

# Factors for Optimum Brine Treatment Process Design

Harshad M. Patel

Olin Corporation  
Charleston, Tennessee, USA

## ABSTRACT

*Brine treatment for chlorine/caustic soda plant application generally consists of reduction of calcium, magnesium, other heavy metals and sulfate impurities from brine. There are significant factors in brine treatment design. Failure to consider these factors during design can result in high capital cost, chemical treatment costs, maintenance costs, and will sometimes result in poor brine quality.*

*The process design discussed is for brine saturation, soda ash and caustic reaction systems, sludge settling, brine filtration and lime treatment. Various examples are cited.*

*The factors to be considered in brine saturator design are salt charging rate, undissolved solids removal, sand carryover, the potential for magnesium spiking and salt caking.*

*Five major factors involved in reactor design are retention time, brine temperature, degree of agitation, excess reactants and supersaturation of precipitates.*

*Sludge settler design is based upon the quality of precipitates and their settling rate. Temperature inversion and slugging of flow should be avoided. Improvement in settling rates can be obtained by using coagulants.*

*The factors to consider in filter design should provide for settler upsets and overloading of the filter. A test procedure is discussed. The relative operating cost due to body feed, precoat versus increased settler capital costs to improve settling should be evaluated.*

*Sulfate in the recirculating brine system is controlled by lime, calcium chloride, barium chloride or barium carbonate. Proper dosage and sizing of equipment is necessary to avoid scaling of lines and piping.*

*Lime is also used to raise the calcium-to-magnesium ratio to improve settling of the magnesium hydroxide precipitate. The optimum calcium/magnesium ratio is discussed.*

## INTRODUCTION

Chlorine and caustic soda producers are one of the largest users of salt produced in the world. The U.S. chlor/alkali industry used 22 million tons of salt, about 55% of the total U.S. salt market in 1981 (Mineral Industry Surveys, 1982).

Chlorine and caustic are produced by feeding sodium chloride brine (about 25 wt.% salt) to electrolytic cells. Three types of electrolytic cell processes are presently in commercial use:

1. Mercury cell
2. Diaphragm cell
3. Membrane cell.

Each of these processes requires brine of high purity with low calcium, magnesium and sulfate. They also have a very low tolerance for other impurities in brine—particularly heavy metals.

Brine is produced by injecting water or recirculated, depleted brine from the cells into the salt dome or by flowing water through the salt bed in properly designed saturators. As nearly all salt contains calcium, magnesium and sulfate, the brine needs to be treated to reduce the impurity levels. If the salt quality changes, it changes brine chemical treatment requirements. Drastic changes in salt quality make it nearly impossible to produce the desired quality brine with brine treatment equipment normally found in chlor/alkali plants.

As an example, a mercury cell plant in Greece was designed to use Italian and Rumanian rock salt. An attempt was then made to use domestic Messolangi solar salt without changing the brine treatment system. The filters could not keep up with the operation because they had to be sluiced every three to four hours. In another example, at one of the Olin mercury cell plants, the rock salt brine treatment system was modified to evaluate the potential use of Spanish solar salt. Manual chemical feed and temporary modifications of the system controls were used for

the test. Although the normal magnesium level of filtered brine was below 1 ppm, they experienced unpredictable spikes of 1.5 ppm magnesium in filtered brine due to admixed quantities of mother liquor from the ponds. Subsequently it was established that with use of automatic, continuous chemical feed, the rock salt system could be converted to use the solar salt.

The purpose of this paper is to review the factors that affect the design of the brine treatment equipment.

### BRINE QUALITY

This is the first and most important step in designing the brine treatment process. The effects of variations in the impurity levels in brine on cell operation (or intended plant) must be thoroughly understood.

Typical brine quality requirements for an electrolytic chlorine/caustic soda plant are given in Table 1.

### BRINE TREATMENT PROCESS

Salt and brine solution mined from a brine well contains considerable amounts of calcium, magnesium and sulfate. The calcium and magnesium are removed by chemical reaction with sodium carbonate and sodium hydroxide. Brine can be purged to control the sulfate level unless there is high concentration of sulfate in the salt, or if salt is expensive, or if environmental restrictions prevent purging. When necessary the reaction of sulfate with barium or calcium chloride is normally used for sulfate removal.

A brine treatment process for utilization of solid salt is shown in Figure 1. Water or recycling brine passes through a salt bed in the saturator. Salt is added continuously or in batches to the saturator from salt storage. The concentrated brine overflows to the reaction tanks where reagents such as soda ash, sodium hydroxide and, if needed,

barium/calcium salt are added. The reaction tanks overflow into a brine settler. Sludge is drained from the bottom. The brine settler overflow is filtered. Then the filtered brine is sent to the electrolytic cell.

### SALT

Before processing the salt quality should be evaluated first. The following analyses are necessary:

- A. Chemical analysis
- B. Caking characteristics
- C. Angle of repose
- D. Screen analysis.

The salt quality varies with the source of salt. Examples of the typical chemical analyses for two types of salts (rock and solar) are shown in Table 2.

Highly purified salt is available in the U.S.A. Typical analysis of the highly purified salt produced by two different suppliers is given in Table 3. The salt is excellent quality for chlor/alkali plants. The advantages are

- Eliminating chemical treatment and capital equipment costs
- Reduces sludge disposal costs
- Improvement in power consumption in chlor/alkali plants

At present, the price of high purity salt is unattractive; however, it is hoped in the future the price will be reduced to a level to make it economical.

The major factors in the salt handling area to be considered are:

- Salt unloading
- Salt storage
- Salt transfer to the saturator

**Salt Unloading.** Salt is usually received by barge, rail car or truck. Salt crystal size can be important in caking during shipment. Coarse salt larger than  $\frac{3}{8}$  inch seldom cakes, and even 8 to 10 mesh salt does not give trouble for short term storage. Salt that cakes, even in transit, can be unloaded from a railroad car by forming a salt slurry and discharging it to a sump. It is then pumped to salt storage as shown in Figure 2.

**Salt Storage.** Salt can be stored outdoors on a pad or in covered storage bins. Often it is stored in the extra large saturators. In wet storage, caking is rarely a problem.

### BRINE SATURATOR

Sodium chloride dissolves quickly in water. With good contact, water is saturated in about ten minutes, as shown

TABLE 1  
Typical Brine Quality for Chlor-Alkali Cells

| Type of Cell Components | Mercury           |                | Membrane* |                   |
|-------------------------|-------------------|----------------|-----------|-------------------|
|                         | Partial Treatment | Full Treatment | Diaphragm | Primary Treatment |
| NaCl gpl                | 310               | 310            | 315       | 305               |
| Ca PPM                  | 400-600           | 10             | 3         | 1                 |
| Mg PPM                  | 2                 | 1              | 0.3       | 0.1               |
| SO <sub>4</sub> gpl†    | 10                | 10             | 10        | 10                |
| Fe PPM                  | 1                 | 1              | 0.1       | 0.1               |
| Heavy Metals            | 0.5               | 0.5            | None      | 0.1               |

\*The primary treatment brine is further processed to reduce Ca + Mg concentration in the ion exchange system.

†Metal anode Chlor/Alkali cells

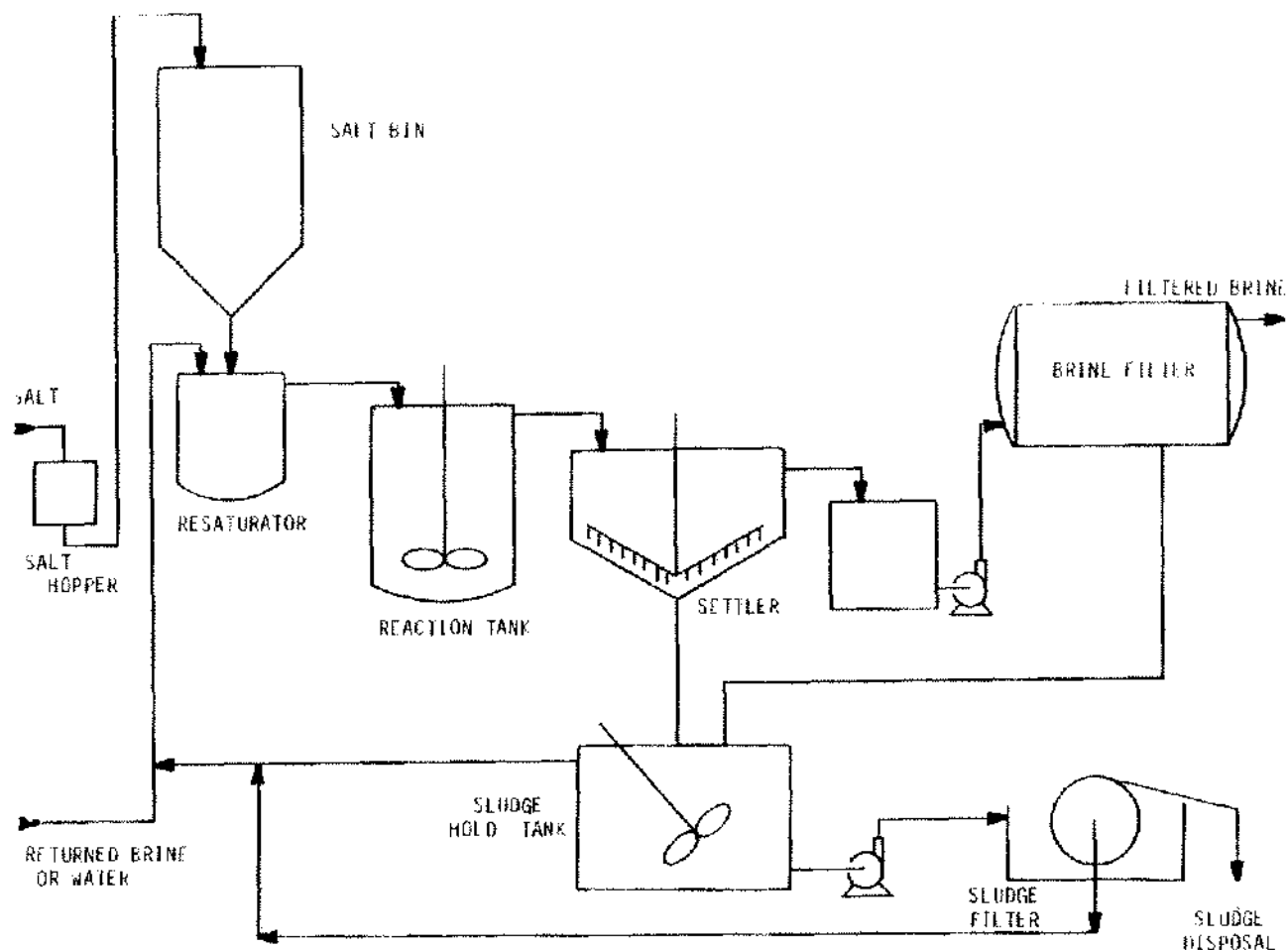


Figure 1. Flow Scheme Brine Treatment

TABLE 2

Salt Analyses—Commercial Grade

|                        | Typical<br>Louisiana<br>Rock Salt | Typical<br>Spanish<br>Solar Salt |
|------------------------|-----------------------------------|----------------------------------|
| NaCl wt. %             | 98.80                             | 98.5                             |
| Water wt. %            | 0.06                              | 1.0                              |
| Water Insolubles wt. % | 0.60                              | 0.1                              |
| Sulfate wt. %          | 0.35                              | 0.22                             |
| Calcium wt. %          | 0.16                              | 0.03                             |
| Magnesium PPM          | 25.                               | 500.                             |

