

Recovery of Sodium Sulphate from Sea Bittern

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ABSTRACT

A simple process has been evolved for the recovery of sodium sulphate from sea bittern employing different ternary, quaternary and quinary phase diagrams. It was seen that sea bittern composition during progressive solar evaporation did not fall in either astrakanite or Glauber's salt field at 25° or 0°C. Thus, it was found not possible to recover sodium sulphate directly from bittern. A method has been evolved to obtain an intermediate salt fraction called Sels Mixtes, a mixture of magnesium sulphate and sodium chloride, by tracing the compositions of bittern during evaporation on phase diagrams of reciprocal salt pairs in the system Na^+ , Mg^{++} , Cl^- and SO_4^{--} and on that of quinary oceanic salt system, Na^+ , K^+ , Mg^{++} , Cl^- and SO_4^{--} .

By using the reciprocal salt pairs diagram at 25° and 0°C, a process was evolved to prepare Glauber's salt from Sels Mixtes. Glauber's salt was converted to anhydrous sodium sulphate by employing a polythermal ternary diagram of the system $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{H}_2\text{O}$. The process yields 98 percent pure sodium sulphate from Sels Mixtes with 67 percent recovery of sulphate.

INTRODUCTION

Out of the many ions present in seawater, very few, especially Ca^{++} , Mg^{++} , Na^+ , K^+ , Cl^- , Br^- and SO_4^{--} are concentrated to a level which permits their economic recovery in the form of different salts. In solution they form a very complex multicomponent system governed by the Phase Rule. Their concentrations are such that after the crystallization of calcium salts, no other salt becomes saturated until most of the sodium chloride is crystallized. However, at the stage of 29.5° Be' density, the concentration of the remaining ions is increased to such an extent that the adhering mother liquor imparts an impurity of magnesium salts to the product, common salt. Hence, the mother liquor, called bittern, is considered as a waste material and is discarded. Various authors (Mehta, 1976; Fernandez-Lozano, 1974) have given figures for the quantities of chemicals which can be recovered from bittern, in relation to the salt produced. This loss of bittern, therefore, assumes a great importance in these days of dwindling mineral resources. Processes have been reported to recover potash salts (Talimadge et al.,

1964) and epsomite (Fernandez-Lozano, 1974) from bittern. The attempt is made here to develop a technology by employing phase diagrams for the production of sodium sulphate from bittern. This product has many industrial uses and great demand.

THE PHASE RULE APPLICATIONS

Evaporation of bittern. The bittern at 29.5° Be' constitutes a quinary system comprised of Na^+ , K^+ , Mg^{++} , Cl^- and SO_4^{--} . However, during progressive solar evaporation of bittern, the following two reciprocal salt pairs play an important role:



When seawater is evaporated, potassium ion remains unsaturated between 25.5° and 34° Be'. The concentration of

potassium ion during this stage is so low that it has no major effect as it follows the course of evaporation according to the former reciprocal salt pair. After that, potassium ion reaches saturation to form a quinary system. Because sodium ion forms no double compounds in the present case but is present instead as a solid phase in the form of sodium chloride, the quinary system may be represented by the latter reciprocal salt pair saturated with sodium chloride.

The equilibrium data of the reciprocal salt systems and quinary systems at different temperatures are reported in the literature (International Critical Tables, 1928). Solubility data for the aqueous system Na^+ , Mg^{++} , Cl^- and SO_4^{--} at 25°C and 0°C have been plotted by Jänecke's method superimposed on each other as shown in Figure 1. The quinary system at 25°C is represented by three ions K_2^{++} , Mg^{++} and SO_4^{--} and plotted on triangular coordinates as given in Figure 2.

