m ³ /t salt | 0,2 m ³ /t salt | 1 m ³ /t salt |

TABLE 4
Calculation of Costs Due to Impurities

| | Evaporated Salt | | Rock Salt (1) | | Rock Salt (2) | |
|--|-----------------|-----------|---------------|-----------|---------------|-----------|
| | kg/t salt | DM/t salt | kg/t salt | DM/t salt | kg/t salt | DM/t salt |
| Case (A) total precipitation | | | | | | |
| *BaCO ₃ consumption DM.6/kg | 1 | 0.6 | 6.25 | 3.7 | 32.5 | 19.5 |
| *Na ₂ CO ₃ consumption DM.3/kg | 0.5 | 0.15 | 10 | 3.0 | — | — |
| *caustic consumption DM.3/kg | 1 | 0.3 | 8 | 2.4 | 8 | 2.4 |
| *sludge treatment DM.2/kg | 1 | 0.2 | 22 | 4.4 | 58 | 11.6 |
| Total cost DM/t salt | | 1.25 | | 13.5 | | 33.6 |
| Case (B) brine purge and precipitation | | | | | | |
| *salt losses DM.05/kg | 8 | 0.4 | 51 | 2.6 | 270 | 13.5 |
| *Na ₂ CO ₃ consumption DM.3/kg | 0.5 | 0.15 | 12 | 3.6 | 14 | 4.2 |
| *caustic consumption DM.3/kg | 1 | 0.3 | 8 | 2.4 | 8 | 2.4 |
| *sludge treatment DM.2/kg | | | | | | |
| purges brine | 0.1 | 0.02 | 16 | 3.2 | 26 | 5.2 |
| *demercurization DM.1/m ³ | 0.03 | 0.03 | 0.2 | 0.2 | 1 | 1 |
| Total cost DM/t salt | | 0.9 | | 12 | | 26.3 |

fer considerably. For example, in Scandinavia depositing mercury containing sludges as landfill is not allowed. The next graph shows the influence of sludge demercurization cost on the total purification cost for impurities (Fig.). Due to its low impurity content, evaporated salt soon becomes very economic as sludge demercurization cost increase.

DIAPHRAGM ELECTROLYSIS

Impurity treatment in diaphragm electrolysis. The scope of the discussion of impurity effects in diaphragm electrolysis is restricted to those plants which have to produce chlorine in markets where natural brine is either absent or unavailable on an economic scale. Hence they are operated on the basis of procured salt. This salt is dissolved in water to produce the saturated brine which will be converted into chlorine gas and diaphragm liquor during the diaphragm electrolysis process.

Although there are operations where diaphragm liquor is converted into sodium carbonate liquor, in a major number of plants, diaphragm liquor is evaporated to 50% caustic liquor. We restrict ourselves to the 50% caustic production.

Effect of sulphate in diaphragm liquor evaporation. During evaporation the concentration of caustic increases, and both solubilities of sodium chloride and sodium sulphate decrease. The impurity effect of sulphate in diaphragm electrolysis is understood when these effects of solubilities during diaphragm liquor evaporation are recognized. The solubilities of sodium sulphate and sodium chloride in diaphragm liquor at 90°C are given in Table 5.

As the salt/caustic ratio in diaphragm liquor is approximately 1.33 kg NaCl/kg NaOH, crystallization of salt will start in the early stages of evaporation. In general the diaphragm liquor will be undersaturated with respect to sodium sulphate until evaporation has proceeded to the point where the water/caustic ratio is 2.5 kg H₂O/kg NaOH.

Thus the evaporation process will produce sulphate-free salt at low caustic concentrations (ratio 6–2.5 kg/kg water/NaOH), but at high caustic concentrations (ratio 2.5–1.0 kg water/kg NaOH) the evaporation process will produce a sulphate-rich salt.

Sodium sulphate is slightly soluble in 50% caustic and solubility of sulphate in 50% caustic and sulphate losses happen to be equal to approximately 400 ppm of sulphate feed in salt. Hence sulphate treatment is superfluous when evaporated salt is used as a salt resource.

The schematic views of a plant operated on the basis of a salt with low sulphate content (evaporated salt) and of a

plant operated on the basis of a sulphate-rich salt are shown in Figures 4 and 5.

