

Brine Preparation for Mercury Cells

Jack H. Nichols

Monsanto Company
800 N. Lindbergh Blvd.
St. Louis, Missouri 63166

ABSTRACT

The subject of preparing brine for mercury cells is covered beginning with brine saturation and including treating steps, filtration, operating parameters in mercury cells, and treatment of depleted brine for resaturation.

Methods of saturation to reduce solubility of impurities as well as treatment to remove sulfates and trace metals from brine are covered. Preparation methods allowing saturated sulfate brine are also outlined.

A section of the paper covers the effect of impurities in brine on cell operation and discusses methods for detection and reduction of the deleterious effects.

A discussion of the different procedures used in preparing brine for graphite anode cells vs. cells with dimensionally stable anodes is covered. The markedly reduced brine feed rates for the dimensionally stable anodes coupled with requirements for less pure brine and the interdependency of concentration, thermal effects, and anode-to-cathode gap are discussed.

INTRODUCTION

Salt production and consumption in the United States now amounts to some 40 million tons per year.

More than two-thirds of the United States salt goes into the chemical industry, about 60% of which is used in the manufacture of chlorine.

Of the 15 million tons a year of salt used in chlorine, about 4 1/2 million is used in mercury cells. Consumption of salt in mercury cells over the past ten years has just about quadrupled, and now

SALT VOLUME IN U.S. PRESENT ESTIMATED USAGES

Annual Salt Production	38,000,000 Tons
Used in Chlorine Products	15,000,000 Tons
Used in Mercury Cells (About 75% from Rock Salt)	4,500,000 Tons

represents over 30 percent of U.S. chlorine capacity. Mercury cells now account for some 50-60% of new chlorine plant construction, and with further improvements in mercury cells such as the new Type M2 cell recently announced by deNora, this percentage of new plant capacity should increase even further.

New chlorine plants are larger each year. Typical of these is the new plant of over 600 tons of chlorine per day which PPG recently started in Lake Charles, Louisiana. (Chem. and Engnr. News, 1969).

Today, chlorine can be said to be the belleweather of industry. Just as steel was many decades ago, sulfuric acid became in the interim period, now chlorine is the harbinger of progress. If one compares the dips and rises in the chlorine production curve with the economic health of industry in the United States over the years, one can find an almost direct relationship with the booms and recessions of industry.

Steel is a finished product and goes directly to the consumer. Sulfuric acid on the other hand, is used almost exclusively as a raw material in other processes. Chlorine has a well-rounded end product pattern, much of which goes directly into the consumer's hands for water treatment, pollution con-

trol, etc., but with a large portion going into the production of other chemicals and finished products such as plastic, organic chemicals, and the like.

The cost of steel in the marketplace is primarily in the conversion costs of a relatively low priced ore. The cost of sulfuric acid is primarily in sulfur value. Chlorine has significant portions of its cost represented by salt value, by power costs, and by the cost of equipment and labor. It should remain in the future, a good yardstick for progress.

COST OF PRODUCING CHLORINE DOLLARS PER CHLORINE UNIT TON

	Cost	%
Power	\$28	37%
Capital Charges	21	28%
Salt	14	20%
Other	12	15%

Typical of today's chlorine costs, is a composite showing approximately 37% of the producer's end cost in electricity. Another 28% is due to capital related charges including taxes, depreciation, maintenance, and other factors directly dependent on the amount of capital used in plant construction. Of the producer's cost, salt makes up about 20% of the input. Other factors, such as labor, handling, chemical treating costs, drying acids, etc., amount to some 15% of the cost of producing chlorine.

Of interest to the salt producer, is the fact that the 1/5 of chlorine production cost due to salt, can vary so widely and can affect the chlorine producer's other costs to such a great extent, that the producer's selection of his salt source is a vitally important matter. For instance, the quality of salt used in the typical owner's plant, while perhaps averaging \$14 per chlorine unit ton, might affect overall chloring costs from 50¢ per ton for very good salt, to \$4 or \$5 per ton for poorer quality salts. With so much of today's production of salt going into chlorine plants, and particularly into mercury cells, the way the chlorine producer uses his salt supply is of real importance to the salt industry.