TABLE 3

Salt Analyses—Highly Purified Salt

| Components            | Purified Salt<br>(U.S. Salt Suppliers) |        |
|-----------------------|--|--------|
|                       | Type I                                 | Type 2 |
| NaCl wt %             | 99.970                                 | 97.72  |
| Water wt %            | 0.013                                  | 1.40   |
| Water Insolubles wt % | 0.015                                  | <0.002 |
| Sulfate wt %          | 0.004                                  | 0.015  |
| Calcium wt %          | 0.010                                  | 0.0001 |
| Magnesium ppm         | 3.                                     | 0.1    |

in Figure 3 (Mitchell, 1969, p. 1). However, impurities such as  $\text{CaSO}_4$  take longer to dissolve. These differential solubility rates are important in designing the saturator. As more contact time for brine is provided in the saturator, more  $\text{CaSO}_4$  dissolves. A test conducted on New York rock salt indicated an increase in  $\text{CaSO}_4$  concentration from 1 to 3 gpl when the contact time was increased from 10 to 60 minutes. Higher temperature and lower pH

also increase the calcium sulfate solubility as shown in Figures 4A, B, and C (Mitchell, 1969, p. 2).

The calcium sulfate dissolution is also affected by the presence of calcium and/or sulfate ion due to the common ion effect. Figure 4D shows this effect on the New York salt sample.

In the Olin mercury cell process, as much as 75 per cent of calcium sulfate present in the feed salt can be retained

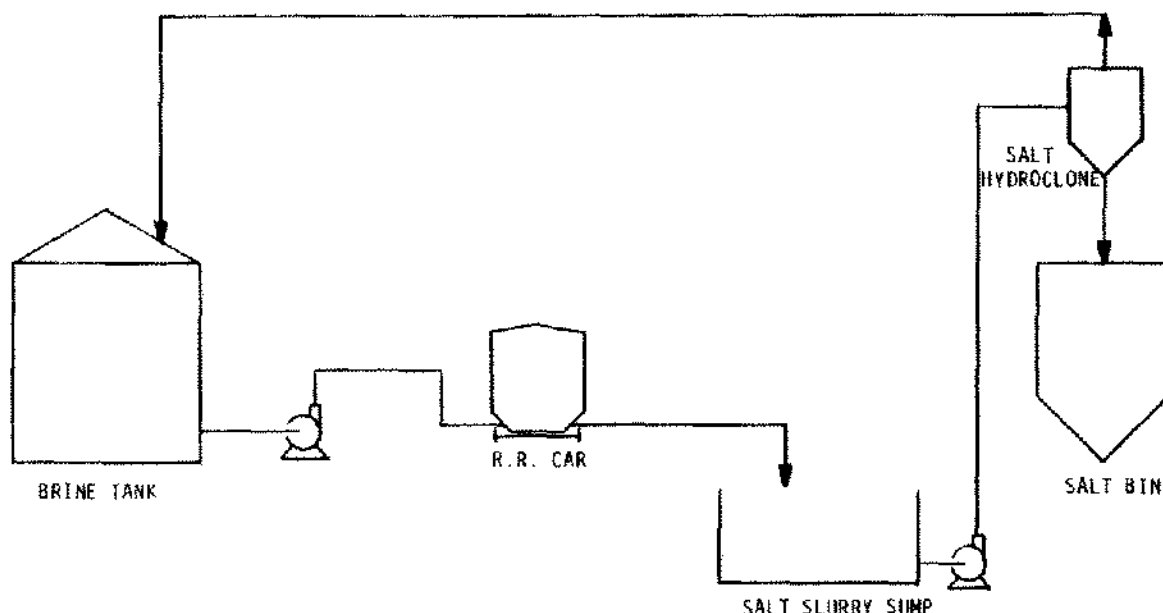


Figure 2. Salt Unloading from R. R. Car in Slurry Form

in the saturator. This is due to short contact time and presence of calcium and sulfate ions in the recycled brine.

The magnesium impurity in the rock salt is usually less than that in solar salt. With solar salt, dried mother liquor high in magnesium is usually present on the surface. The surface magnesium dissolves rapidly in brine resulting in magnesium spikes in the saturated brine. As soon as the surface magnesium has been removed, the magnesium concentration in the brine begins to fall. When salt is added to the saturator in batches, magnesium spikes are often observed. Makhteshim Chemical Works, Israel, conducted the following test using Dead Sea salt. Seven tons of solar salt was charged to a saturator in 10 minutes. The weak brine flow was 24 M<sup>3</sup>/hour requiring one ton of salt per hour to resaturate. The magnesium concentration in the overflow brine versus time is shown in Figure 5. As is seen, the magnesium level returned to normal in about two hours. Salt charging must be properly designed to avoid magnesium spiking in order to prevent upset in the chemical treatment step.

Often the saturators are designed for salt storage also. An economic evaluation should be made of the increase in the treatment costs, due to the longer brine contact vs. the additional cost of dry storage.

In the saturator design the following parameters should be considered:

1. Salt bed depth—Salt dissolves rapidly in a saturator, as we do not require a thick salt bed. About 1 to 1.5 meter height provides saturated brine, even at fairly high flow rates. Room for the insolubles, which remain in the saturator, should be provided.

2. Superficial velocity—Two opposite factors should be considered in deciding the superficial velocity: (1) need for high velocity to reduce the contact time with salt impurity, and (2) need for low velocity so that undissolved impurities stay in the saturator. A 20–25 M<sup>3</sup>/hr/M<sup>2</sup> velocity balances between these two opposite requirements for rock salt.
3. Sludge removal—Undissolved solids build up in the bottom of the saturator. Continuous removal of the sludge can be used, but salt is lost with the residues, and maintenance cost is high. The sludge can be physically cleaned by periodically cleaning the saturator.
4. Skimmer—If the salt carries light oily impurities, a skimmer should be provided.

## REACTION TANKS

Calcium and magnesium are major impurities in salt that should be removed almost completely. Calcium is removed by reaction with soda ash, and magnesium is removed by reaction with caustic soda or lime. Both reactions are straightforward. However, the CaCO<sub>3</sub> and Mg(OH)<sub>2</sub> suspension is very sensitive to the concentration of calcium and magnesium in the brine and also to the conditions of the precipitation.

This and other significant factors for the brine treatment design are discussed below.

**Reaction Rates.** In calcium treatment, the stoichiometric addition of soda ash takes several hours of agitation to complete the precipitation to the CaCO<sub>3</sub> solubility end

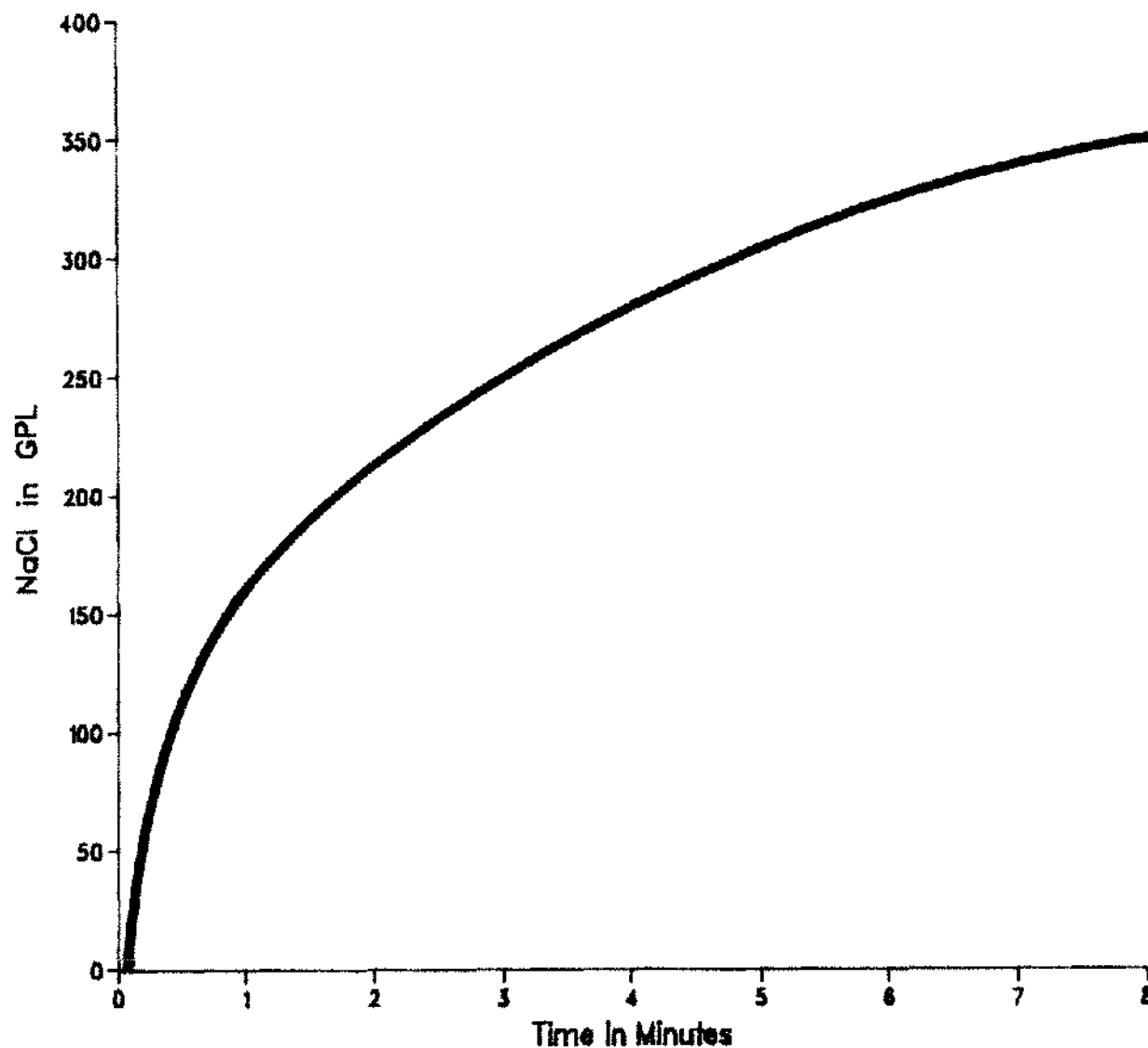


Figure 3. Rock Salt Saturation in Water

point. If, however, an excess of 0.8 gpl soda ash is used, better than 80 per cent reaction occurs in 15 minutes and practically all is completed in one hour with less than 1 PPM Ca remaining in solution.