The composition of bittern at 29.5° Be' falls at point P in Figure 1. This point lies in the sodium chloride field at

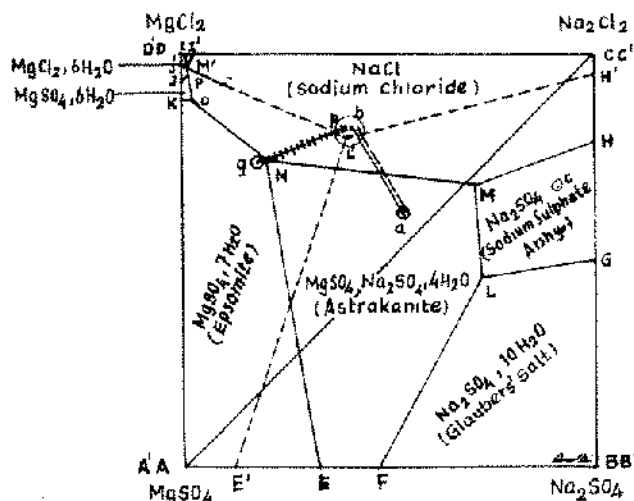


Figure 1. Crystallization of crude salt and Glauber's salt shown on a Jänecke diagram for the system $\text{Na}^+ - \text{Mg}^{++} - \text{Cl}^- - \text{SO}_4^{--} - \text{H}_2\text{O}$. Isotherm at 0°C = -----; isotherm at 25°C = _____.

