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Chemicals from Inland Solid Bittern by the Cyclic Process

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ABSTRACT

Inland solid bitterns from saline lakes are utilised in the development of an integrated process leading to the recovery of useful chemicals. The application of relevant phase equilibria systems at varying temperature cycles, differences in the solubility data relationship and recycling of mother liquors in the process have contributed towards a higher yield and purity of the product. The process realised an overall 70–80% yield in terms of sodium sulphate, sodium nitrate and potassium nitrate.

INTRODUCTION

Sambhar and Didwana are the major saline inland lakes of India. They cover an approximate area around 234 and 25.6 km^2, respectively, in the desert belt of Rajasthan as reported by Mataprasad (1950). Sambhar town is about 80 km away from Jaipur, the State Capital, and is linked by a railway line.

Sea water and similar brines of world famous saline lakes contain potassium chloride as one of the constituents along with other oceanic salts. However, the inland brines of Rajasthan are unique in having a single cation of sodium and all other anions as chloride, sulphate, carbonate and bicarbonate.

Statistical data published by the Salt Department (1990) indicate that more than 1×10^5 t of common salt is recovered every season from the regions of the saline lakes. Aggarwal (1951) has reported that for many decades a huge quantity of 1.2554–1.261 specific gravity bittern is discarded to nearby areas. Bitterns that evaporate in a severely hot climate into solar evaporites are referred as "inland solid bittern". In fact, it is a concentrated natural source of sodium sulphate as compared with bitterns. An average composition of the inland brine bittern and solid bittern is presented in Table 1.

Seshadri and Buch (1959a) and Gohil and coworkers (1990) have studied the recovery of sodium sulphate from inland bitterns and evaporites. In the present study an integrated approach is investigated for processing solid bittern into useful chemicals such as sodium sulphate, sodium nitrate and potassium nitrate. The main stages of the integrated process are as follows:

1. Isolation of a sodium sulphate enriched solid phase and its processing to anhydrous sodium sulphate and sodium nitrate.
2. Processing of sodium nitrate enriched mother liquor to potassium nitrate.

TABLE 1

Composition of inland brine, bittern and solid bittern

Particulars	Sambhar brine	Didwana brine	Bittern	Solid bittern
Specific gravity	1.1983	1.1885	1.261	–
Composition %	By vol.	By vol.	By vol.	By weight
Constituents				
NaCl	18.3	16.1	25.9	49.5
Na_2SO_4	5.4	7.6	9.1	35.3
Na_2CO_3*	1.4	1.0	4.9	4.5
Insolubles	–	–	–	3.2

*Bicarbonate is expressed as carbonate.

METHODS AND DISCUSSION

The carbonates, because of their inherently low concentration, are not accounted for in the present study. The relevant phase systems employed at different stages in the process are summarized and presented along with experimental data of the typical experiment.

Sodium sulphate enriched solid phase

System NaCl–Na_2SO_4–H_2O at 30 and 50°C

The comparative values of the brines as given by Siedell (1953) are presented in Table 2. A distinct difference in the solubility of sodium chloride is observed in the brines at 30 and 50°C. Accordingly, sodium chloride dissolves nearly three times more than sodium sulphate on reaching the equilibrium phase of the system at 50°C, as the solubility of sodium sulphate is decreased to minimum.

In the present study, the two raw materials in terms of inland brine specific gravity 1.1866 and solid bittern were treated in the required ratios and stirred continuously for 3 h at 50°C to attain an equilibrium phase of the system. The solid phase was centrifuged, washed with a little hot water and collected. Experimental results are presented in Table 3. Several experiments were carried out in a similar manner to generate a sodium sulphate enriched product.

During the prolonged dissolution process every 100 ml of the solution extracted about 10.0 g of sodium chloride on reaching the equilibrium phase at 50°C. It had a liquid phase enriched with sodium chloride and a solid phase enriched with sodium sulphate. The mother liquor, highly enriched with sodium chloride, is utilized in the usual manner for the recovery of common salt.