The magnesium and caustic soda or lime reaction is instantaneous. However, the magnesium hydroxide floc is very delicate. The use of lime instead of caustic soda gives better settling floc but requires subsequent removal of calcium, which requires vigorous agitation during reaction with soda ash (Hine, 1959, pp. 769-773). This results in breaking of the delicate floc, requiring longer settling time. Complete magnesium hydroxide precipitation is accomplished at 10.5-11 pH.

**Supersaturation of  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ .** On addition of soda ash and caustic soda to the calcium-magnesium-

containing brine, microscopic particles of amorphous  $\text{CaCO}_3$  coated with a layer of  $\text{Mg}(\text{OH})_2$  are formed. The mixture is a homogeneous milky fluid. With time the particles grow to  $10^{-4}$  mm diameter forming a colloidal suspension. In the next phase amorphous, nuclei crystallize out and form the elementary particles of the slurry.

Shortly after crystallization, the measured solubility of  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  is several times the equilibrium concentration forming a supersaturated solution. The rate of desaturation depends upon (a) calcium-to-magnesium ratio, (b) agitation and (c) temperature.

Test results have indicated that the size of these particles depends on the condition of precipitation (Pribicevic and Stancic, 1970, pp. 363-368). Normally a  $\text{CaCO}_3$  particle reaches 1 micron in diameter, but in the presence of

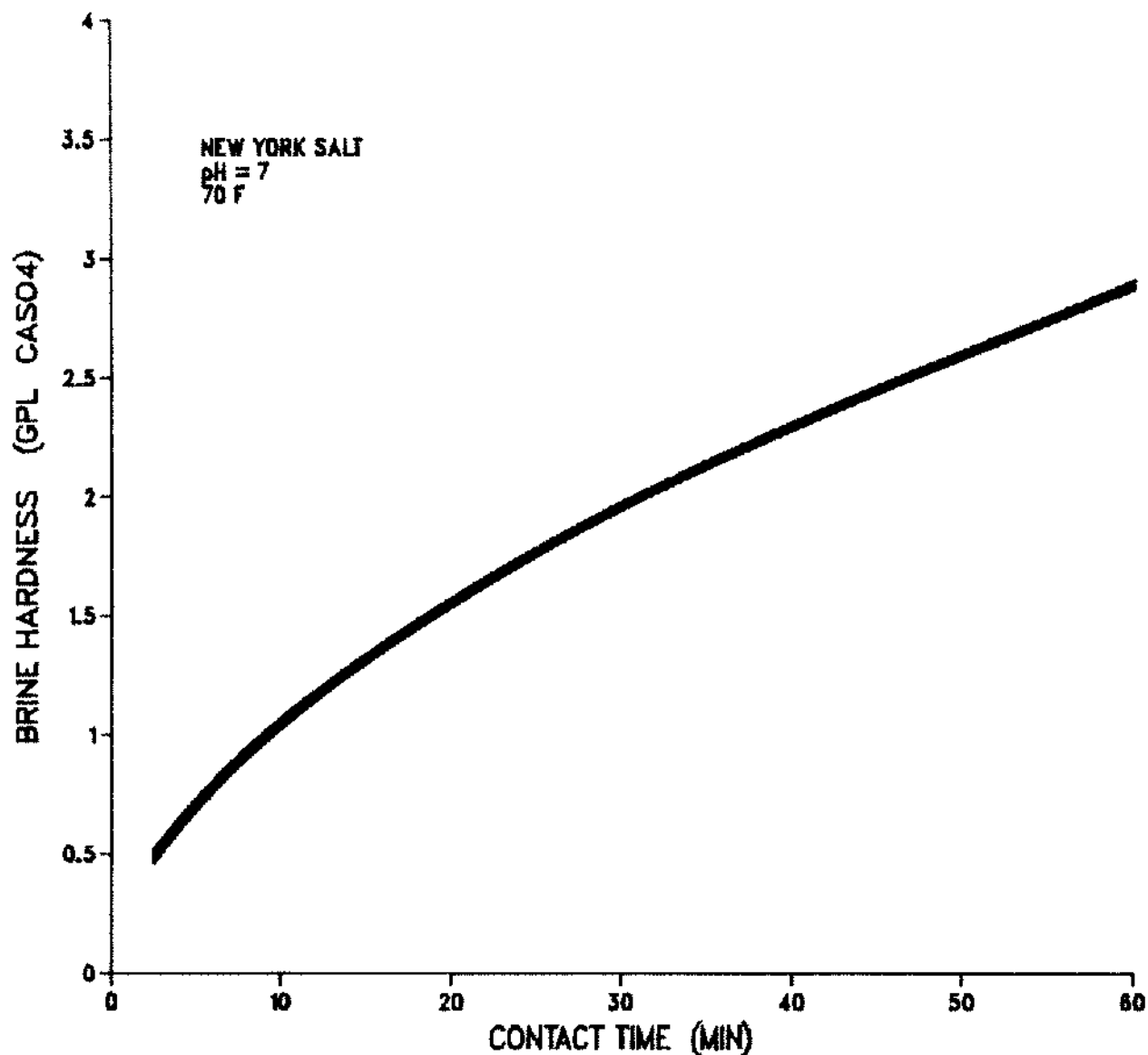


Figure 4A. Rate of Calcium Sulfate Dissolution in Brine

Mg it can vary by a factor of 300 to 400. Microscopic particles adhere to each other and form stable floccules which settle to the bottom.

As shown in Figure 6, the maximum precipitation rate is achieved at 80-90 per cent Ca in the Ca + Mg mixture. At Mg below 10-15 per cent, the precipitation rate decreased sharply. Apparently the low concentration of  $Mg(OH)_2$  does not provide adequate binding for  $CaCO_3$  precipitate.

**Solubility Product.** In a saturated solution of a salt, there is an equilibrium between the ions in the solution and the excess salt. For saturated solution of barium sulfate the equilibrium is represented as follows:



for which

$$[Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10} = K_{sp}.$$

Such an equilibrium constant is called a solubility product and is designated  $K_{sp}$ . In the operating plant often there is no equilibrium of ions with excess salt, but a constant concentration ionic product is formed. We will call this the Pseudo Solubility Product ( $K_{sp}'$ ). This is obtained by measuring the ionic concentration when it has reached equilibrium and multiplying the ionic concentrations. This principle can be used to

1. Determine excess reagent requirements to achieve permissible impurity levels in the finished brine
2. Determine which impurity will precipitate first.

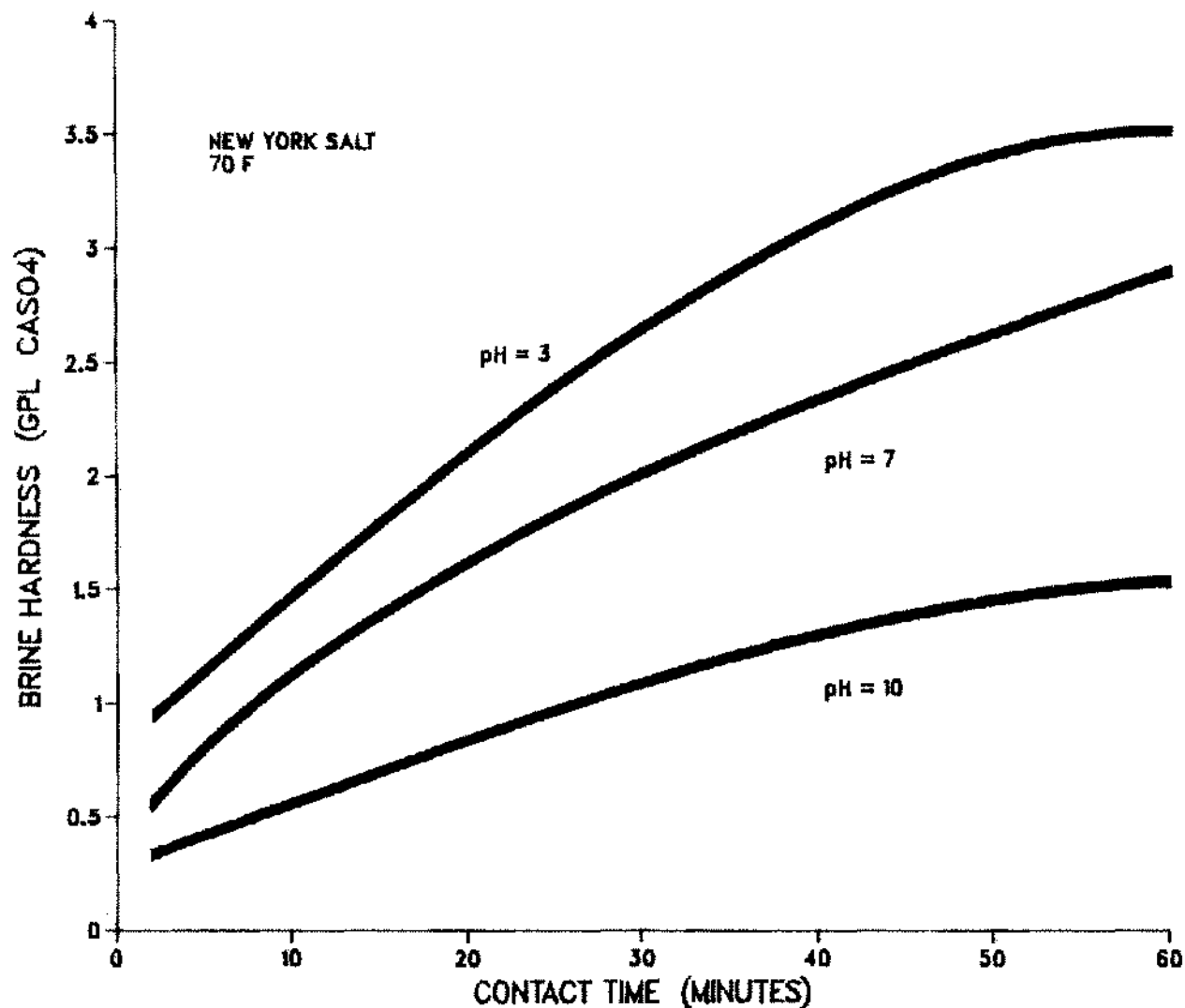


Figure 4B. Effect of pH on Rate of Calcium Sulfate Dissolution in Brine

1. *Excess reagent requirement.* For brine system design, if 10 PPM calcium is desired, the excess carbonate requirement will be 0.21 g/liter as shown below.

