

Separation of Sodium Sulfate from Salt-Caustic Brines

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ABSTRACT

In the electrolysis of sodium chloride, sodium sulfate is an undesirable impurity which at one stage or another has to be removed from the system. The precipitation of sodium sulfate can be accomplished by using certain solvents possessing high dielectric constants. Solvents, such as ammonia and methanol, that have a free pair of unshared electrons, are Lewis bases and as such have a coordinating effect on the ions present in solution. The addition of such a solvent to an aqueous solution of sodium chloride and sodium sulfate reduces the dielectric constant of the solvent medium and increases dipole-dipole interaction. This brings about the precipitation of sodium sulfate. The amount of sodium sulfate precipitated depends on its initial concentration and the amount of solvent used.

The solubility of sodium sulfate in the systems: $\text{NaCl-H}_2\text{O-Methanol}$, $\text{NaCl-H}_2\text{O-NH}_3$, $\text{NaCl-NaOH-H}_2\text{O-NH}_3$ has been investigated. Using these data, it is possible to design separation processes to remove sodium sulfate from the system.

INTRODUCTION

Salt brine derived by solution mining for chlorine and caustic soda production is invariably contaminated with impurities, such as, calcium, magnesium, iron and sulfate.

High purity salt can be produced (Theilgard, 1963) by recrystallization with no chemical treatment. However, where chlorine and caustic soda are produced by the diaphragm cell, chemical treatment of the salt brine is necessary. Magnesium and iron are precipitated with a lime slurry or diaphragm cell effluent caustic soda (Kaufman, 1960); calcium is precipitated by soda ash addition. The resulting brine will contain sodium sulfate, which may be treated out with barium chloride, or more commonly, left in solution.

The sulfate can be removed at two places in the electrolytic process: from the brine entering the diaphragm cell or from the cell effluent caustic soda.

Diaphragm cell effluent caustic soda contains a considerable amount of sodium chloride and lesser amounts of sodium sulfate. As cell effluent caustic soda is evaporated, sodium chloride is the first salt to crystallize from solution. This is followed by a mixture of sodium chloride and sodium sulfate.

Sodium sulfate must be removed from the evaporator salt prior to recycle back to the diaphragm cell to prevent a sulfate build-up in the system. Various methods (Vassenberg et al, 1939 and Sharples Corp., 1955) have been devised for this purpose.

This paper deals with the effect of certain solvents, such as methanol and ammonia, on the solubility of sodium sulfate in salt-caustic brines. Having a free pair of unshared electrons, these solvents exhibit a marked coordinating effect on the ions present in solution and are classed as Lewis bases.

Some of the solubility data presented here are from the literature, the rest were obtained during this work. These data are used to show that processes may be designed to separate sodium sulfate either from the diaphragm cell feed solution or from the cell effluent.

THE EFFECT OF SOLVENTS ON THE SOLUBILITY OF SODIUM SULFATE

The removal of sodium sulfate from a brine depends on a host of variables. The most important one, however, is the activity of water, or stating in simple terms, how much "free" water is there to solvate the ions constituting the sodium sulfate molecule. Any tampering with the activity of water, be it evaporation, cooling or addition of another salt to the system will have a corresponding effect on the solubility of sodium sulfate. The reason this happens is the fact that the solubility of sodium sulfate is more water-activity dependent than that of sodium chloride. The cation-anion interaction between sodium and sulfate ions is higher than between sodium and chloride ions mainly by virtue of the charge difference. Higher activities of water are required to keep the sodium sulfate in solution.

A convenient way to reduce the activity of water in solution is to add a solvent which would promote dipole-dipole interaction (both solvent molecules being dipoles) and reduce the activity of water. Since the dielectric constant of the added solvent is lower than that of water, the resulting solvent will have a dielectric constant lower than the original one. This will promote ion-ion interaction and encourage salt precipitation.

The addition of ammonia or methanol to a system, such as $\text{Na}_2\text{SO}_4\text{-NaCl-H}_2\text{O}$, reduces the activity of water and promotes the precipitation of Na_2SO_4 . The fact that Na_2SO_4 precipitates as the anhydrous salt and not a hydrate emphasizes the point that the activity of water is reduced in the presence of such solvents. In addition, solvents, such as ammonia, possess a pair of free electrons and have the ability to coordinate the ions constituting the NaCl molecules. This is particularly well illustrated in the system $\text{KCl-NaCl-NH}_3\text{-H}_2\text{O}$ (Gaska, et al., 1965), where the addition of NH_3 to the system lowers the solubility of KCl , but increases the solubility of sodium chloride. Figure 1 illustrates this effect. In this situation, ammonia can be used very effectively to