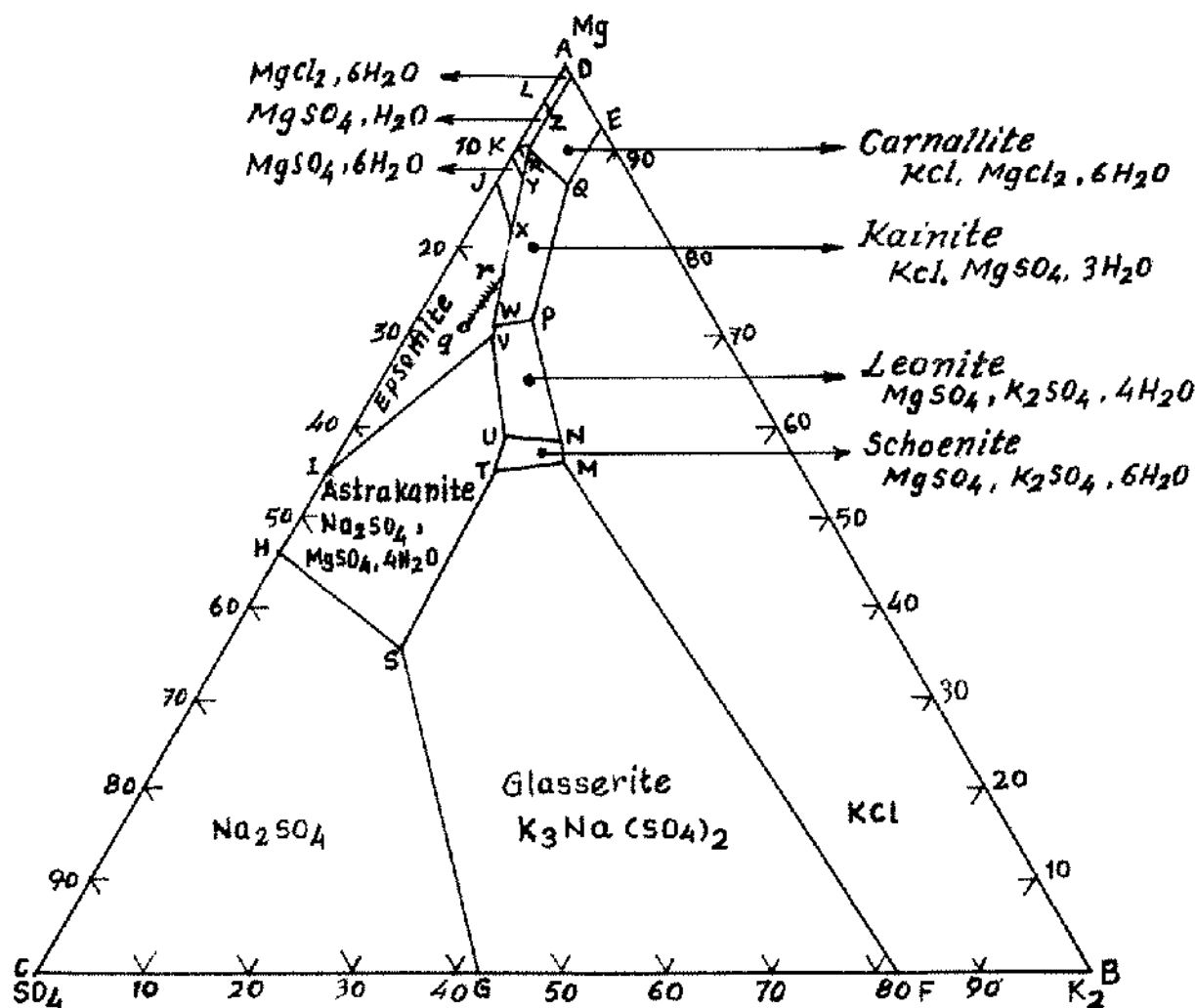


Figure 2. Crystallization of Seles Mixtes shown on a triangular diagram for the system $[\text{Na}^+, \text{K}^+, \text{Mg}^{++}][\text{Cl}^-, \text{SO}_4^{--}] \text{H}_2\text{O}$ at 25°C .

25°C as well as at 0°C. Thus, the composition represented by P on isothermal evaporation at 25°C traverses a path away from the Na_2Cl_2 corner in the sodium chloride field reaching Q when magnesium sulphate saturates. Hence, from P to Q the bittern obtained at any stage during the course of isothermal evaporation between P and Q does not fall into the Glauber's salt field either at 25°C or at 0°C but it falls in epsom salt field at 0°C. Consequently, if the bittern is chilled (once concentrated by isothermal evaporation), it yields only epsom salt (Fernandez-Lozano, 1974). It is not possible to produce sodium sulphate by chilling the bittern of any density to 0°C.

Removing the crystallized sodium chloride and evaporating the bittern beyond Q would give a mixture of epsom salt and sodium chloride along the line N-O (Figure 1). However, as the potassium ion approaches saturation at this stage, the path has to be traced on a diagram of the quinary system (Figure 2) in which the bittern composition also falls in the epsom salt field. It reaches R on further evaporation, during which a mixture of epsom salt and sodium chloride called 'Sels Mixtes' is obtained. On reaching R, kainite starts crystallizing along with epsom salt and sodium chloride. The composition of the bittern moves in the direction of rXY. The mixture obtained is mixed salt (Bhat, et al., 1965). It can be processed for potash recovery (Seshadri, et al., 1970).

Recovery of sodium sulphate from Sels Mixtes. The composition of a mixture of salts obtained between points Q and R falls on the diagonal $\text{Na}_2\text{Cl}_2 - \text{MgSO}_4$ (Figure 1). A portion of it crosses the Astrakanite field at 25°C, but nearly all of it crosses the Glauber's salt field at 0°C. A solution of such a mixture yields Glauber's salt on chilling. As the Glauber's salt removes the water of crystallization, the composition of the mother liquor moves away from the Na_2SO_4 corner (Figure 1). The dehydration of the Glauber's salt is carried out by considering a ternary system comprised of $\text{Na}_2\text{Cl}_2 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$ represented by the line BC (Figure 1). The Glauber's salt composition represented by Na_2SO_4 corner on addition of sodium chloride moves towards C. Sodium chloride has to be sufficient to bring the composition of the end liquor into the anhydrous sodium sulphate field. The transition temperature of Glauber's salt to anhydrous sodium sulphate is lowered from 32.4°C (point G) to 17.9°C (point F) as is seen in the polythermal diagram of the system: $\text{NaCl} - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$ (Figure 3).

EXPERIMENTAL

Solar evaporation of sea bittern. Laboratory experiments were carried out to systematically collect the different fractions of salt from bittern. The first fraction contains predominantly sodium chloride which crystallizes when the composition of bittern fell in the Sodium chloride field (Fig. 1). The second fraction of the mixture of magnesium