For a brine system in a chlor/alkali plant operating at 60°C, the pseudo solubility product found for  $\text{CaCO}_3$  is as follows:

$$\begin{aligned} K_{sp'} &= [\text{Ca}][\text{CO}_3] = 1.06 \times 10^{-6} \\ &= [2.95 \times 10^{-4}][\text{CO}_3] = 1.06 \times 10^{-6} \\ [\text{CO}_3] &= 3.53 \times 10^{-3} \text{ gm moles/liter.} \end{aligned}$$

2. *The precipitates with the lowest solubility products for commonly encountered impurities are given in Table 4.* It is apparent that between  $\text{BaSO}_4$  and  $\text{CaSO}_4$  co-precipitation  $\text{BaSO}_4$  should precipitate first.

The Pseudo Solubility Product actually achieved in the plant depends upon temperature, flowrates and equipment design. It is possible to maintain the same level of

one ion impurity of a compound by changing the concentration of the other ion in the circulating brine system.

**Agitation.** Agitation is desirable for calcium carbonate precipitation. It helps to increase crystal size, as well as to keep them in suspension. Larger size crystals will sink faster in the settler.

Data obtained in a laboratory bench scale test reactor using 300 gpl brine (rock salt) was treated with excess 0.6 gpl soda ash (Olin test data 1). After settling, the top 100 ml of solution was withdrawn for analysis. Figure 7 shows the relative effects of 5 minutes and 60 minutes agitation on the sludge settling rate.

The optimum agitator speed was found to be less than 4 ft/sec. tip velocity. Sixty minutes reaction time was selected in the design.

Magnesium precipitates are delicate and should not be vigorously agitated to avoid precipitate breakup resulting in slow settling of precipitates. Magnesium, therefore, is

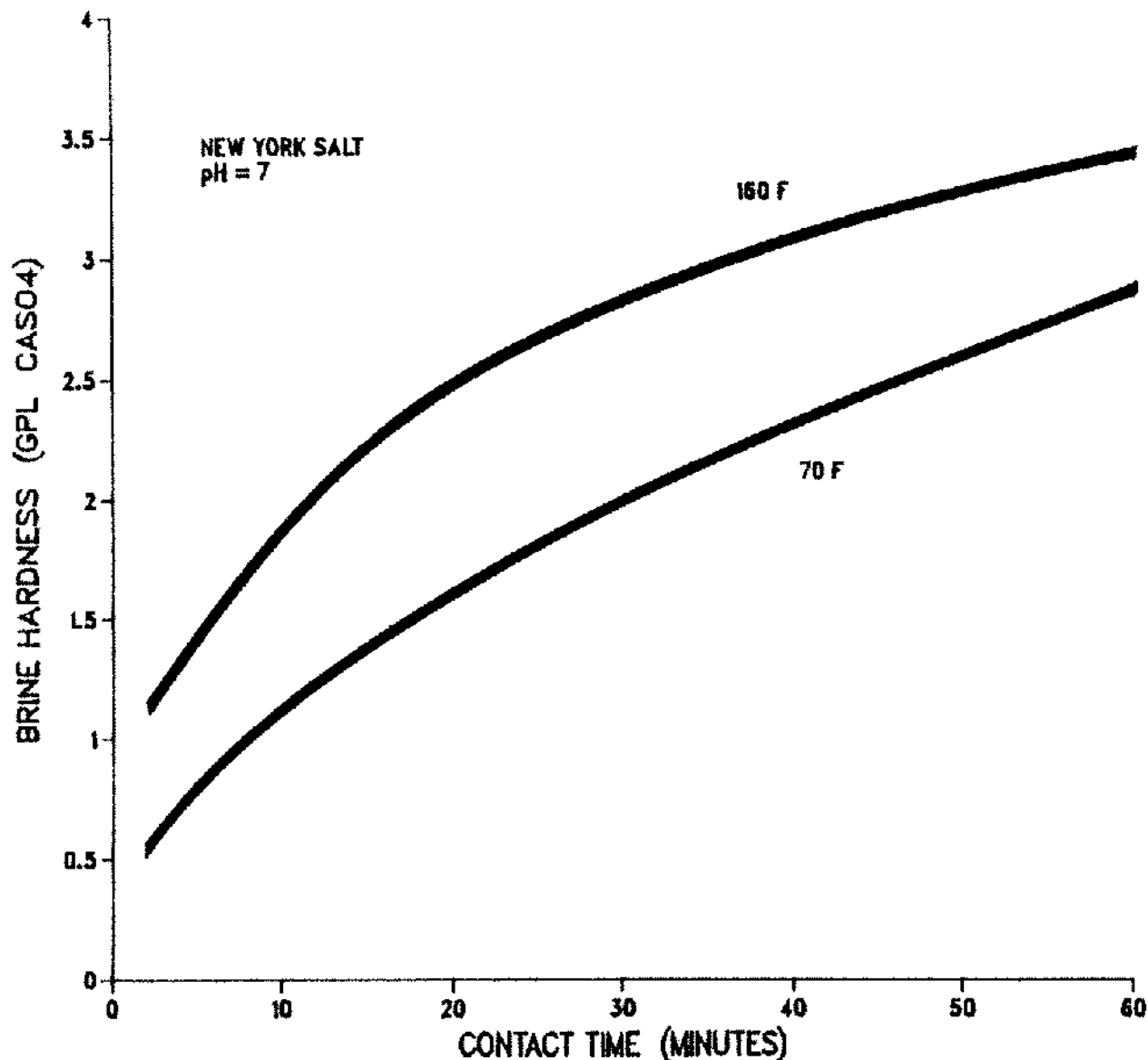


Figure 4C. Effect of Temperature on Rate of Calcium Sulfate Dissolution in Brine

precipitated by slow stirring to provide mixing of the reagent and it is precipitated at the last moment before the brine is sent to the settler (Vijayaraghavan, 1961, p. 468).

**Settling  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ .** Most rock salt contains low magnesium and little effect on settling can be expected. The magnesium effect on settling during the design phase can be disregarded for all practical purposes.

In solar salt, where high magnesium is present, the Ca:Mg ratio is critical. The presence of  $\text{Mg}(\text{OH})_2$  precipitate assists the binding of  $\text{CaCO}_3$  precipitate. At the same time, the presence of  $\text{CaCO}_3$  helps the fluffy sodium hydroxide precipitate to be dragged down. The preferred Ca:Mg ratio is 3-5 calcium to 1 magnesium.

Vijayaraghavan has shown that there is a reduction in the settling rate with an increase in magnesium concentration (Vijayaraghavan, 1961, p. 469). This is apparent in Figure 8. The study of Pribicevic and Stancic has shown that the optimum Ca:Mg ratio is 0.8:0.2. Addition of lime to increase the calcium concentration will increase the settling rate. This is further discussed in the settler design.

**Temperature.** Hine has pointed out that the solution temperature affects the reaction rate (Hine, 1958). At low temperatures initial precipitation requires a long time. Once the process of settling begins, however, rapid precipitation at a fixed rate occurs, showing little effect of temperature.

During the equipment design stage additional reaction



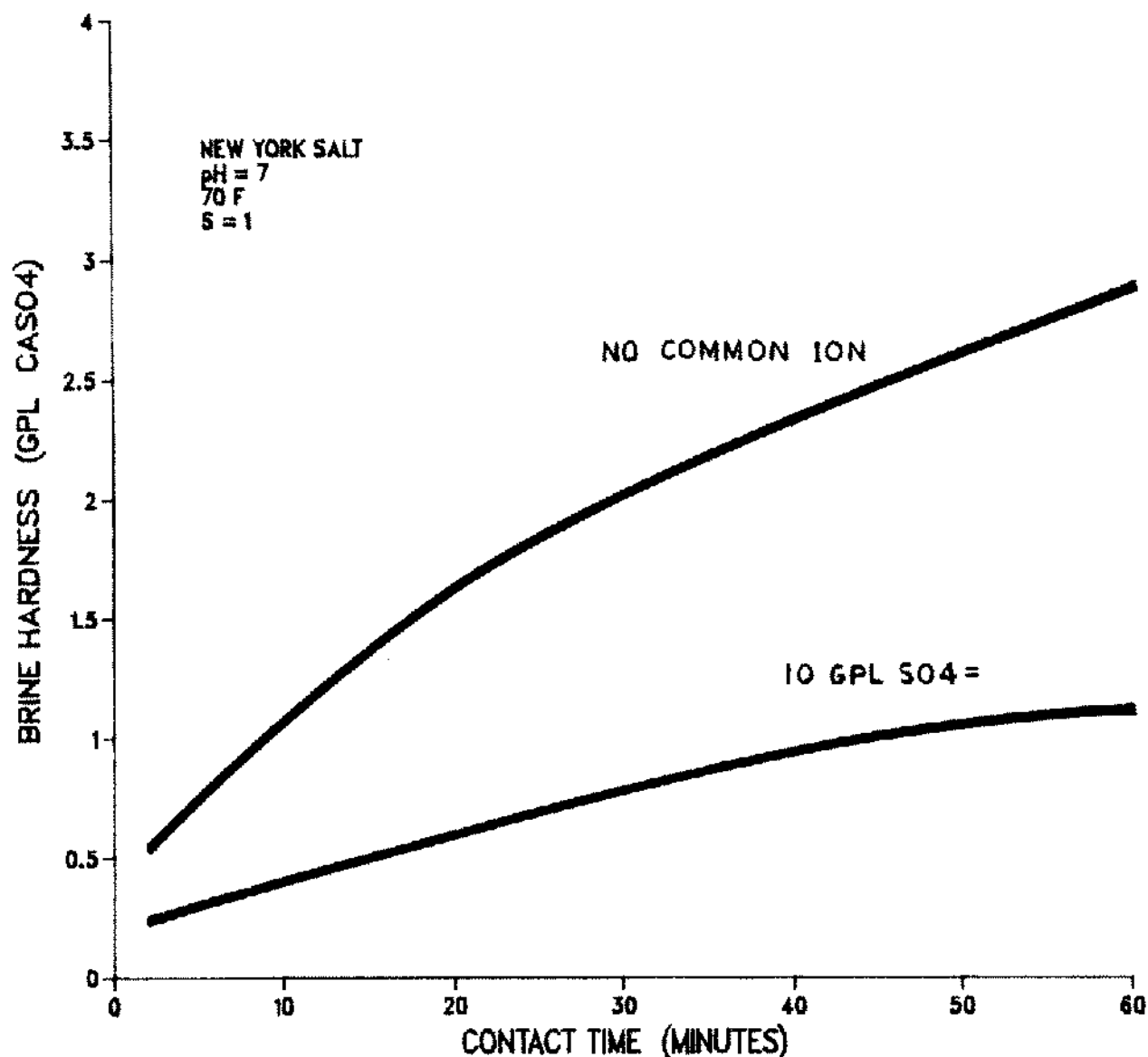


Figure 4D. Common Ion Effect on Calcium Sulfate Dissolution Rate in Brine

time should be provided in case the treatment is carried out at low temperatures. In the 40°C-70°C temperature range, however, there is no significant difference in reaction time observed.