METHODS OF BRINE MAKING FOR MERCURY CELLS

By far, the greater number of mercury cell plants in the United States, produce chlorine from rock salt. Most of these plants use traditional salt dissolving systems, where salt is charged into a large unit called a saturator and weak brine slowly flows up through the salt bed, over-flowing to fur-

ther processing equipment. Some of the newer rock salt dissolving plants have utilized a rapid saturation system, where depleted brine is fed rapidly through a small bed of salt, continuously charged from a large salt hopper.

METHODS OF BRINE MAKING FOR MERCURY CELLS

From Rock Salt

Salt Dissolving
Rapid Saturation

From Well Brine

Evaporation of Well Brine
Resaturation Mining

From Evaporated Salt

From Diaphragm Cells
From Purchased Salt

A much smaller number of mercury cell chlorine plants use brine from wells. The greater number of these plants incorporate brine evaporation systems. The salt is crystallized from well brine in a relatively pure crystal. Also employed in the United States is at least one plant using resaturation mining, where the weak brine from the cells is pumped into the ground and saturated brine taken out for treatment and fresh feed to the cells. (Sanders, Gerdiner, and Wood)

An increasing number of mercury cell plants are using evaporated salt. Many of these plants use salt which has been recovered in nickel, or nickel lined evaporators, producing 50% caustic soda from the cell liquor effluent from diaphragm cell plants. A number of plants also operate on evaporated salt purchased on the market.

SELECTIVE SATURATION OF BRINE IN SALT BEDS

For the balance of this discussion, we will limit our thoughts to the preparation of brine from rock salt. Important factors in making brine from rock salt include sodium chloride content, the calcium sulfate content, the crystalline structure, the average particle size and size distribution of the salt that is received in the user's plant.

One of the main constituents (and an unwanted one) in rock salt is calcium and its salts, primarily calcium sulfate. If an excess of salt and calcium sulfate are dissolved in a water solution, the more rapidly soluble sodium chloride will go into solution first, and will rapidly saturate the liquid phase.

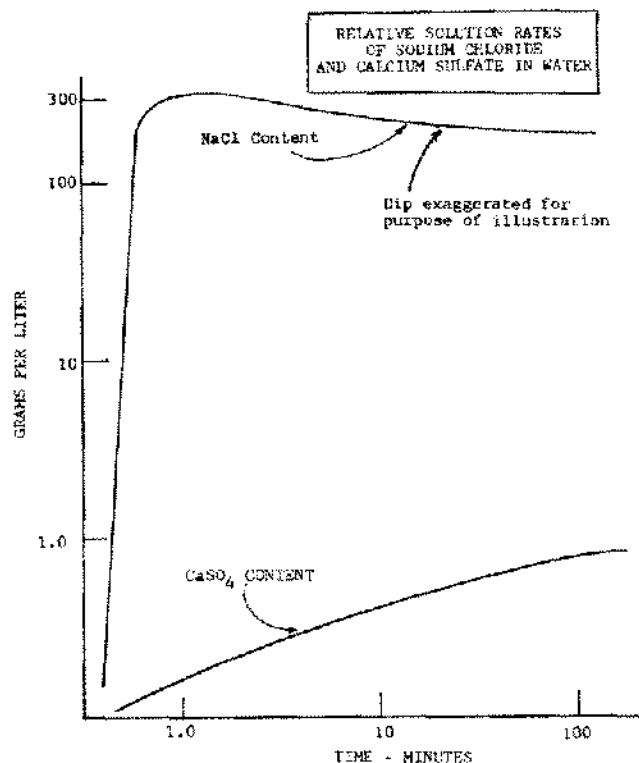


Figure 1.

Solution equilibria, however, dictate that some 3-5 gpl of a resulting equilibrium solution will be a calcium sulfate. Thus, after saturation with NaCl, if the solution is kept in contact with the undissolved salts, the calcium sulfate content will rise to between 3 and 5 gpl. It is the principle of rapid saturating equipment, to get the saturated solution of sodium chloride out of contact with the solid phase as soon as possible.

Note, that if the rapid saturator is small enough to get the brine out of contact with the salt in ten minutes, the CaSO_4 pickup is only half what it is in two hours, and is only 20% if the time can be cut to one minute. (Gardner and Ward, U.S. Patent 2,787,591)

Installation of rapid saturation equipment can be quite complicated. It involves not only the usual elevated hopper and controlled gate, for continuously feeding salt from overhead into the quite small saturator vessel itself, but also an efficient means of removing undissolved salts from the unit almost continuously to avoid the carry over of solids into the brine system where they would then dissolve anyway.