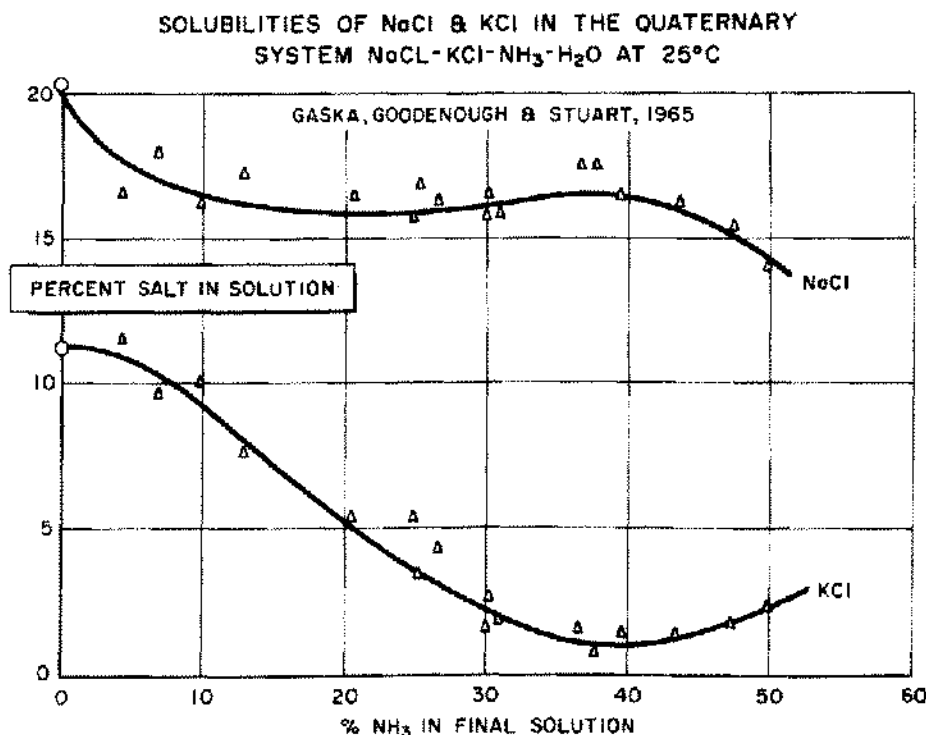


Figure 1

separate KCl from a KCl-NaCl solution. What happens here is that ammonia reduces the activity of water, generally lowering the solubility of salts in the resulting solution, but possessing the capacity to coordinate sodium ions, thereby maintaining the solubility of NaCl.

A similar situation exists in the system: Na_2SO_4 -NaCl- NH_3 - H_2O . Even though the presence of ammonia lowers the activity of water and the dielectric constant of solution, the solubility of NaCl is not affected because of the coordinating effect of NH_3 . The solubility of Na_2SO_4 drops because the new solvent does not possess the energy needed to solvate the ions making up the sodium sulfate molecule and keep them apart. Precipitation of sodium sulfate results.

The presence of NaOH in the system does not change the picture much. Its presence increases the ionic strength of solution, thereby lowering the activity of water. Therefore, in the presence of caustic soda, the resulting solubility of sodium sulfate is even lower than without it.

The use of methanol as a solvent to separate sodium sulfate from a NaCl brine is very similar to the separation accomplished by the use of ammonia. Methanol, however, does not coordinate NaCl to the degree ammonia does, therefore, a slight decrease in the sodium chloride solubility should be expected.

The major variables affecting the solubility of sodium sulfate are the ones that affect the activity of water. Lower temperature, higher ionic strength of solution and higher solvent concentration would favor lower solubility of sodium sulfate.

THE SYSTEM: NaCl - Na_2SO_4 - H_2O

The polythermal solubility data for the system: NaCl - Na_2SO_4 - H_2O are reported in the literature (Purdon and Slater, 1946 and Landolt-Börnstein, 1962). The ternary diagram for the system at the 25°C. isotherm is shown in Fig. 2. The only points of interest in the polythermal data