When a sulphate-rich salt feed is utilized (more than 500 ppm sulphate in salt) the completely separated salt handling systems are in operation in order to ensure complete separation of the so-called sulphate poor salt and the sulphate-rich salt. The sulphate-rich salt is a mixture of two crystals: sodium chloride and triple salt, $\text{NaCl} \cdot \text{Na}_2\text{SO}_4 \cdot \text{NaOH}$. The decomposition of triple salt requires special and complicated washing techniques. Moreover sodium sulphate is reclaimed in a glauber salt crystallization unit.

Investments in these separate salt handling systems, the sulphate treatment plants are DM 7 million for a plant producing 250,000 tons chlorine per year. Moreover, the sulphate treatment plant will consume about 0.2 t steam/t chlorine and thus the treatment cost difference due to sulphate between evaporated salt and sulphate-rich salt resources, will vary from approximately DM 8–9/ton salt in large-scale operations up to DM 10–11/ton salt in smaller scale operations.

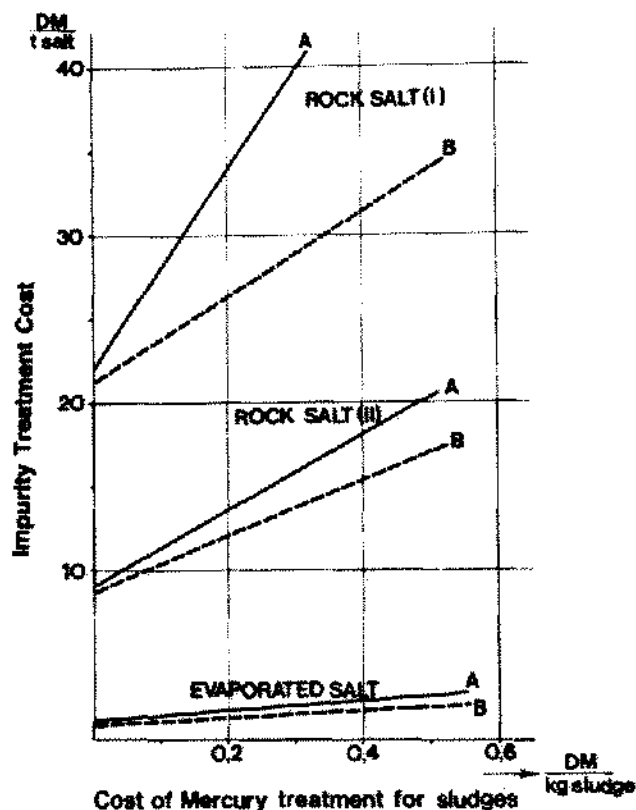


Figure 2. Loss of impurity treatment in chlorine production by mercury electrolysis versus cost of sludge demercuration.

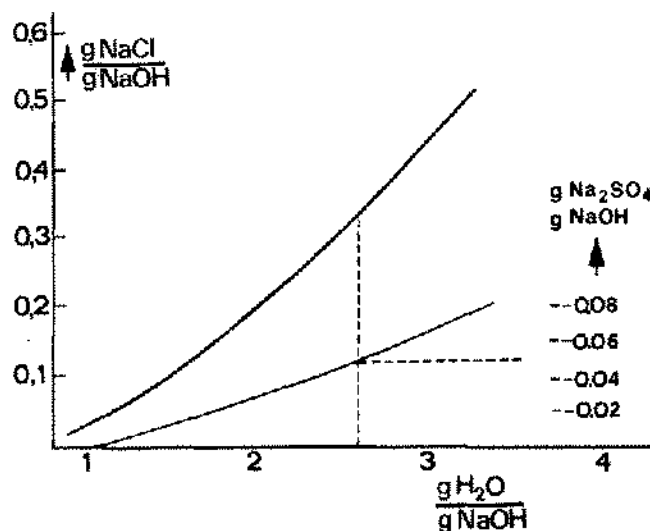


Figure 3. Solubilities of sodium chloride and sodium sulphate in caustic at 90°C.

TABLE 5
Typical Analysis of Diaphragm Liquor

| Constituents | On the Basis of Sulphate Containing Rock Salt (10,000 ppm SO_4) | On the Basis of Evaporated Salt (400 ppm SO_4) |
|--|---|--|
| NaOH | 120 kg/m ³ | 120 kg/m ³ |
| NaCl | 160 kg/m ³ | 160 kg/m ³ |
| Na_2SO_4 | 6 | 0.12 |
| Ratio NaCl/NaOH | 1.33 kg/kg | 1.33 kg/kg |
| Ratio $\text{Na}_2\text{SO}_4/\text{NaOH}$ | 0.05 kg/kg | 0.001 kg/kg |

Effects of calcium and magnesium in diaphragm electrolysis. The effect of calcium as an impurity in diaphragm electrolysis feed brine is understood when the diaphragm is recognized as a resistance to brine flow through the cells. Cells are operated at constant brine flow and consequently

the head of brine above the catholyte will rise when flow resistance increases.