For the plant operator who does not use rapid saturation, there are other means of selective solu-

tion processes for saturation of brine with sodium chloride and exclusion of other unwanted salts.

One method of selective dissolving consists of using an agent to inhibit the solubility rate of calcium sulfate into the brine solution. One such method uses one or more of the polyphosphates. One of the better known polyphosphates for such use is sodium hexametaphosphate. This process has received wide-spread publicity and its reported advantages over simple solution of rock salt can be shown by a simple curve. (Roland and Ralston, U.S. Patent 2,906,600)

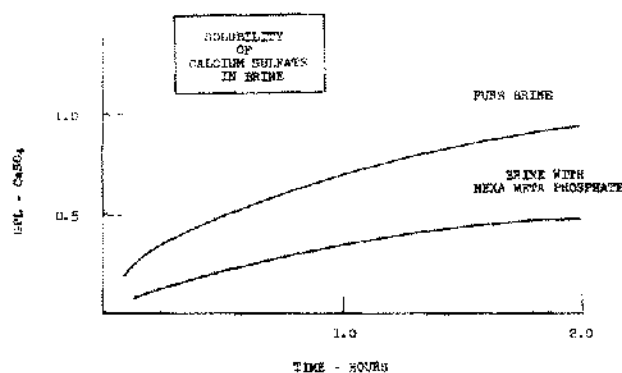


Figure 2.

In the example shown here, the data represent solution phenomena in brine with a pH of about 10. Here, sodium hexametaphosphate will reduce the calcium sulfate dissolved by about 1/2 for any time period up to two hours. Other tests, for example, at pH=7, the CaSO_4 solubility is about double, but the HMP curve remains constant, thus effecting about 75% suppression of CaSO_4 pickup.

In most mercury cell plant brine systems requiring higher pH levels for metals removal, some of the HMP advantages are therefore probably lost.

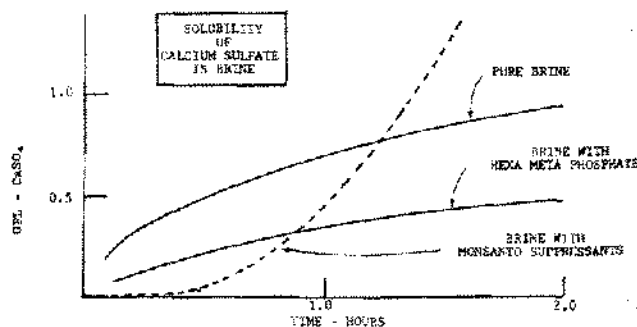


Figure 3.

Another process used in many mercury cell plants in the United States, is that developed by Monsanto. Monsanto's own agents are used for inhibiting the rate of solution of calcium sulfate from salt beds in flowing brine solutions. While the solubility advantages of this process are not so good with long sojourn times in the salt bed, the effects are extremely good with retention periods less than one hour. The process has good advantage when used in dissolving rock salt for mercury cells with no deleterious effects on cell operation.

A final method of selective solution allows calcium sulfate to go to saturation in the brine thus avoiding further pickup. (Gardner and Ward, U.S. Patent 2,787,591)

Due to the common ion effect, calcium and sulfate ions will exist in a solution in a ratio of about 1 to 1.5 gpl of calcium and 2.5 to 4 gpl of the SO_4 ion. While calcium content of brine is acceptable only up to about 50 ppm in most mercury cells, if it is allowed to increase above 700 ppm (0.6 gpl) it offers a buffering effect to hydrogen formation and again (with some disadvantages) becomes tolerable. By allowing the calcium content to rise to and stay nearly at saturation, the method, while causing the plant operator some headaches with its effect on cell operation, does limit the sulfate content of the brine to an acceptable level of 3-4 gpl as SO_4 .

Another method using this principle involves removal of calcium only, allowing the reaction product, sodium sulfate to increase markedly. This is undesirable in mercury cells since rapid oxidation attack on graphite anodes is progressively evident as the SO_4 ion increases above about 7 or 8 gpl, but it is used by some operators.

BRINE TREATMENT

To remove calcium and sulfate ions.