Mirabilite by the cyclic process

System NaCl–Na_2SO_4–H_2O at 10 and 30°C

The comparative values of two brines given by Siedell (1953) are presented in Table 2. The solubility of sodium chloride progressively increased in the system at 10°C, whereas the corresponding solubility of sodium sulphate remains at an almost constant value. However, the solubility of sodium sulphate at 30°C increased to its maximum value. On the basis of the above data, an optimum concentration of the respective salt is established at a varying temperature, to run the cyclic operation of mother liquor

In the present study, a sodium sulphate enriched solution, the mother liquor from a previous cycle, and water were mixed in the required ratios and stirred uniformly at about 30°C to dissolve the added solid phase as sodium sulphate. The clear filtrate was then cooled to 10±2°C and maintained for about 30 min. The crystallised mirabilite was centrifuged, washed with a little water and collected. The mother liquor was again made up to optimum values and recycled in a similar manner to stock up the material. The experimental results are presented in Table 4.

TABLE 2

System NaCl–Na_2SO_4–H_2O at 10, 30 and 50°C (g/100 g solution)

Temperature in °C					
10°		30°		50°	
NaCl	Na_2SO_4	NaCl	Na_2SO_4	NaCl	Na_2SO_4
26.3	0.0	2.3	26.0	7.8	20.0
23.6	3.3	5.7	25.0	16.3	11.3
17.3	3.1	12.2	16.2	24.1	5.5
13.1	3.3	18.0	9.7	25.4	2.5
3.8	5.8	23.0	6.7	28.8	–
0.0	8.4	26.5	–	–	31.8
–	–	–	29.0	–	–

TABLE 3

Sodium sulphate enriched solid phase

Particulars (Raw material)			Qty. (kg/l)
Inland solid bittern (% by weight)			13.0
NaCl	Na_2SO_4	Na_2CO_3	
49.5	35.3	4.5	
Brine S.G. 1.1866 (% by volume)			75.0
17.7	6.2	2.6	
Sodium sulphate enriched solid phase (% by weight)			5.2
3.5	79.1	0.2	
Mother liquor S.G. 1.2341 (% by volume)			72.0
27.5	7.0	3.5	

TABLE 4

Mirabilite by cyclic process

Particulars (Raw material)			Qty. (kg/l)
Mother liquor S.G. 1.0919 (% by volume)			25.0 + 10.0 (water)
NaCl	Na_2SO_4	Na_2CO_3	
6.5	7.0	0.18	
Sodium sulphate enriched solid phase (% by weight)			5.0
3.5	79.5	0.2	
Mirabilite (% by weight)			10.0
1.0	37.5	–	
Mother liquor S.G. 1.103 (% by volume)			25.0
6.2	6.5	0.2	

Yield of sodium sulphate as enriched phase: 89.0%; as mirabilite: 94.0%; as thenardite 88.0%. Overall yield: 71.0%.

TABLE 5

System $NaCl–NaNO_3–H_2O$ at 25 and 100°C (g/100 g solution)

Temperature in °C			
25°		100°	
NaCl	$NaNO_3$	NaCl	$NaNO_3$
26.0	0.0	28.6	0.0
22.6	9.7	17.6	24.0
18.9	18.8	13.4	33.9
13.3	32.6	8.2	48.7
9.6	36.0	5.6	57.4
3.1	43.7	2.2	60.0
0.0	47.8	0.0	69.7

In the cyclic process, every 100 ml of the solution crystallised 38–40 g of mirabilite. The mother liquor is recycled in the process until the concentration of sodium chloride builds up to an optimum value of 18–20% NaCl by volume, then a fresh mother liquor is taken. A measured volume of water is initially added in the process to supplement the water removed in the formation of decahydrate.

Anhydrous sodium sulphate

A weighed quantity of mirabilite was incongruently dissolved in its water of crystallisation at 50°C. The slurry was uniformly stirred and the thenardite was salted out by adding a calculated ratio of sodium chloride, as also reported by Seshadri and Buch (1959b). The finished product was then analysed as 99.0% Na_2SO_4 by weight.