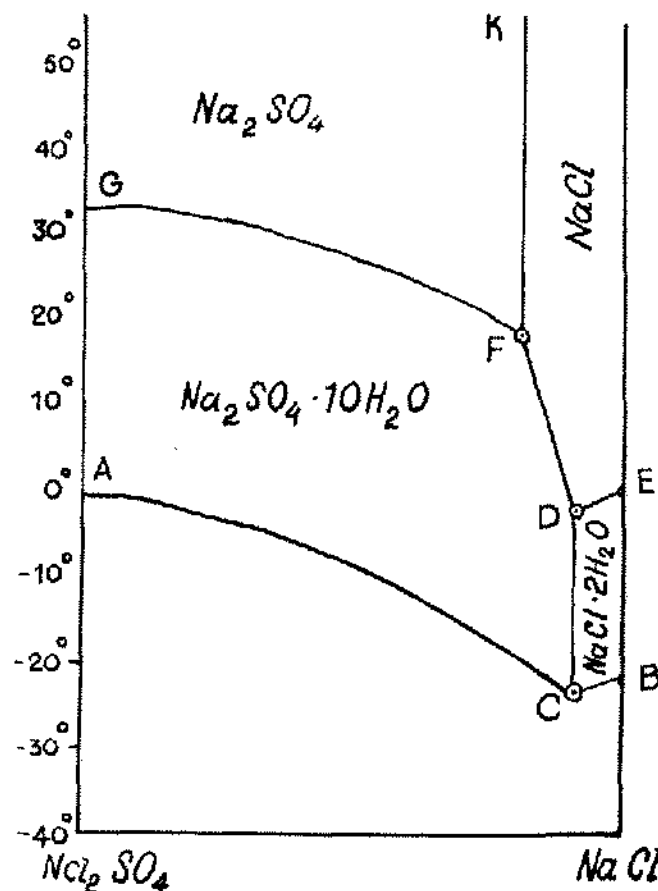


Figure 3. Polythermal diagram of the system $\text{Na}_2\text{SO}_4 - \text{NaCl} - \text{H}_2\text{O}$ at various temperatures.

sulphate and sodium chloride crystallizes when the path of crystallization passed through the epsom salt field (Fig. 2). Definite volumes of 29.5° Be' bittern were solar evaporated in cement pans to obtain quantitative data. The samples of bittern were analyzed for each degree rise in density and the compositions were traced on the phase diagrams to obtain sharp fractions of these salts. At the time of collection, the salt was heaped, allowed to drain and sun-dried for two days. It was then weighed and analyzed.

The compositions of bittern and salt fractions of a typical experiment are given in Tables 1 and 2. The solid salt fraction obtained during bittern evaporation between 29.5° Be' and 34.1° Be' (i.e. points P and Q in Figure 1) contained predominantly sodium chloride and impurities of magnesium sulphate and magnesium chloride from the adhering liquor. This can be termed a crude salt. On further evaporation of bittern between 34.1° Be' and 35.2° Be' (i.e. points Q and R, Figure 2) Sels Mixtes, having a composition of MgSO_4 28.0%, NaCl 39.5%, MgCl_2 2.9% and KCl 2.4% was obtained.

Recovery of sodium sulphate from Sels Mixtes. The process consisted of three stages 1) dissolution of Sels Mixtes and filtration, 2) chilling of Sels Mixtes solution for

TABLE 1
Composition and Volume of Sea Bittern at
Different Densities During Progressive Solar Evaporation

Density 'Be'	Volume in Liters	Point in Fig. 1 X or 2	Composition in M/1000 M H ₂ O			
			MgSO ₄	Na ₂ Cl ₂	MgCl ₂	K ₂ Cl ₂
29.5	1000	P	10.30	23.14	22.92	2.89
30.7	831		11.61	21.06	27.71	3.30
32.2	682		16.82	15.57	38.71	4.63
33.3	626		18.44	14.90	39.20	4.78
34.1	581	Q	20.06	13.85	42.85	4.99
35.2	422	R	17.42	6.70	56.62	5.86

TABLE 2
Compositions of Crude Salt and Sels Mixtes Recovered
During Solar Evaporation of Sea Bittern

Description	Density Range of Recovery	Salt Separated T/1000 T Bittern	Composition g/100 g Wet Basis			
			MgSO ₄	NaCl	MgCl ₂	KCl
Crude Salt	29.5°– 34.1° Be'	81.5	1.6	84.2	2.4	0.4
Sels Mixtes	34.1°– 35.2° Be'	58.4	28.0	39.5	2.9	2.4

TABLE 3
Composition of Solutions During Conversion of
Sels Mixtes to Sodium Sulphate

Description	Point in Fig. 1	Composition in M/1000 M of Water			
		MgSO ₄	Na ₂ Cl ₂	MgCl ₂	Na ₂ SO ₄
Sels Mixtes Solution	A	25.6	36.7	5.0	—
Glauber's Salt Mother Liquor (m.l. 1)	B	10.6	25.6	25.7	—
Dehydration of Mother Liquor (m.l. 2)	C	4.7	40.4	—	14.0

recovery of Glauber's salt and 3) dehydration of Glauber's salt to anhydrous sodium sulphate.