#### SETTLER

The precipitated impurities are separated in a settler and then followed by filtration to get the purified brine. When the salt has relatively little impurity or high magnesium, which is difficult to settle (magnesium hydroxide precipitates), the settler can be replaced by total filtration of solids.

In a settler, the particle settles by free and hindered settling. Initially, individual particles are far apart in a

dilute suspension. The particles with the density higher than that of fluid will settle. *Free settling* occurs when individual particles start settling independently. The free settling rate is directly dependent upon size and density of the particles and decreases with increasing upward liquid velocity.

When a particle moves downward in a suspension an equal volume of fluid is displaced upward. As settling progresses, the distance between individual particles will decrease in the lower part of the suspension. This means that the displaced fluid will have a decreased cross-sectional area available for upward flow that results in a higher upward fluid velocity. The higher upward fluid velocity will decrease the settling rate of the particles as the

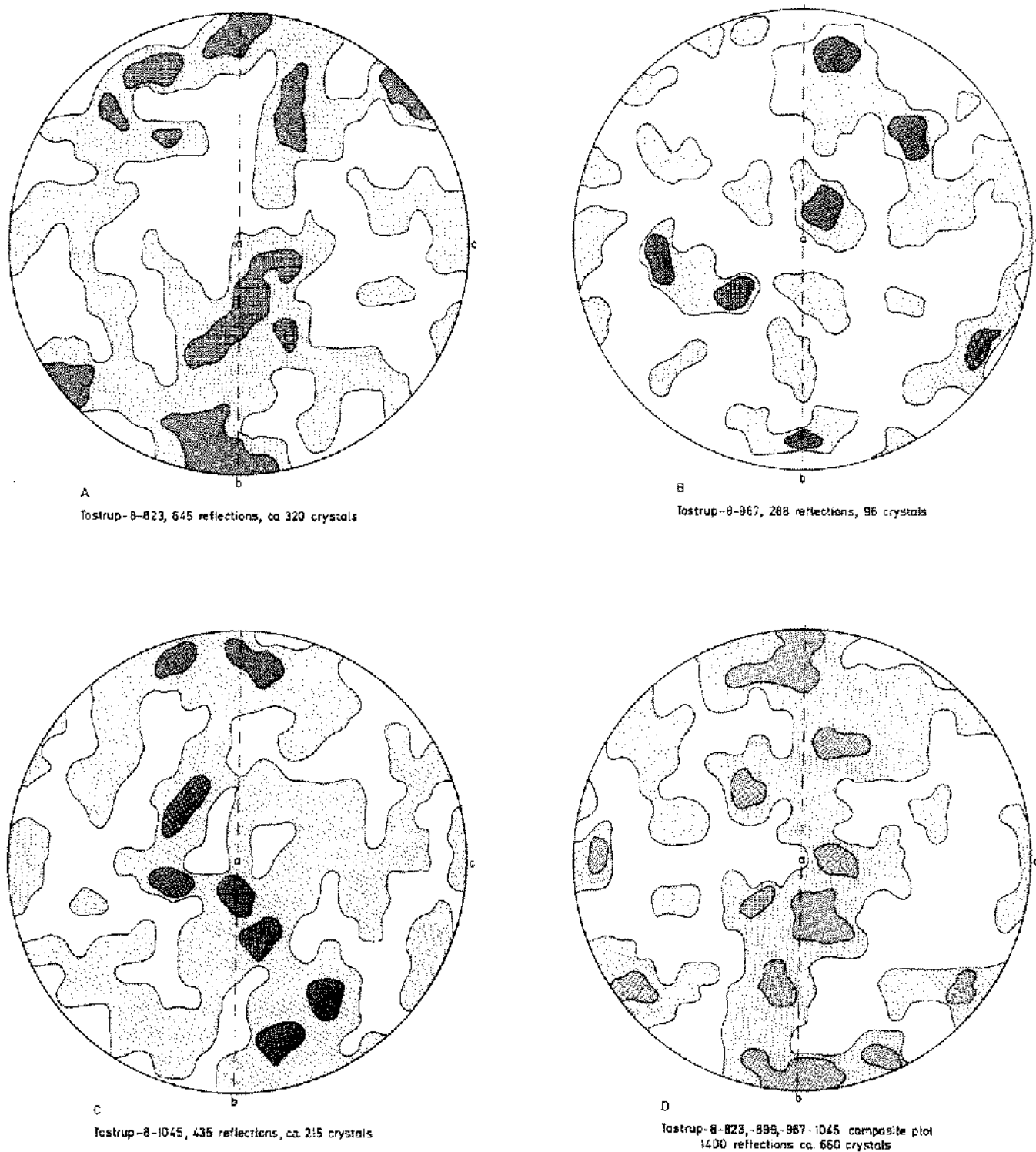


Figure 5. Magnesium Dissolution with Single Charge of Solar Salt

concentration of particles in the lower part of the suspension increases. A loose structure results in which particles are trapped, and this eventually forces all particles to settle with the same velocity irrespective of size and shape. This type of settling is called *Hindered Settling*. As all par-

ticles during hindered settling have the same velocity, a sharp interface between clear liquid and slurry will form. Sometimes there is no sharp distinction between clear liquid and slurry. This is particularly true in solar salt precipitates.

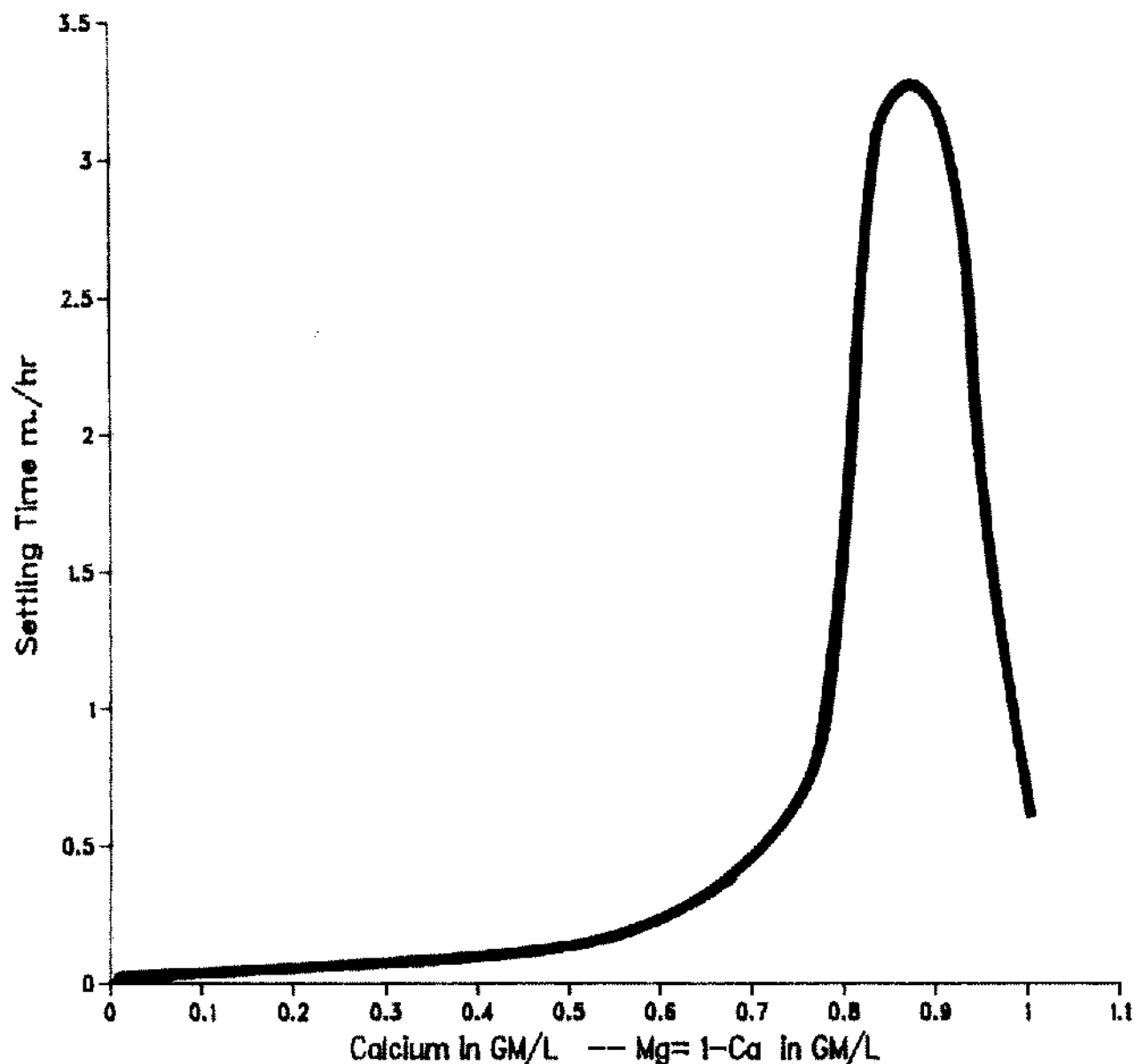


Figure 6. Dependence of the Precipitation of the Suspension on the Ca/Mg Ratio

TABLE 4  
Solubility Products

| Compounds  | $K_{sp}$              |
|------------|-----------------------|
| $Al(OH)_3$ | $1.1 \times 10^{-15}$ |
| $BaCO_3$   | $7.0 \times 10^{-9}$  |
| $BaSO_4$   | $1.1 \times 10^{-10}$ |
| $CaCO_3$   | $1.2 \times 10^{-8}$  |
| $CaSO_4$   | $6.4 \times 10^{-5}$  |
| $Fe(OH)_3$ | $1.5 \times 10^{-36}$ |
| $Fe(OH)_2$ | $1.6 \times 10^{-14}$ |
| $MgCO_3$   | $4.0 \times 10^{-5}$  |
| $Mg(OH)_2$ | $1.2 \times 10^{-11}$ |

Solubility product data in water: (Ion concentrations are in gmm moles/liter.

In order to design a settler, the rate of settling should be established based upon laboratory tests. If the precipitates do not settle but stay in suspension, flocculating agents are used. This improves the settling rate and can substantially reduce the size of the settler required. The selection of the flocculating agents should be made carefully. Some chemicals are detrimental to the process, e.g., amino compounds, and they should be avoided.

The free settling characteristic usually determines the overflow quality while the hindered settling determines the quality of the underflow.