Sodium nitrate by cyclic process

System $NaCl–NaNO_3–H_2O$ at 25 and 100°C

The comparative values of two brines given by Siedell (1953) are presented in Table 5. Unlike sodium chloride, a marked difference in the solubility of sodium nitrate is evident at the said temperature. A saturated system at 100°C is therefore employed to achieve a controlled dissolution of sodium nitrate and also for separation of the excess sodium chloride. Similarly, the dissolved sodium nitrate is crystallised on cooling the system to room temperature (28°C). The optimum parameters for the relative solubility differences of the two salts have been established to run the mother liquor in a cyclic manner.

Sodium nitrate was produced in the present study according to the known chemical reaction between sodium sulphate and calcium nitrate in an aqueous medium at elevated temperatures. Accordingly, a measured volume of the sodium sulphate stock solution (prepared by dissolution of a sodium sulphate enriched phase) and the mother liquor from a previous cycle were mixed and stirred continuously at above 90°C. A calculated ratio of calcium nitrate slurry (prepared by neutralizing limestone with nitric acid similar to the average composition in the by-product of the nitrophosphate unit) was then added in an equivalent proportion of sulphate ions.

After filtering out gypsum, the clear solution was concentrated to the desired volume and again hot filtered to remove the separated sodium chloride and residual gypsum. The saturated brine was later cooled to room temperature (28°C) to crystallise sodium nitrate. The product was centrifuged, washed free of adhering mother liquor and collected. The mother liquor was recycled in a similar manner to stock up the material. The experimental results are presented in Table 6.

It is observed that the precipitated gypsum is coarse, presumably because formation of bassanite ($CaSO_4·0.5H_2O$) produced rapid filtration and later hot water washing of the gypsum cake. The saturated solution is normally evaporated a little below the volume mark and is again made up with water to unsaturate the brine for sodium chloride and calcium sulphate, thereby preventing its separation along with the product when cooled to room temperature (28°C). Experimental data indicated that every 100 ml of the saturated solution crystallised 22–25 g of sodium nitrate in the cyclic process. The relative concentration of about 3–5% $Ca(NO_3)_2$ by volume in excess of stoichiometry is maintained in the mother liquor to ensure a total desulphatization of the system.

Technical grade sodium nitrate

The product obtained was crystallised from a hot saturated solution based on solubility differences at 30 and 90°C, as given by Siedell (1953). The mother liquor was recycled in the process until the concentration of sodium chloride built up to 2.0% NaCl by volume. The finished product then analysed as 99.3% $NaNO_3$ by weight.

Potassium nitrate by cyclic process

Phase system Cl^-, NO_3^-, Na^+, K^+ at 25 and 100°C

Findlay (1951) studied the chemical reaction to produce nitrate based on the phase system in aqueous media. The invariant values of the two phase systems are given in the International Critical Tables (Washburn, 1928) and are graphically plotted in Figs. 1 and 2.

The relevant points of the saturated phase system

TABLE 6
Sodium nitrate by cyclic process

Particulars (Raw material)								Qty. (kg/l)
Mother liquor S.G. 1.3943 (% by volume)								20.0
	NaCl	Na_2SO_4	Na_2CO_3	$Ca(NO_3)_2$	$NaNO_3$	$CaSO_4$	$CaSO_3$	
	13.0	–	–	5.0	41.2	0.8	–	
Sodium sulphate stock solution S.G. 1.1600 (% by volume)								30.0
	1.0	17.8	0.82	–	–	–	–	
Calcium nitrate slurry S.G. 1.5431 (% by volume)								7.8
	–	–	–	80.0	–	–	–	
Gypsum (per cent by weight)								7.3
	2.0	–	–		2.0	70.1	1.24	
Desulphated solution S.G. 1.2064 (% by volume)								58.5
	5.2	–	–	1.7	20.0	0.86	–	
Residue (% by weight)								0.2
	56.0	–	–	–	6.5	10.0	–	
Product sodium nitrate (% by weight)								6.4
	0.5	–	–	–	95.2	–	–	
Mother liquor S.G. 1.4168 (% by volume)								20.0
	13.2	–	–	5.0	41.2	0.8	–	

Yield of sodium nitrate = 93.9%. Overall yield 84.0%.