Based on the laboratory experiments, a number of bench scale experiments were made and the results of one typical experiment are given in Tables 3 and 4.

Sels Mixtes was dissolved in water to prepare its solution which was saturated with sodium chloride. The composition of the solution obtained is given in Table 3. It fell at point a (Figure 1). It was then filtered through a filter press. The dissolution efficiency with respect to MgSO₄ was 100 percent.

The Sels Mixtes solution was then chilled to –5°C in the chilling tank under vigorous agitation with stirrers. The de-

cision to chill the Sels Mixtes solution to –5°C was made after various cooling experiments performed during the course of preliminary studies. The product, Glauber's salt, was filtered through a vacuum filter. The efficiency of conversion of MgSO₄ in Sels Mixtes to sodium sulphate at this stage was 72 percent. The composition of the mother liquor 1 (m.l. 1) obtained is given in Table 3 and is represented by point B in Figure 1.

The Glauber's salt was then dehydrated by adding calculated quantity of sodium chloride under uniform stirring and raising the temperature to 50°C. It melted and partly dissolved in its water of crystallization. Anhydrous sodium sulphate was precipitated. The contents were centrifuged and

TABLE 4
Compositions of Glauber's Salt and
Anhydrous Sodium Sulphate Obtained from Sels Mixtes

	Glauber's Salt %	Anhydrous Sodium Sulphate %
Na_2SO_4	39.3	98.3
NaCl	7.5	1.4
MgSO_4	2.4	1.0
R_2O_3	<0.007	<0.007
Iron as Fe	<0.007	<0.007
pH	—	8.3

freed of the adhering liquor by a washing with water in the centrifuge. The composition of the mother liquor 2 (m.l. 2) is given in Table 3 and is represented by point C (Fig. 1). The efficiency of dehydration of Glauber's salt to anhydrous sodium sulphate was 83.4 percent and combined efficiency of dissolution, chilling and dehydration came to 60 percent.

The compositions of Glauber's Salt and anhydrous sodium sulphate are given in Table 4.

The mother liquor 2 contained 10 percent sodium sulphate with reference to input of SO_4^{--} ion in Sels Mixtes taken. It was chilled to 0°C . The efficiency of recovery of sodium sulphate from recycled solution was 75 percent. Thus, the overall efficiency came to 67 percent. The alternate use of this solution is to chill it along with the Sels Mixtes solution.

CONCLUSIONS

Based on these results, a flow sheet, showing operations involved in this process yielding 8 tons per day sodium sulphate technical grade, is given in Figure 4. The process has great potential because it recovers sulphate content in the form of an industrially useful product sodium sulphate from bittern and leaves mother liquor for the recovery of potash by known methods.

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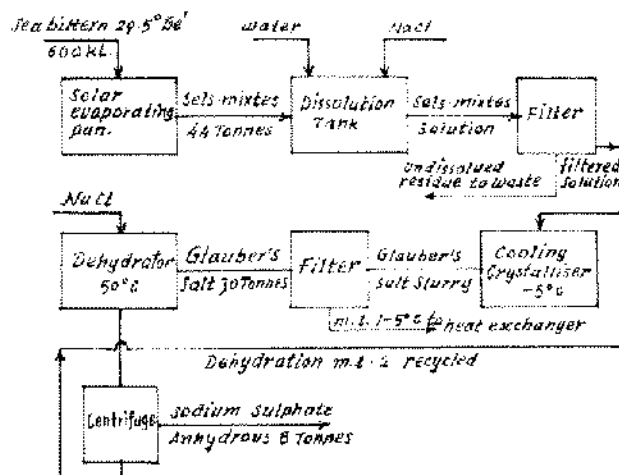


Figure 4. Flow diagram for the process of conversion of Sels Mixtes to sodium sulphate.

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