There are various settling test procedures available. The Parkson Company uses the following test procedure

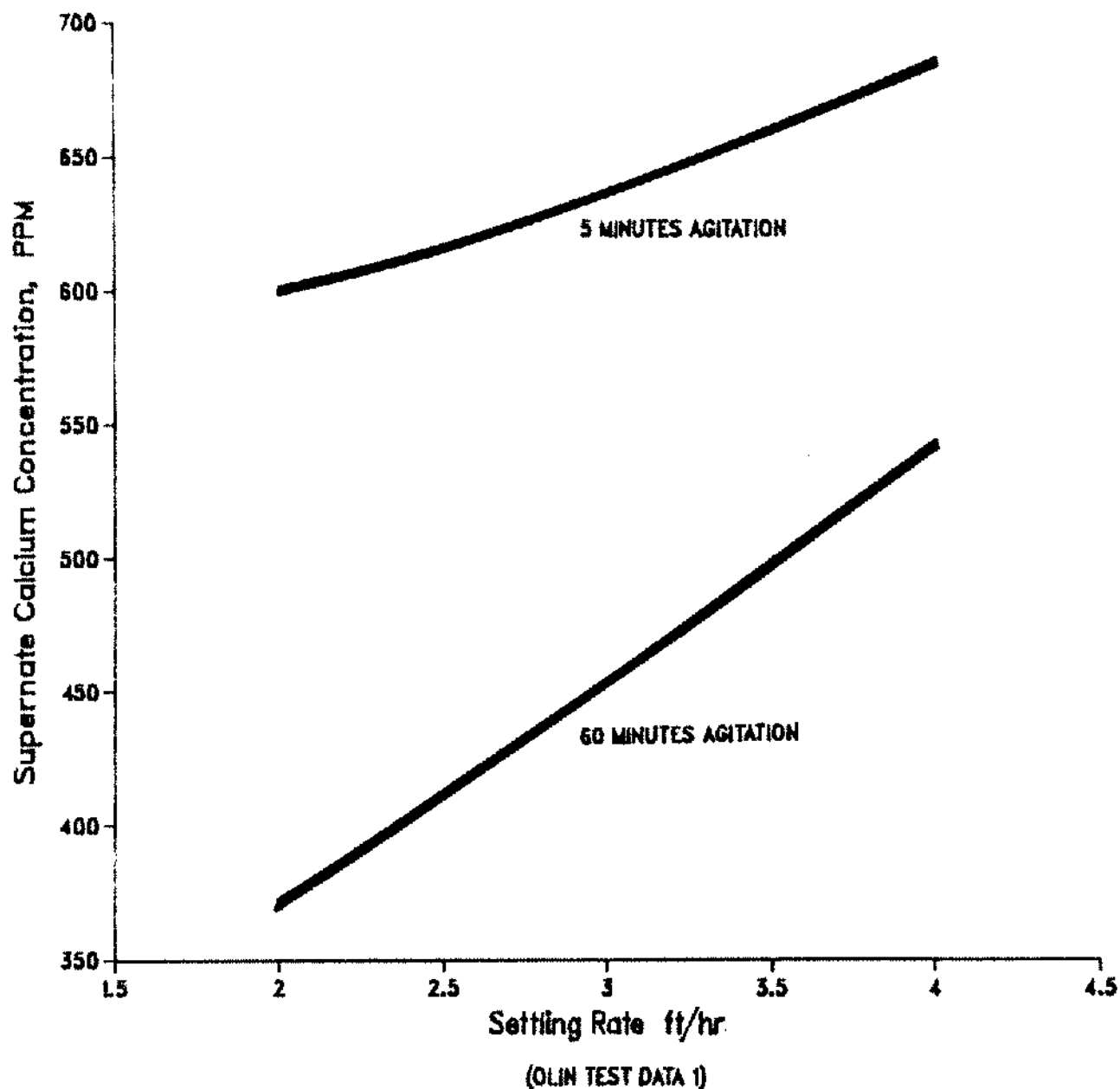


Figure 7. Calcium Concentration vs. Settling Rate of Calcium Carbonate

which was used at Olin in one of our designs (Olin test data 2).

As shown in Figure 9, five graduated cylinders were maintained at 70°C. Brine, after reaction with soda ash and caustic soda, was poured into the five graduated cylinders. The pH of brine had been adjusted to 11.2.

Prior to settling, a sample of brine was analyzed for Ca and Mg—giving 276 and 41.8 mg/liter respectively.

The brine poured into the graduate cylinder was approximately 20 cm high (I.D. of each cylinders—1⅜"). Then the top 100 ml of sample was siphoned after 2, 6, 10, 14, and 18 minutes settling and was analyzed for Ca and Mg. The results obtained are presented in Table 5.

The settling rate for each time period was calculated from Table 5. A plot of ppm Ca and Mg concentration as a function of settling time was drawn (see Figure 10). From the plot it indicates that after approximately 6 minutes of settling the concentration of Ca and Mg drops to 30 and 10 ppm, respectively. For a 1000-gpm settler, the rise rate of 2.84 ft/hr would mean that we would select a 60-foot-diameter settler. The height of the brine sludge settler is about 10 feet straight side. The bottom can be curved or a 45° cone can be used.

Temperature changes, fluctuating loading rates and flow changes affect the settling process substantially. A change in temperature produces thermal currents, result-

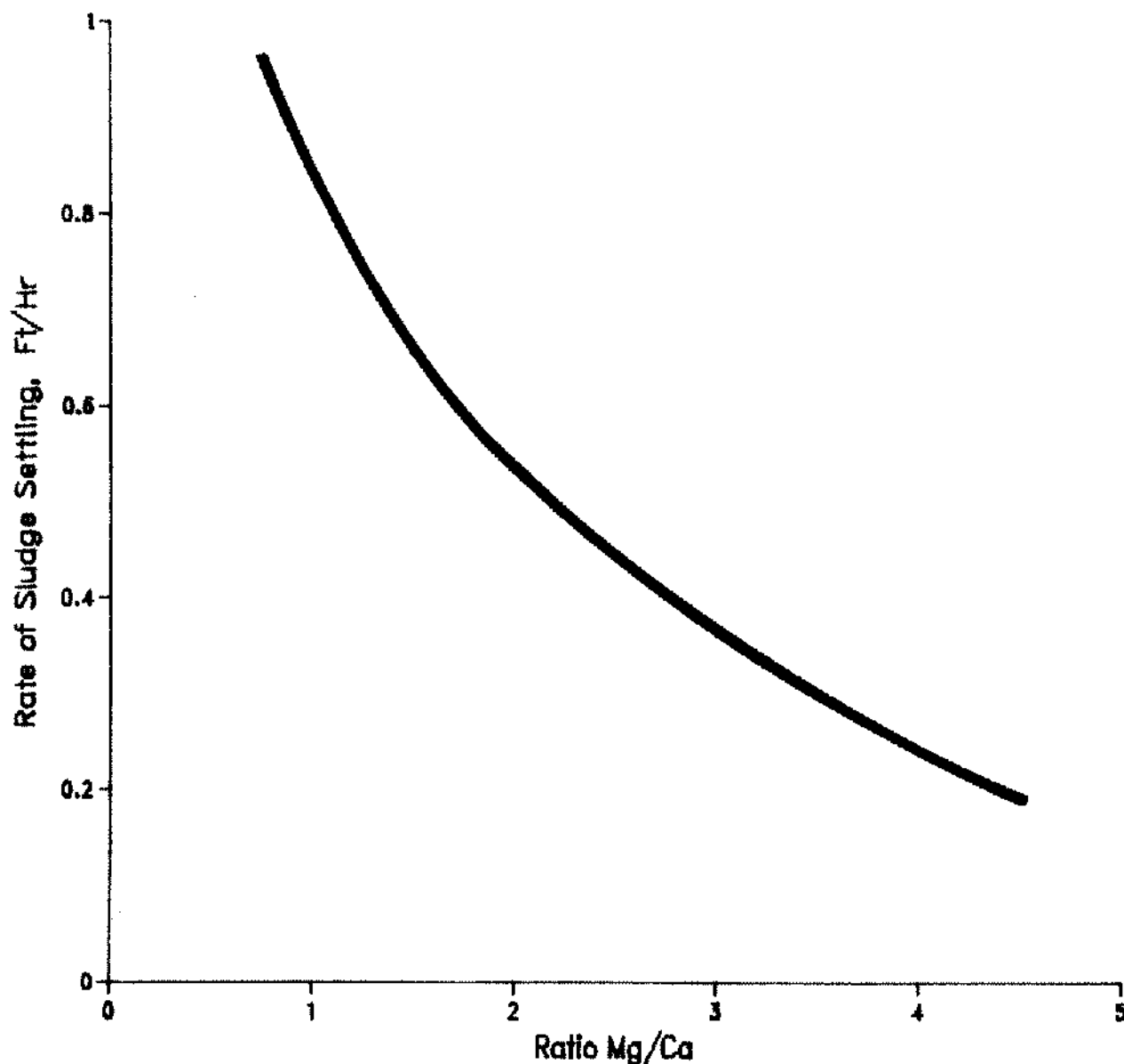


Figure 8. Mg/Ca Settling Rate

ing in short circuiting the precipitates. Surges of flow will result in excessive turbulence and disturbance in the settler feed well. This also causes short circuiting of feed to the settler proper.

The settled sludge is moved toward the center of the settler by a rotating rake. Care must be taken so that all precipitates can be pushed gently toward the center without causing undue turbulence.

Occasionally, considerable solid build-up on the rake arms is observed. Eventually these solids fall off. The solids will cause a considerable unbalanced strain on the arm and also impair sludge movement. Proper design of the support arm well, clear of the cake blades, minimizes this problem. Also monitoring the rake motor amps gives an indication of sludge buildup.

#### BRINE FILTER

The filtration step is necessary to remove final traces of both calcium and magnesium precipitate from the brine.

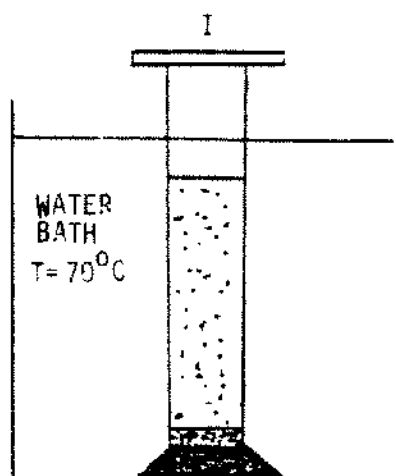
The equilibrium solubility of  $\text{CaCO}_3$  and magnesium hydroxide is on the order of 0.5–0.8 mg/liter and 0.1–0.2 mg/liter, respectively. The settler overflow, under ideal operation, is about 15 mg/liter Ca plus Mg. This indicates that most of the  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  impurity is undissolved solids.

There are various types of filters in operation: sand filters, precoat filters, cartridge filters, etc. The filter type is selected, based upon cake characteristics, potential filter media contamination in the filtrate and desired brine quality.