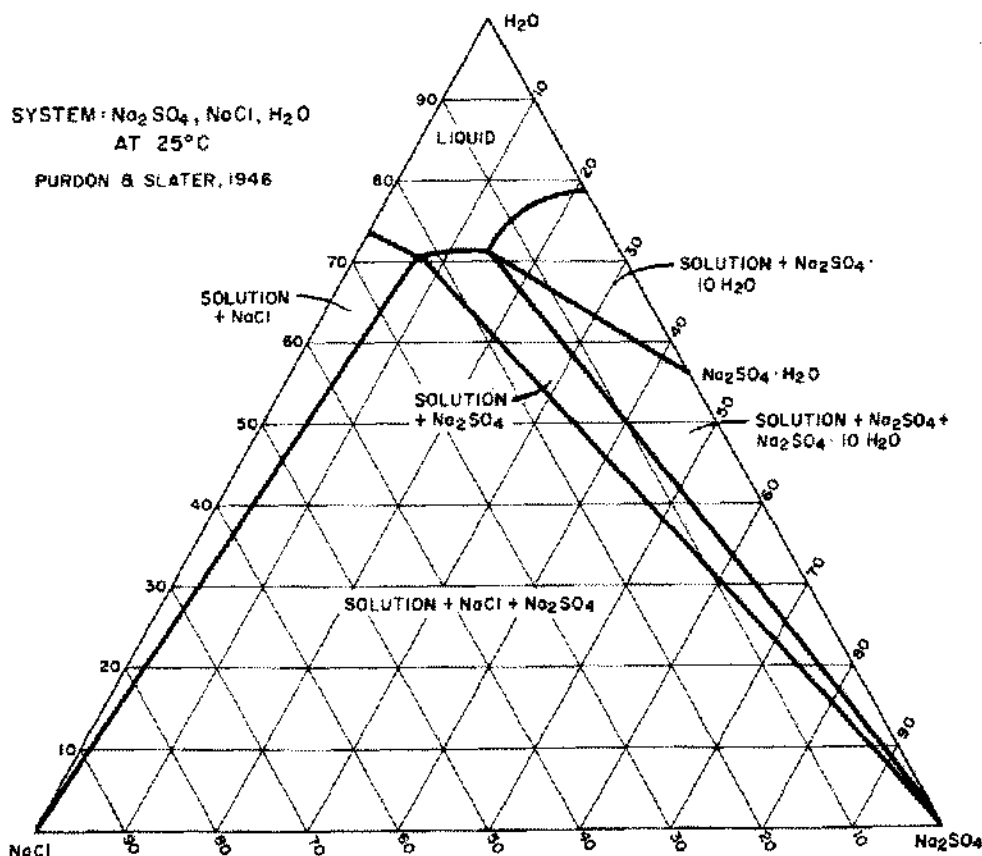


Figure 2

the ternary system are: the transition of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ to NaCl at -2.85°C .; $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ to $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$ at 17.5°C .; and the transition of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ to Na_2SO_4 at 32.5°C .

THE SYSTEM: $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{NH}_3-\text{H}_2\text{O}$

More recently, Nenno and Drozin (Nenno and Drozin, 1955) have published the solubility data for the quaternary system: $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{NH}_3-\text{H}_2\text{O}$ at the 35 and 60°C . isotherms shown in Figs. 3 and 4.

Figure 5 is a replot of their data using the points where the system is mutually saturated in respect to both salts. The above authors claim that with increasing ammonia concentration, the solubility of sodium sulfate becomes independent of temperature. This, however, may not be the case outside these temperature limits. Examination of Fig. 5 shows that at a concentration of $\frac{1}{2}\%$ NH_3 , the solubility of Na_2SO_4 is essentially the same for the two isotherms. The solubility of sodium chloride is slightly temperature and ammonia-concentration dependent. For example, at 60°C . the following $\text{H}_2\text{O}-\text{NaCl}$ weight ratios prevail.

% NH_3	Ratio, $\text{H}_2\text{O}/\text{NaCl}$
10	2.91
15	3.01
17	3.04

Therefore, to be sure that the quaternary system is saturated with respect to sodium chloride in the presence of ammonia, a back projection of the water ternary system should be done.

In the recovery of sodium sulfate from a salt brine, a number of combinations are possible, depending on the composition of the starting solution. Three cases are presented in Fig. 6 where

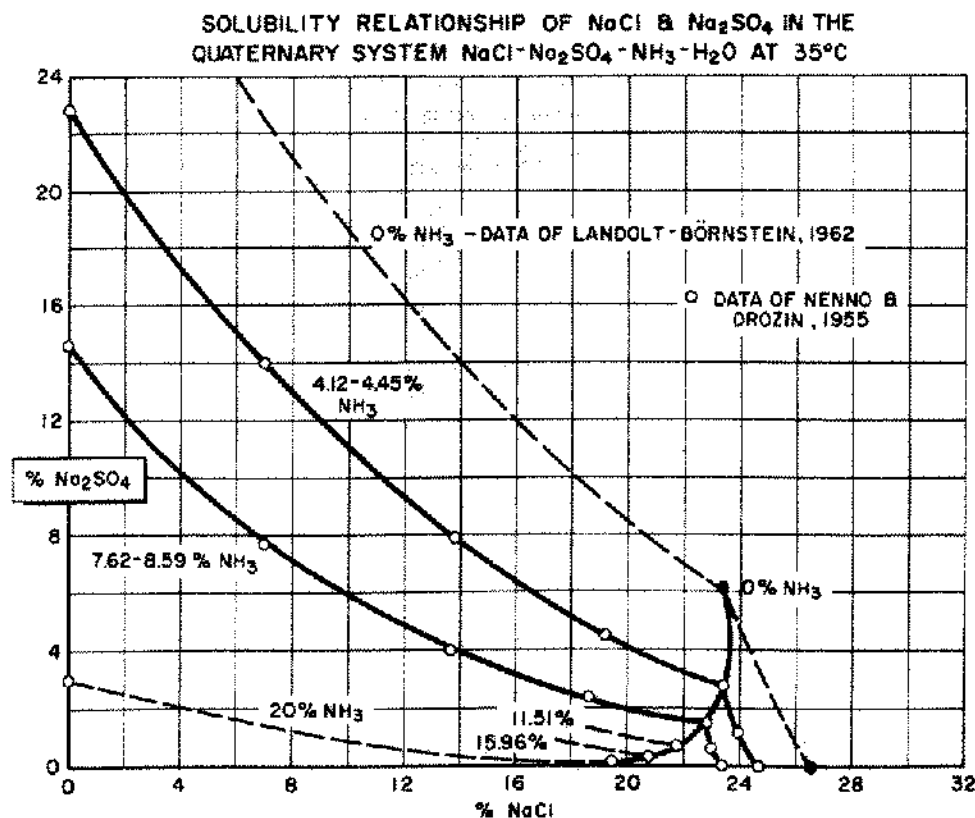


Figure 3

SOLUBILITY RELATIONSHIP IN THE QUATERNARY SYSTEM
 $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{NH}_3-\text{H}_2\text{O}$ AT 60°C