Calcium is normally removed from brine to a residual level of about 50 gpl or less by precipitation with sodium carbonate in an alkaline solution. If the reaction product, sodium sulfate, is to be removed, it is precipitated with finely divided barium carbonate via surface reaction at the interface of the barium carbonate crystals. It was once thought necessary to prolong the barium carbonate reaction for periods of two hours or more, but in recent years, the process has been shortened considerably by the availability of finely divided barium carbonate. Even now, if large amounts of sulfate are to be removed, reaction times as long as thirty minutes are desirable. The precipitates of

calcium carbonate and barium sulfate are removed primarily by settling in clarifiers whose rise rates range from 0.5 gpm per square foot, down to as low as 0.2 gpm per square foot.

To remove metal oxides.

In brine containing appreciable amounts of magnesium iron and other light metals, it is desirable to carry the metal oxides out of solution at a pH above nine.

To remove trace metals.

Removal of heavy metal such as vanadium, titanium, chromium, molybdenum and the like, is important. It has been found that these metals form fine particulate insoluble oxides which are settled only if enough flocculate material is available in the settling step. With Louisiana rock salt, the volume of calcium and barium salts has normally been large enough to act as a flocculant for the trace metals. However, in a number of cases, additional flocculant such as ferrous sulfate and some of the synthetic flocs have been used.

With brine systems which use an efficient inhibiting agent or a rapid dissolving system good enough to preclude the dissolving of any large amount of calcium sulfate, the need for subsequent chemical treatment with sodium and barium carbonates is greatly reduced. Cost of producing brine in this way can, therefore, be reduced considerably. However, one must realize that when efficient inhibitors are used, very little flocculant in the settling step is available and in many cases, additional flocculants are required for heavy metals removal.

Feeding salt.

An important factor with respect to brine treatment by the classical process is the upset condition in treating equipment which can be caused at the instance of salt charging into a large saturator filled with brine solution. The addition of solid salt at a high rate causes an incidence of heavy flow of brine from the saturator into treating equipment. The resulting disproportionality between feed of brine treating chemicals and the salt rate creates an out of balance situation where sufficient treating chemicals are not available to a significant portion of the brine. The use of inhibiting agents in the feed to the saturator obviates this problem, since such agents are already present in the solution filling the saturator and the small amount of calcium sulfate carried over with the overflow is normally not great enough to upset any subsequent addition

of treating chemicals. With the classical process and with rapid saturation dissolvers, it is necessary for the plant owner to provide elaborate tankage and pumping equipment to compensate for excess flow when charging salt to the saturator.

Crystal size.

Another problem of this type which cannot easily be compensated by the cell operator is the high incidence of impurities at short periods when salt of varying crystal size is introduced. With constant feed of brine treating chemicals, the plant is upset if a batch of fine salt is introduced, this, because fine salt may contain more CaSO_4 than the average of a shipment.

For hours, or even days, after feeding a charge of fine salt, the plant operation will experience problems.

Even the use of a selective solution process will have trouble—because all such processes, even rapid saturation depend for their performance on the rate of solution, and rate depends on surface area, which is larger with fine crystals. So, with fine salt, both the high CaSO_4 content, and the high surface area of CaSO_4 present dissolving problems.

Filtration.

After chemical treatment and settling, finished brine is normally filtered in any one of several conventional filtration steps. Many smaller plants use pressure feed gravity bed filters of the sand or anthra-filt type. Many larger plants use some form of pressure leaf filter for removal of the fine particles not removed in the settling step.

EFFECT OF IMPURITIES ON CELL OPERATION

The effect of sodium sulfate on anode wear in mercury cells has already been discussed.

The effect of metals on mercury cell operation depends primarily on their solubility in mercury. Calcium for instance, can be tolerated in cells up to 50 ppm without real problem. However, as calcium increases, it is precipitated on the surface of the mercury in the cell, forming an emulsion which tends to build up as cell operations continue, and must be cleaned out at intervals to prevent interruption of mercury flow and possible cell shorting. Other metals such as zinc, copper, magnesium, and the like, have essentially the same effect but at different levels.