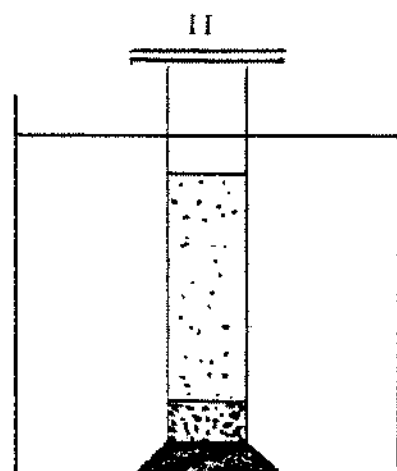
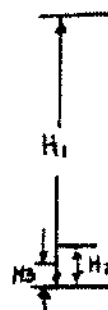
BRINE HEIGHT  
H1 = 20 cm

SLUDGE HEIGHT  
H3 = 1 cm

H2 = 2.5 cm

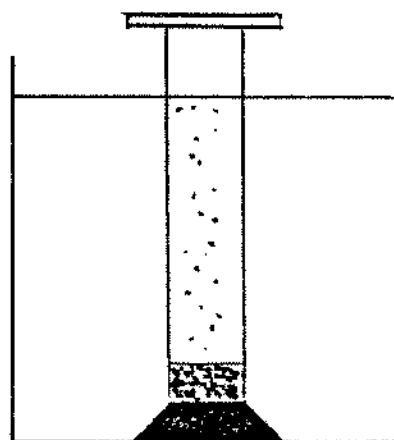


SETTLING TIME,  $t = 2$  mins.



SETTLING TIME,  $t = 6$  mins.

III



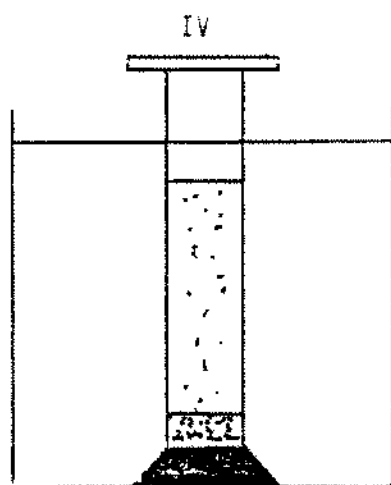
SETTLING TIME,  $t = 10$  mins.



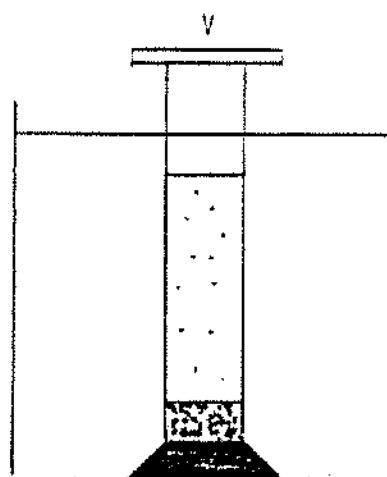
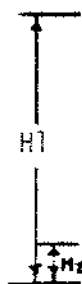
BRINE HEIGHT  
H1 = 22 cm  
SLUDGE HEIGHT  
H2 = 2.5 cm

BRINE HEIGHT  
H1 = 20 cm

SLUDGE HEIGHT  
H2 = 2.5 cm



SETTLING TIME,  $t = 14$  mins.



SETTLING TIME,  $t = 18$  mins.

Figure 9. Solar Salt Brine Sludge Settling Test (Olin Test Data—2)

TABLE 5  
Solar Salt Settling Tests  
(Olin test data—2)

| Test Nos. | Settling Time, T "mins." | Brine Height "cm" | Sludge Settled Height "cm" | Analysis PPM |      | Settling Rate Ft/Hr |
|-----------|--------------------------|-------------------|----------------------------|--------------|------|---------------------|
|           |                          |                   |                            | Ca           | Mg   |                     |
| 1         | 2                        | 20                | 1.0                        | 179          | 45.3 | 10.3                |
| 2         | 6                        | 20                | 2.5                        | 24.6         | 5.0  | 3.43                |
| 3         | 10                       | 22                | 2.5                        | 17.5         | 2.9  | 2.1                 |
| 4         | 14                       | 20                | 2.5                        | 13.6         | 2.1  | 1.47                |
| 5         | 18                       | 20                | 2.5                        | 10.1         | 1.4  | 1.14                |

5:1—Ca:Mg at T = 70°C

Treated Brine:

Ca = 276 mg/liter (234 ppm)

Mg = 41.8 mg/liter (35 ppm)

Diameter of each Graduate Cylinders =  $1\frac{3}{8}$ " = 3.49 cms.

Selection of filtration rates can be based upon laboratory tests. A bomb test filter is often used to conduct these laboratory scale tests. A bomb test filter, as developed by Great Lake Carbon Corporation, is shown in Figure 11. It has a filter leaf covered with filter cloth. Air is supplied to maintain desired filtration pressure. The slurry to be filtered is charged to the filters, the filtration pressure set, and the volume of filtration measured vs. time, as seen in Figure 12.

A typical filtration test for an unsettled solar salt brine conducted at Olin (Mota, 1981) follows: The brine was slowly agitated to obtain a homogeneous solution. Approximately 2.5 liters of this brine was poured into the "Bomb Filter" and three filtration tests using filteraid "Dicalite 476" as body feed were conducted at 10 psig pressure. The results of the three tests conducted at 5, 10, and 20 lbs filteraid per 1000 gal brine were plotted in Figure 12 (filtrate volume vs. time).

The filtration rate is calculated as follows:

$$\text{Filteraid Use} = 5 \text{ lb}/1000 \text{ gal.}$$

From Figure 12.

For 8-hr cycle, filtrate collected = 770 ml at P1 = 10 psig

$$\text{GPH}/\text{ft}^2 = \frac{\text{Filtrate collected for 8 hr, ml}}{8 \text{ Hr}} \times \text{leaf factor}^{(1)}$$

$$= \frac{770 \text{ ml}}{8 \text{ hr.}} \times 0.0485 = 4.67 \text{ gph}/\text{ft}^2 = F1$$

To obtain a flow (F2) at P2 = 30 psig

$$F_2 = F1 \times P2/P1 = 4.67 \text{ gph}/\text{ft}^2 \times 30/10 = 8.09 \text{ gph}/\text{ft}^2 = 0.135 \text{ gpm}/\text{ft}^2.$$

<sup>(1)</sup>Leaf factor is conversion factor to gph/ft<sup>2</sup>.

The filtration rates for the three tests were 4.67, 5.82 and 8.79 gph/ft<sup>2</sup>, respectively. The concentration of Ca and Mg in the filtrate for each test was 3 and .05 ppm, respectively.

Brine with high magnesium forms colloidal precipitates which are difficult to filter. A precoat filter is often used for this type of filtration.

Selection of precoat is important because it sometimes allows leaching of undesirable impurities (Hine, 1979, p. 507). The 10-micron cartridge filter can produce about 0.9 ppm calcium brine, while it can be reduced to about 0.5 ppm by 1-micron cartridge filters. These filters have high pressure drop and require frequent backwashing. Because of this problem, in a full-scale plant automated backwashing or a sluicing system is recommended.

The backwash from the filter is normally settled. If dry cake is desired, the supernatant liquid is decanted and the bottom portion is filtered in a vacuum or a plate and frame type filter. A high magnesium salt backwash takes a fairly long time to settle. Special attention should be given in the design so that adequate time is provided for the settling. The thin slurry is difficult to filter. Sometimes filteraid is added to improve its filterability.

## SULFATE TREATMENT

Various methods are available for the sulfate treatment. The criteria of selecting the appropriate methods include (a) desired level of control, (b) sludge disposal restriction, (c) treatment cost. The most commonly used methods are:

- A. Calcium treatment
- B. Barium treatment
- C. Purge.

**A. Calcium treatment.** This process uses the solubility product principle for control of sulfate:



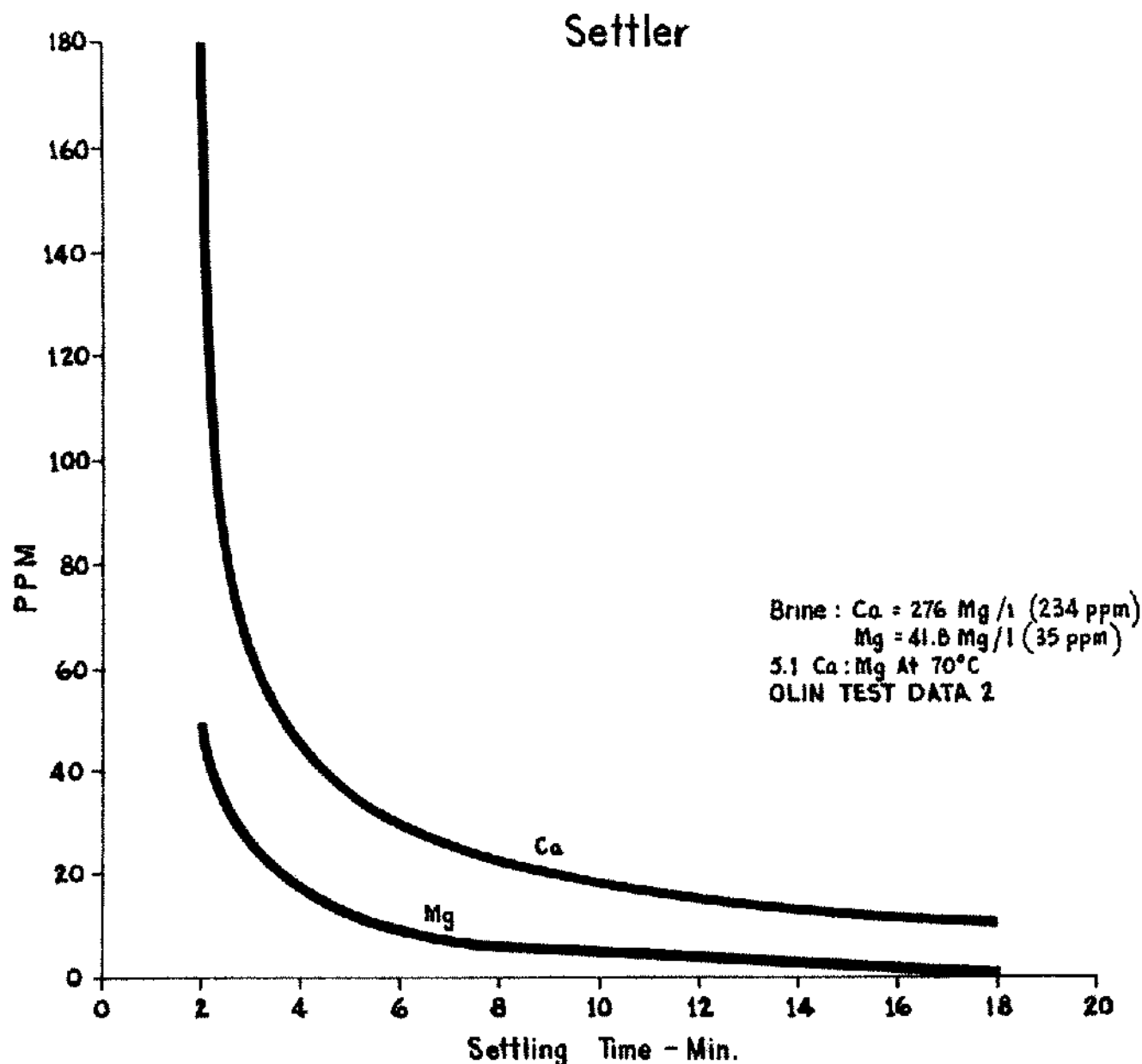
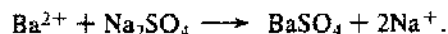


Figure 10. Bench Scale Settling Test for Settler Design

In order to attain the desired  $\text{SO}_4$  level, calcium chloride or lime is added. Gypsum is formed, but anhydrite is preferred. The optimum conditions for anhydrite formation are:

1. High concentration of NaCl
2. High pH
3. High temperature
4. High concentration of anhydrite slurry as solid phase (Olin has used this principle successfully).