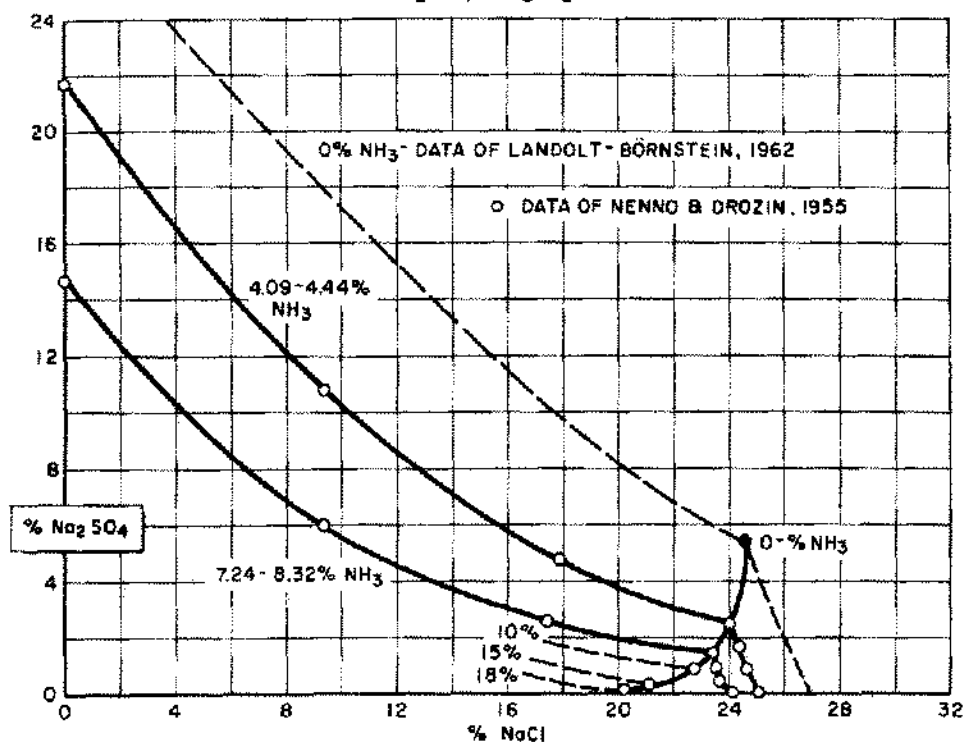


Figure 4

SYSTEM: $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{NH}_3-\text{H}_2\text{O}$ AT 35 & 60°C .
 SYSTEM AT MUTUAL SATURATION