Diaphragm cell construction allows a head of approximately 80 cm brine; when brine rises beyond this head, the diaphragm should be changed. The influence of calcium on brine head on top of the catholyte in diaphragm cells is shown below (brine flow and cell load without any interruption).

A slightly increasing slope is needed and thus the stationary level should be 3–4 mg/l, which is reached with evaporated salt (12 ppm Ca) without any brine purification, whereas in case of impure salt brine treatment is necessary.

Cost of this well-known brine treatment with sodium carbonate and caustic depend on the scale of operation, of the calcium content in salt and the price of sodium carbonate and amount from 4 DM/ton salt in large scale units up to 8 or 9 DM/ton salt in small scale operations.

CONCLUSIONS

Choice of a specific salt resource as a raw material for chlorine-caustic manufacturing is made on a basis of economic evaluations. In these evaluations price of salt,

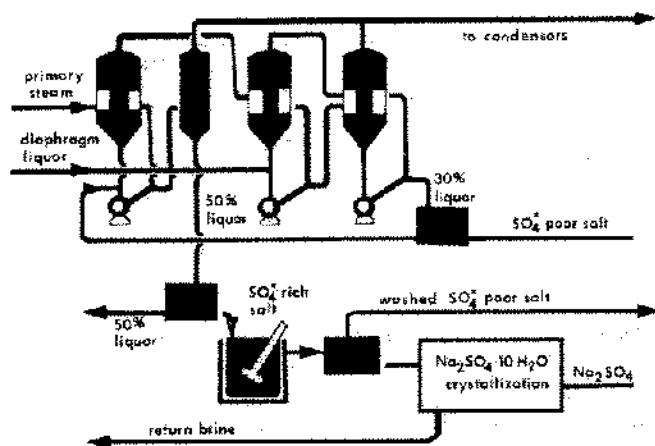


Figure 4. Diaphragm liquor evaporator for sulphate rich diaphragm liquor.