**B. Barium treatment.** Barium carbonate or barium chloride is reacted with sulfate to produce barium sulfate precipitates:



Barium carbonate sludge requires secured landfill disposal. If there is no secured landfill available with the barium treatment, the calcium treatment should be used. With the barium treatment the process should be designed so that there is no excess barium left in brine during the soda ash treatment.

**C. Purge.** In the diaphragm cell chlor-alkali process, about 12 per cent caustic is produced mixed with 13 per cent salt solution. During evaporation of caustic, salt containing sodium sulfate crystallizes and separates. The salt is washed and 5-7 per cent concentration sodium sulfate solution is produced and can be purged.



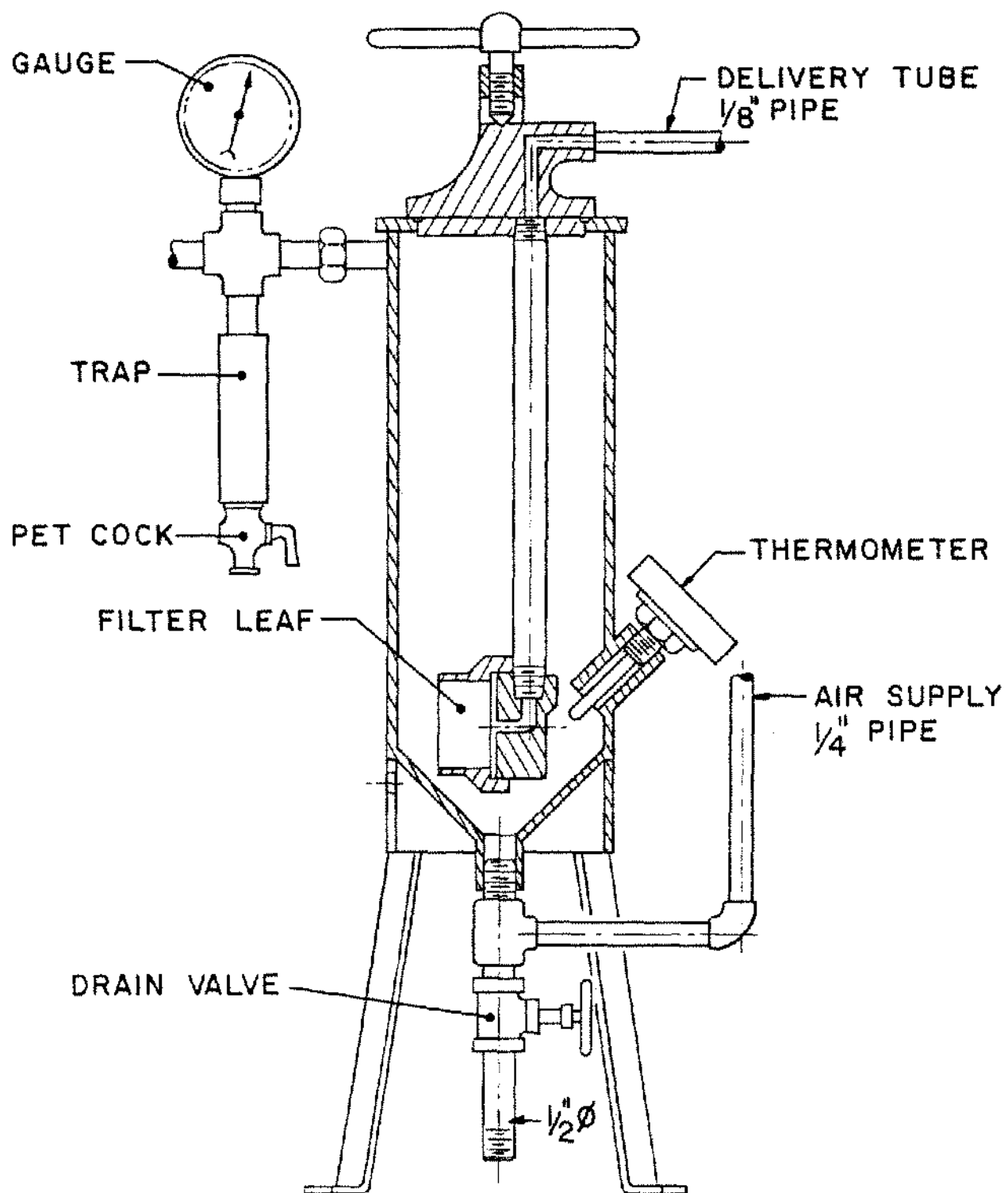


Figure 11. Bomb Filter Press

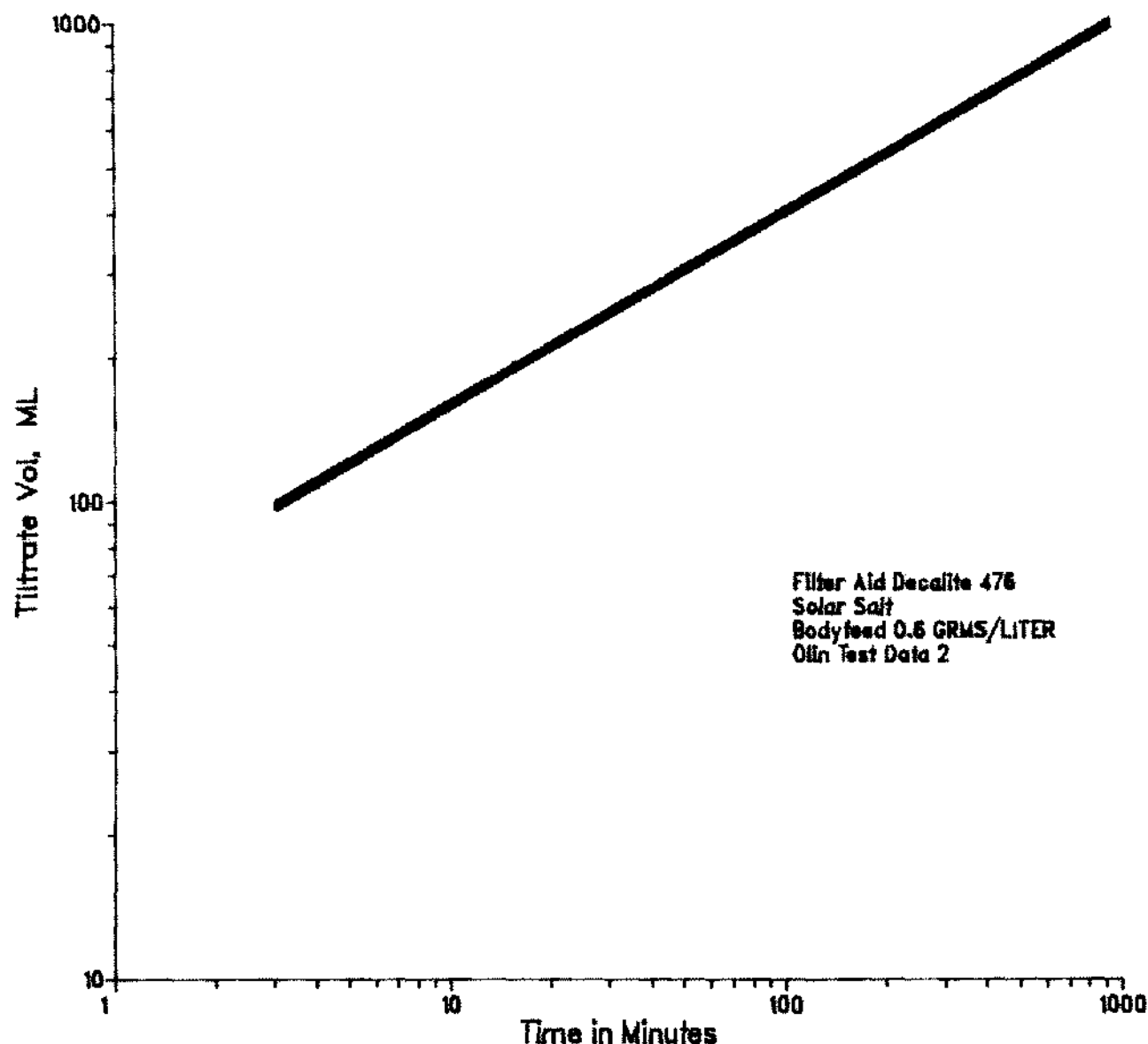


Figure 12. Brine Filter Test

### CLOSING COMMENTS

The optimum brine treatment process selection is dependent upon the type of salt and the economics of the plant. Salt analysis and bench scale laboratory tests can provide significant information for design. The factors outlined in this paper are critical in designing a reliable brine treatment process.

Calcium-magnesium concentration plays a major role in selecting reaction tank and settler design. The conventional treatment involves soda ash and caustic soda reaction. Use of lime in magnesium treatment is practical where the cost of soda ash is low.

The calcium and magnesium concentration can be re-

duced economically, below 1 ppm and 0.1 PPM level, respectively, by proper selection of reaction system settling and filtration.

Sulfate is controlled by (1) crystallization as sodium sulfate, (2) purge, or (3) chemical treatment with calcium or barium.

### ACKNOWLEDGMENT

I would like to thank Olin Management for allowing the publication of this paper; also, I would like to thank K. E. Woodard and P. W. Breaux from Olin, and J. L. Wood, consultant, for their valuable suggestions. A special thanks to L. S. Casteel of Olin for his encouragement and assistance in writing this paper.

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