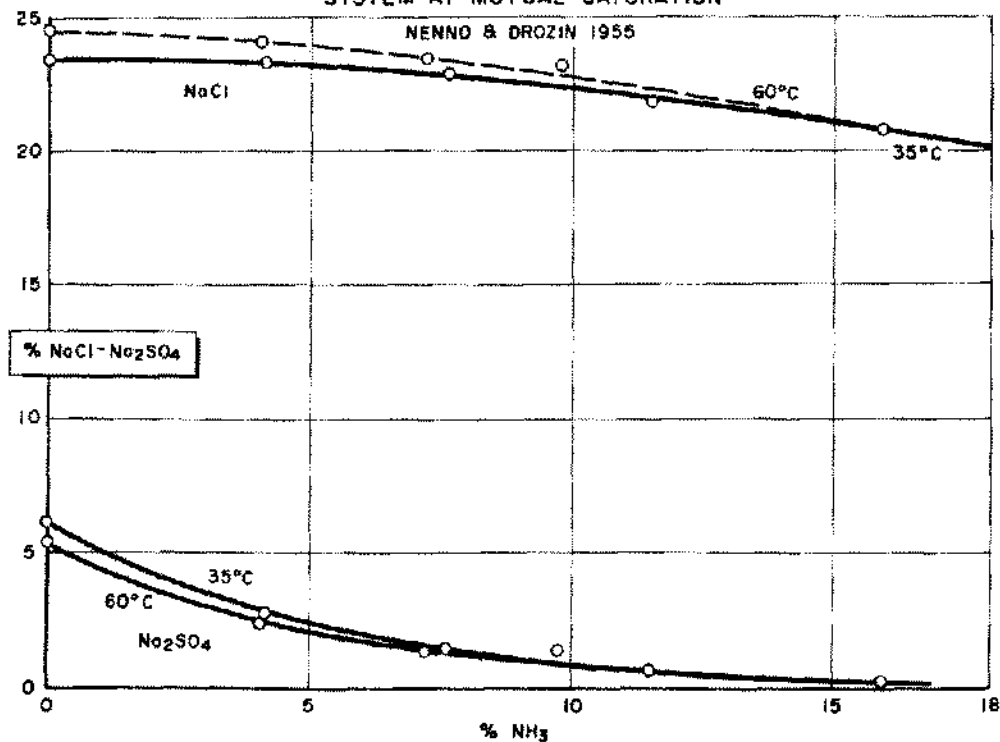


Figure 5

SEPARATION OF Na_2SO_4 FROM CONCENTRATED BRINE SOLUTIONS

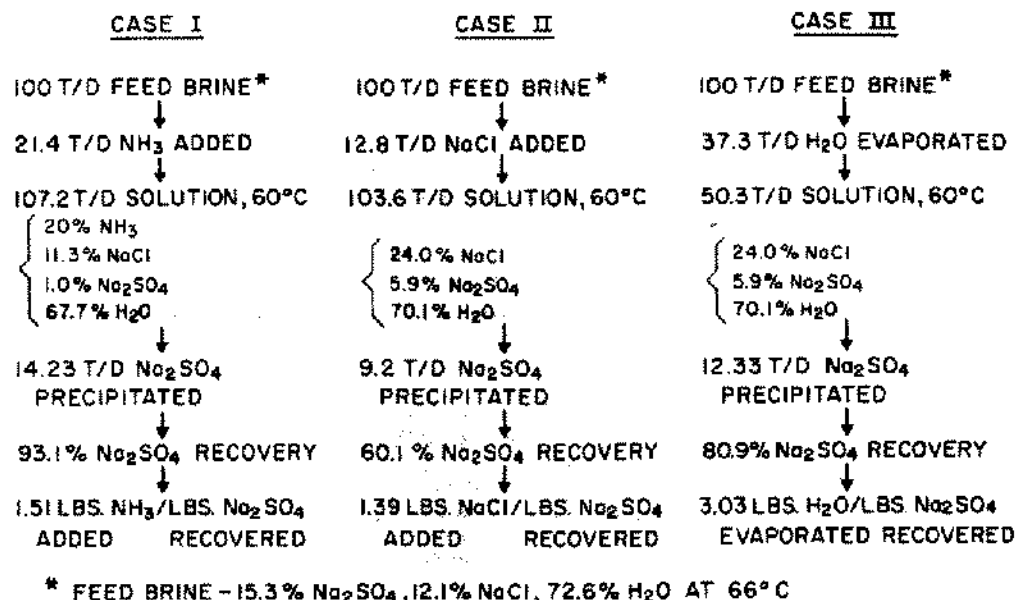


Figure 6

Common feed solution is treated in different manners. The cases used are as follows: (1) ammoniation, no evaporation or salt addition; (2) salt addition, no ammoniation or evaporation; (3) evaporation, no ammoniation or salt addition. The use of ammonia has two distinct advantages: (1) the recovery of sodium sulfate is more efficient; and (2) ammonia used can easily be reused after its distillation from the mother liquor.

THE SYSTEM: $\text{NaOH}-\text{NaCl}-\text{Na}_2\text{SO}_4-\text{NH}_3-\text{H}_2\text{O}$

The quaternary system: $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{NaOH}-\text{H}_2\text{O}$ has been of considerable interest to those companies producing caustic soda, especially by the diaphragm cell method. The polythermal data are not reproduced here for the sake of brevity, but two points are worth noting: the existence of $\text{OH} \cdot \text{H}_2\text{O}$ as a solid phase at a temperature below 60°C.; and, the existence of the triple salt, $\text{Cl} \cdot \text{Na}_2\text{SO}_4 \cdot \text{NaOH}$, which is temperature and concentration dependent.

Laboratory work was performed in examining the influence of ammonia on the quaternary system: $\text{NaOH}-\text{NaCl}-\text{Na}_2\text{SO}_4-\text{H}_2\text{O}$. The purpose of this work was to investigate a system where the activity of water is further affected by the presence of NaOH . A salt-caustic brine containing the following weight percent composition was chosen at random:

68.5% H_2O
 16.5% NaOH
 13.0% NaCl
 2.0% Na_2SO_4
 $t = 60^\circ\text{C}.$

Gaseous ammonia was bubbled into the apparatus shown in Fig. 7, containing a sample of the above salt-caustic brine. The apparatus was weighed before and after ammonia addition to determine the weight of ammonia added. The vessel was agitated and kept in a constant temperature bath until steady-state conditions were reached. A sample was withdrawn from the vessel at the end of each run, by trapping the ammonia solution in a preweighed quantity of standardized HCl ,