The insoluble metals such as the heavy metals named above, iron and some others, tend to cause an ion exchange condition with the flowing mer-

cury amalgam. As a metal ion is precipitated at the cathode surface, it loses its charge to the cathode and forming the oxide, is immediately redissolved in the brine solution. When this occurs, another ion is discharged, an atom of hydrogen is formed, dissociating an equivalent amount of sodium from the mercury amalgam. The result is the creation of hydrogen gas which dilutes the chlorine and of caustic soda which immediately reacts with chlorine in the brine to form sodium chlorate, another injurious agent, causing anode oxidation and also corrosive attack on brine handling equipment. (DeNora, Vittorio, and Gallone, 1964)

An extensive amount of work illustrating the above has been done by Gosta Angel and Tage Lunden, of Sweden. Gallone has followed this work with an extensive study using the Soltest method, to determine the qualitative effects of metal constituents in the feed to mercury cells. It is important for the cell owner to be aware of the existence of dangerous metal impurities and to practice the proper means for their removal. (Angel and Lunden)

In the non-metals category, the chlorine plant operator should beware of the presence of fixed nitrogen compounds in the brine system.

Fixed nitrogen such as that arising from unexploded dynamite charges in the salt face will remain in the salt and contaminate the brine from the saturator. Passing into the cell, the nitrogen ions will form a complex with chlorine resulting in a buildup of nitrogen trichloride. This substance will leave the cells with the chlorine gas, and will concentrate somewhere around the chlorine liquefaction system, particularly in any liquid chlorine scrubbers utilized to clean the gas being fed to compressors. Nitrogen trichloride is highly explosive and if allowed to build up above 300 or 400 ppm, is a serious safety hazard.

Fixed nitrogen should be kept out of brine systems. If it is present, however, it may be removed by operating the brine system with a high free chlorine which will cause the nitrogen compounds to break down before electrolysis, followed by air stripping to remove the NCl_3 . It should be noted that a nitrogen content of 1 ppm in brine can result in an NCl_3 content of 50 ppm in chlorine gas from the cells.

DEPLETED BRINE HANDLING

The mercury cell operator using rock salt will find it desirable to dechlorinate brine from the cells to a level of 100 ppm free chlorine or less.

The dechlorination step may include vacuum stripping, steam distillation, air stripping, or a combination of any two or more of these methods.

The necessity for dechlorination is evident in that subsequent addition of sodium hydroxide for removal of impurities, will react with any free chlorine present to form first sodium hypochlorite, and finally sodium chlorate. As has been noted above, sodium chlorate is quite corrosive to most equipment and is particularly dangerous when used in a plant where equipment linings are in poor condition or where increases in capacity have caused high localized velocity, situations in equipment and piping.

It would, of course, be desirable to avoid if possible, the caustic addition step in the brine system. This practice is possible in plants using evaporated salt or salt from diaphragm cells, as long as a bleed stream is provided for removal of sufficient by-pass quantity of brine for disposal or for treatment and return to the system.

CONCLUSIONS

As has been pointed out earlier in this discussion, the cost of handling brine is to a major extent, dependent on the quality of salt provided to the mercury cell plant. Relatively pure salt such as diaphragm cell salt, evaporated salt, and even solar salt beds, can be handled in the owner's plant much more economically than can the rock salts, which contain progressively higher amounts of calcium sulfate and other impurities as one moves in a northerly direction in the U.S. Means for compensating for impurities in salt have been devised and are being used in the form of rapid saturation methods, inhibitors for selective dissolving of sodium chloride, and in improved methods for treating. However, it should be evident that salts of better quality should be much more economical to the user than poorer quality salt when the owner looks at the overall economics of its use. Even the question of salt yield is important when one considers the fact that with every ton of sludge he must discard from the salt treatment system, a large quantity of both solid salt and brine is also lost. In Monsanto, we normally assume that yield

on a salt containing 1% impurities must also allow for another 1% loss in the form of salt crystals and brine discharged with the sludges.

In summary, we might make the following statements:

1. Almost 40% of U.S. salt goes to chlorine.
2. During the past two decades the portion of production going to mercury cells has increased from 1/25 to 1/3 of the chlorine bound salt.
3. Although the mercury cell plant can treat to use most any salt, its extra costs in using an inferior salt can go as high as 10 to 20% of its total chlorine production cost.
4. There are methods operators can use to reduce these costs—all based on some process of selective solution.
5. The prime help the salt producer can give (after assuring good quality), is in maintaining uniform shipments and uniform salt size distribution.

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