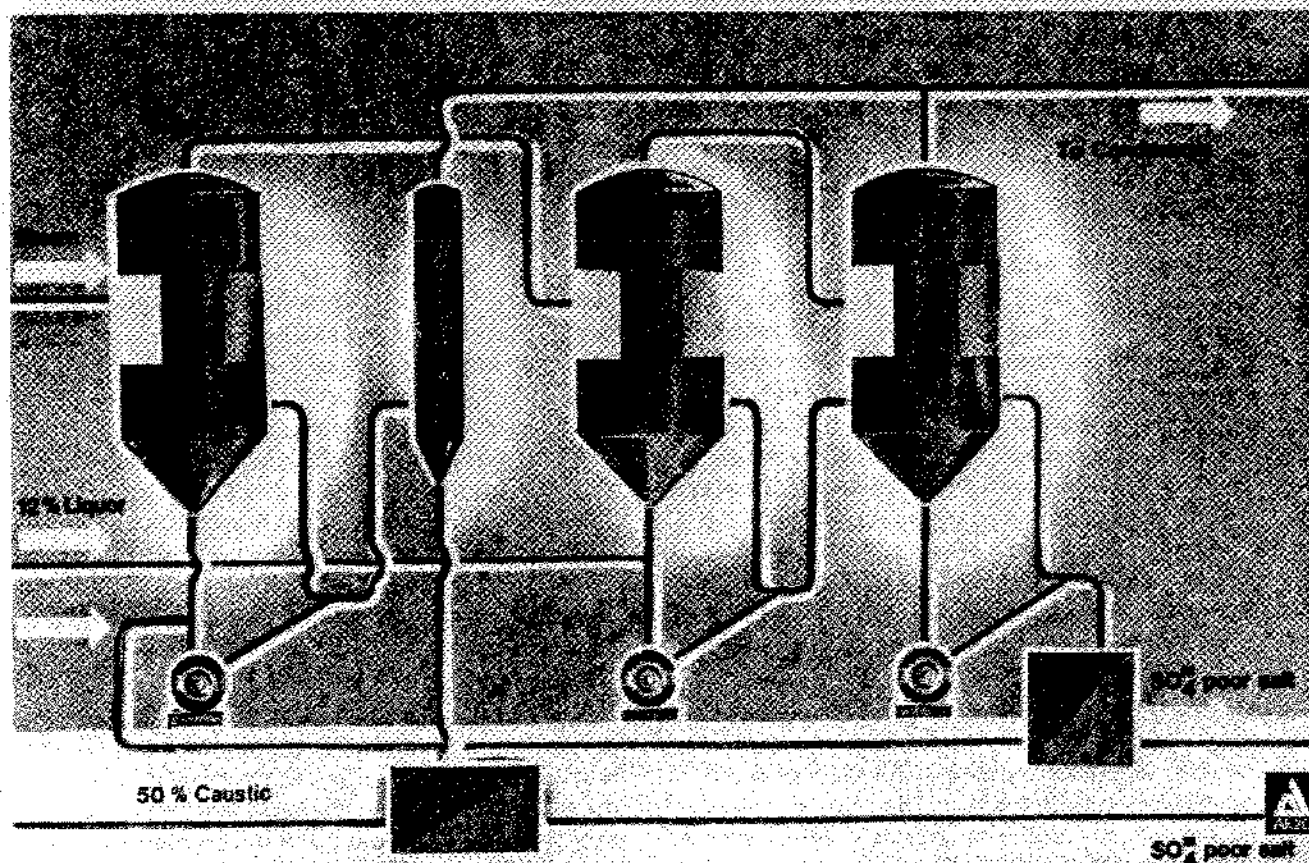


Figure 5. Diaphragm liquor evaporator for sulphate poor diaphragm liquor.

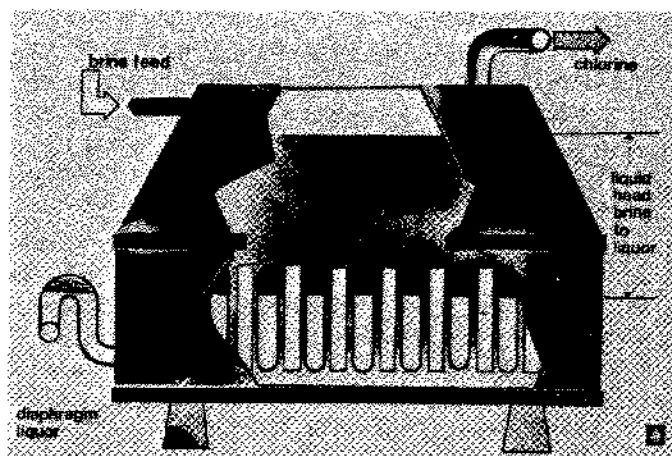


Figure 6. Schematic view of diaphragm cell for chlorine caustic production.

transportation cost and cost of purification present in the salt, have to be taken into consideration.

Important developments of the last ten years are the increase in mercury cost of treatment for mercury in brine purge and sludges due to the increasing strength of mercury pollution restricting measures; and chlorine caustic produc-

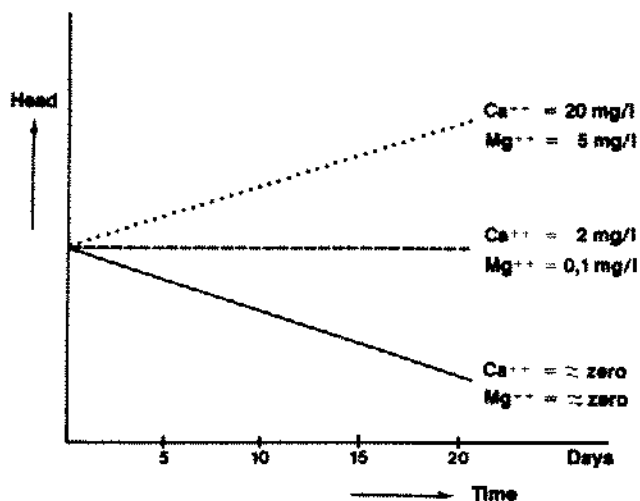


Figure 7. Influence of brine feed analysis on increase of head during chlorine production by the diaphragm process.

tion by the asbestos diaphragm cell process in markets where natural brine is unavailable. In these plants effects of sulphate in diaphragm liquor evaporation and of calcium in diaphragm cells are major items, the cost of which must be calculated in order to make a proper selection of salt resource.