APPARATUS FOR EQUILIBRATING AND SAMPLING NaCl-Na₂SO₄-NaOH-NH₃-H₂O SYSTEM UNDER PRESSURE

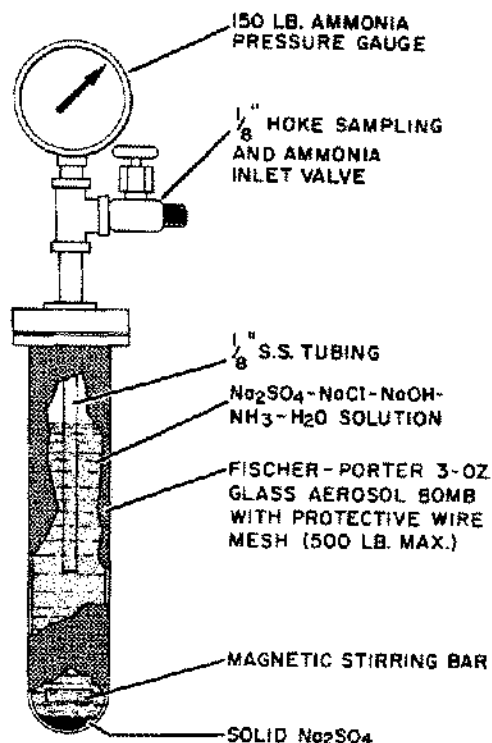


Figure 7

contained in a glass-stoppered weigh-bottle. After determining the net weight of the sample taken, sodium sulfate was determined by titrating the solution with standardized BaCl₂ to the tetrahydroquinone end point. The results of this solubility study are shown in Fig. 8. The total pressure exerted by this system at various ammonia concentrations is shown in Fig. 9.

THE SYSTEM: Na₂SO₄-NaCl-Methanol-H₂O

A partial phase solubility diagram at 25°C. is shown in Fig. 10. The methanol-free system is shown for reference. As in previous cases, the system is always saturated with respect to one salt. In the presence of methanol, the solubility of sodium sulfate is lowered considerably and the solid phase in equilibrium with the solution is anhydrous sodium sulfate and not a hydrate as is the case in a pure aqueous system.

Figure 11 shows some of the data obtained at 0°C. The solubility of sodium sulfate is lowered to concentrations below 1%. It is evident that ammonia is able to suppress the solubility of sodium sulfate much more than does methanol.

PROCESS CONSIDERATIONS

Examining the solubility data of the above systems it is quite evident that the use of solvents such as ammonia or methanol reduces the solubility of sodium sulfate to a very low residual level. Furthermore, the precipitated sodium sulfate is not hydrated and is of relatively high quality. These factors offer enough incentive to utilize such solubility relationships and to incorporate them in sodium sulfate removal and recovery processes.

To illustrate the feasibility of the removal of sodium sulfate from salt-caustic brines, one process will be examined in detail. It is designed to remove sodium sulfate from NaCl-NaOH-H₂O

THE SOLUBILITY OF SODIUM SULFATE AS A FUNCTION OF AMMONIA CONCENTRATION IN THE SYSTEM:
NaCl-NaOH-NH₃-H₂O AT 60° C

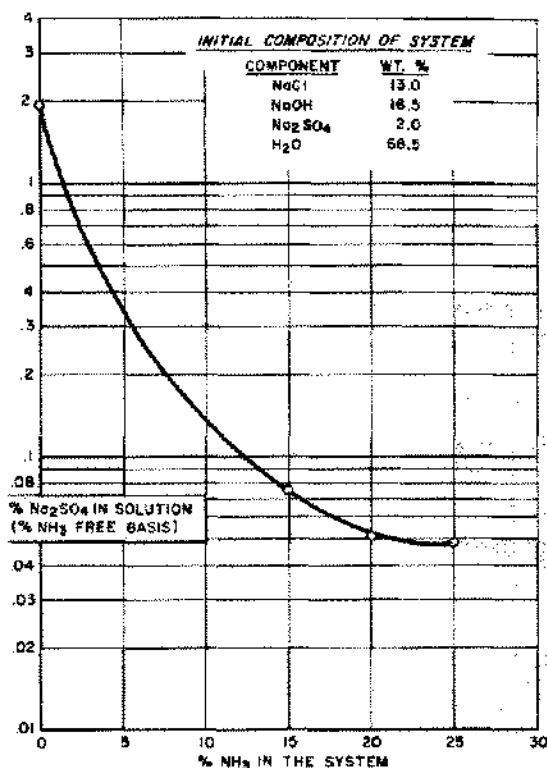


Figure 8

TOTAL PRESSURE IN THE SYSTEM AS A FUNCTION OF AMMONIA CONCENTRATION AT 60° C

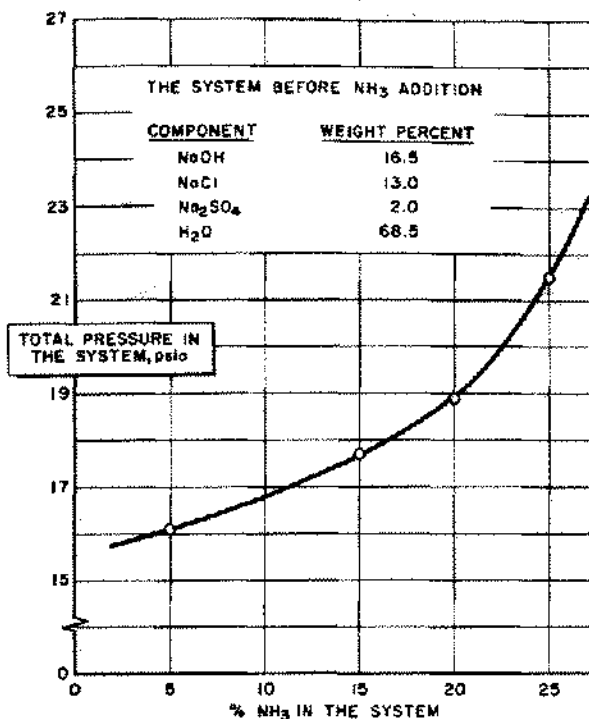


Figure 9

SOLUBILITY RELATIONSHIP IN THE SYSTEM
Na₂SO₄-NaCl-METHANOL-WATER
TEMPERATURE 25° C

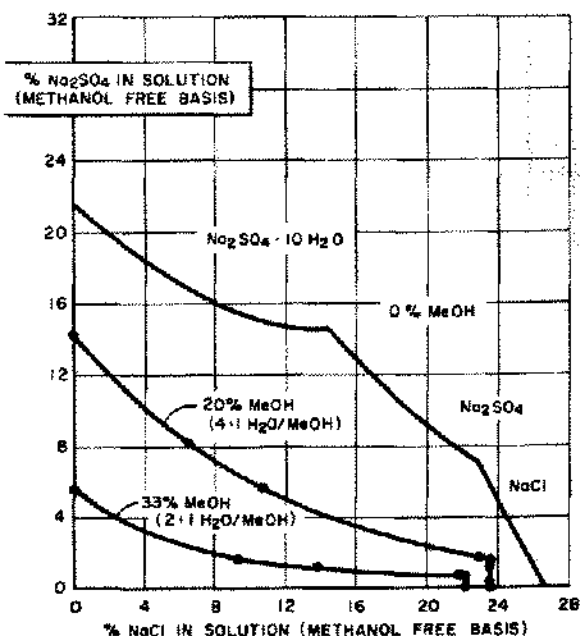


Figure 10

solutions using ammonia as a solvent. The solvent is recovered from the mother liquor in a distillation step and reused in the process on a continuous basis.

Starting with a caustic brine containing 16.5% NaOH, 13.0% NaCl and 2.0% Na₂SO₄, and ammoniating to the 10.6% NH₃ level at 60°C., the solubility of sodium sulfate drops to the 0.126% Na₂SO₄ level on an ammonia-free basis. This represents a 93.7% recovery of sodium sulfate.

Again, it is obvious that a number of combinations are possible for the separation of sodium sulfate, where each system must be examined independently. A flow sheet predicted on the above solubility data is given in Fig. 12. This schematic flow diagram can be broken down into thirteen basic process steps. They are outlined below with the suggested material of construction and design pressure for each piece of equipment shown in parenthesis:

1. Ammonia storage (steel, 300 psig.)
2. Mixing tank, agitated and baffled (steel, 50 psig.)

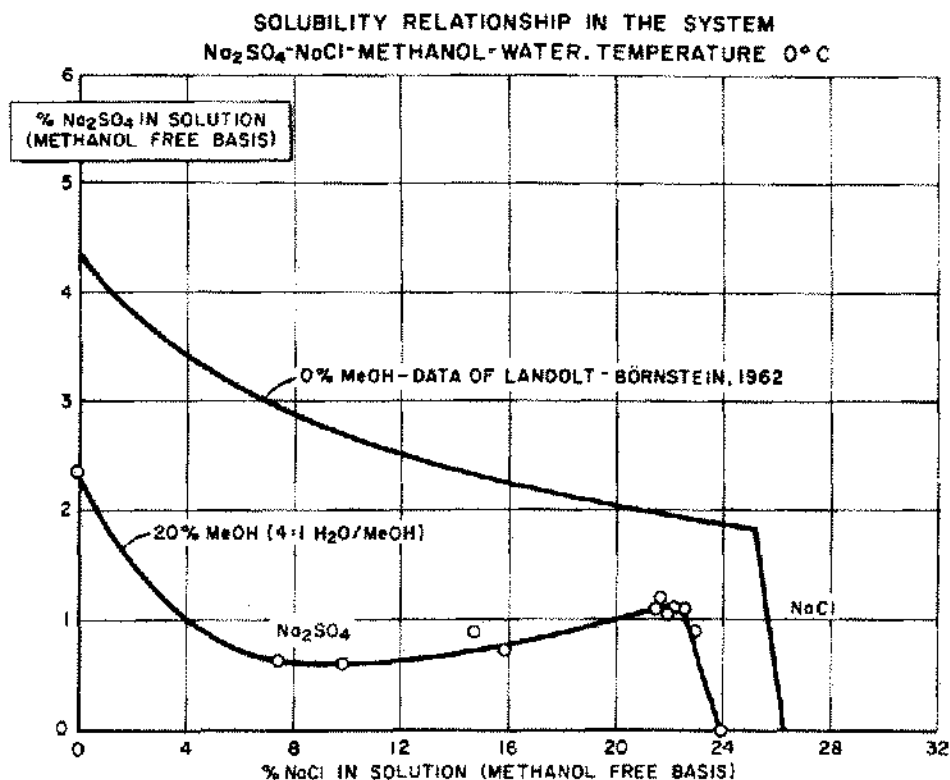


Figure 11

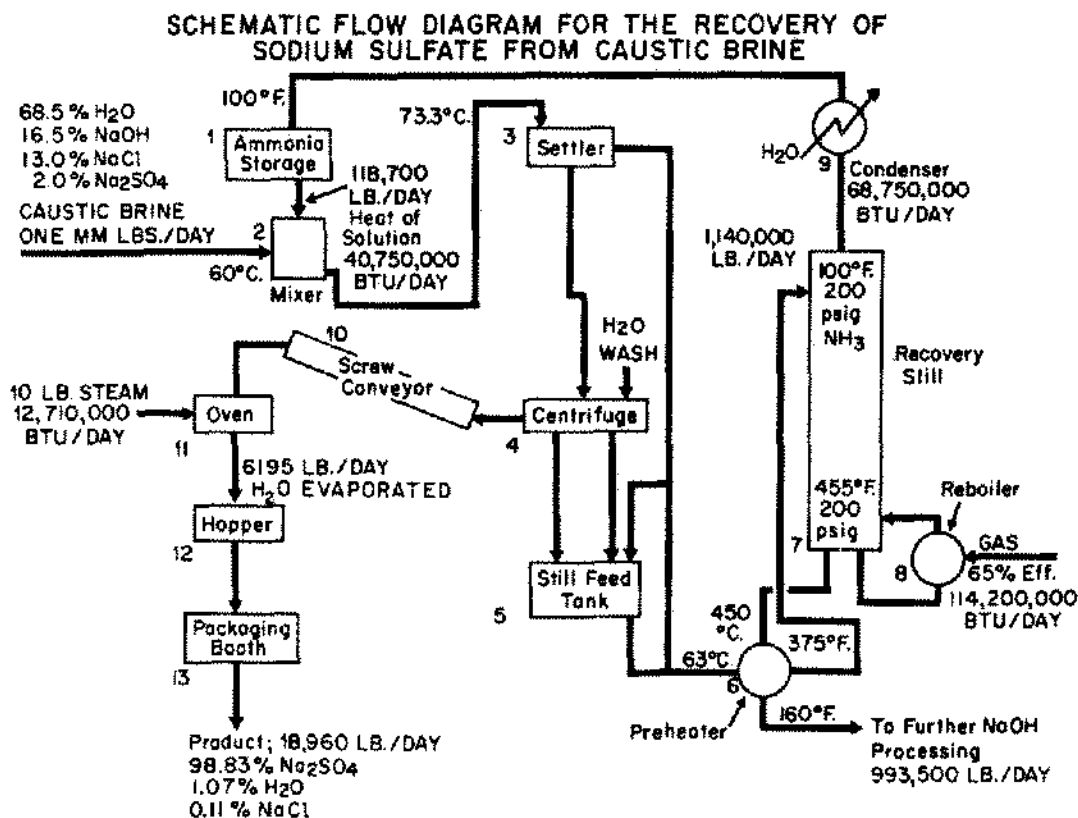


Figure 12

3. Settler, with rake mechanism (steel, 50 psig.)
4. Pressure centrifuge (steel, 50 psig.)
5. Still feed tank (steel, 50 psig.)
6. Preheater (steel)
7. Ammonia recovery still (steel, 300 psig.)
8. Reboiler (steel, 350 psig.)
9. Condenser (steel, 300 psig.)
10. Screw conveyor (steel)
11. Drier (steel)
12. Storage hopper (steel)
13. Product packaging station (steel)

Brine ammoniation can be carried out in conventional equipment where cooling can be applied. This latter step is necessary to remove the heat of solution of ammonia. The residence time in the mixing tank will be dictated by the particle size (Na_2SO_4) desired.

A hindered settler is indicated to concentrate the slurry prior to centrifugation. Since the slurry being filtered is under a slight positive pressure, a pressure centrifuge is needed. A water wash of the filter cake is needed for mother liquor displacement.

The combined wash and mother liquor solution from the filtration step is preheated in a heat exchanger with the still bottoms from the ammonia recovery still.

Heat is supplied to the ammonia recovery still by a fuel gas direct-fired reboiler. Ammonia is condensed overhead by a water-cooled condenser. Condensation of ammonia required lower steam consumption, but higher cooling requirements than compression. In sections of the country where cooling water is at a premium, compression of ammonia would likely be chosen. A 99.9% recovery of ammonia on a recycle basis is possible in such a system.

The washed filter cake from the centrifugation step can be dried in a continuous rotary drier that is vented to a brine scrubber. Ammonia absorbed in the scrubber is recycled to the ammonia recovery still.

Product storage and packaging represent standard equipment.

SUMMARY

Certain water-miscible, polar solvents can have a significant effect on the solubility of sodium sulfate in NaCl and NaCl-NaOH solutions. The addition of solvents, such as ammonia or methanol, cause sodium sulfate to precipitate from salt-caustic brines to a much greater extent than is the case using a NaCl salting-out procedure. Based on the data presented in this paper it is possible to design a process for an efficient separation of sodium sulfate from salt-caustic brines. The use of such a separation process appears to offer some economic advantages and operating flexibilities not possible in other processing schemes.

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