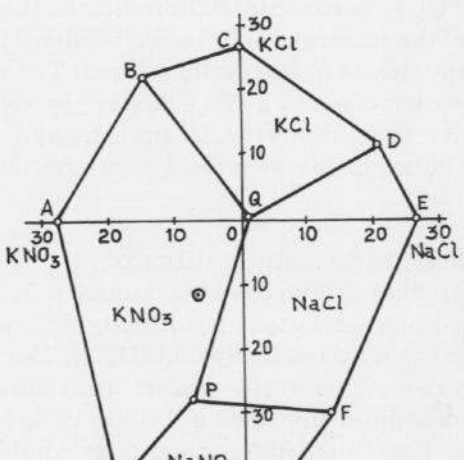

Fig. 1. System Cl^-, NO_3^-, Na^+ and K^+ at 25°C (g/100 g solution).

falling in the respective fields PFEDQ at 100°C and AQPH at 25°C indicate solid phases as sodium chloride and potassium nitrate in the brine. Accordingly, the optimum parameters are established to run the cyclic concentration of the mother liquor.

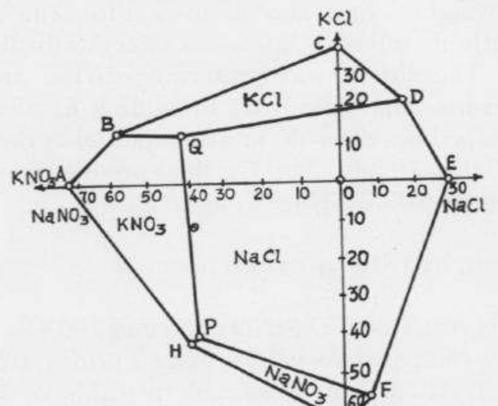

Fig. 2. System Cl^-, NO_3^-, Na^+ and K^+ at 100°C (g/100 g solution).

In the present study, a measured volume of the sodium nitrate enriched mother liquor rejected from the recrystallisation phase, the mother liquor from a previous cycle, and water were mixed together in required ratios and the temperature was raised to about 100°C. Potassium chloride was then added to the system in equivalent proportion to the sodium nitrate present in the enriched mother liquor. The clear solution was continuously stirred and concen-

TABLE 7

Potassium nitrate by cyclic process

Particulars (Raw material)				Qty. (kg/l)
Mother liquor S.G. 1.4321 (% by volume)				15.0
KNO_3	$NaNO_3$	NaCl	KCl	
26.6	16.5	15.0	–	
Sodium nitrate enriched mother liquor S.G. 1.3552 (% by volume)				15.0
–	40.8	1.7	–	
Potassium chloride (% by weight)				6.0
–	–	1.0	96.0	
Residue (% by weight)				6.7
3.5	0.5	85.2	–	
Product potassium nitrate (% by weight)				7.5
97.5	–	0.2	–	
Mother liquor S.G. 1.4328 (% by volume)				15.0
27.0	16.9	15.5	–	

Yield of sodium nitrate: 93.5% (on basis of potassium chloride).

trated to the desired volume mark. An identical procedure to that described for the sodium nitrate process was then followed. The experimental results are presented in Table 7. The finished product then analysed as 99.5% KNO_3 by weight.

The respective observed points in the fields at 100 and 25°C are converted into the required values and shown by the 'O' mark in Figs. 1 and 2. Experimental data indicated that every 100 ml of saturated brine crystallised 38–40 g potassium nitrate in the cyclic concentration process as also earlier found by Gohil et al. (1986).

CONCLUSION

According to the projected data, an inland salt works producing 1×10^5 t of common salt per annum would also yield about 38,000 t of inland solid bittern equivalent to 10,000 t of sodium sulphate.

By an integrated process, half of the total sodium sulphate is to be recovered in terms of sodium nitrate and potassium nitrate with an overall production of 5,000 t of sodium sulphate, 7,500 t of sodium nitrate and 2,200 t of potassium nitrate as products of

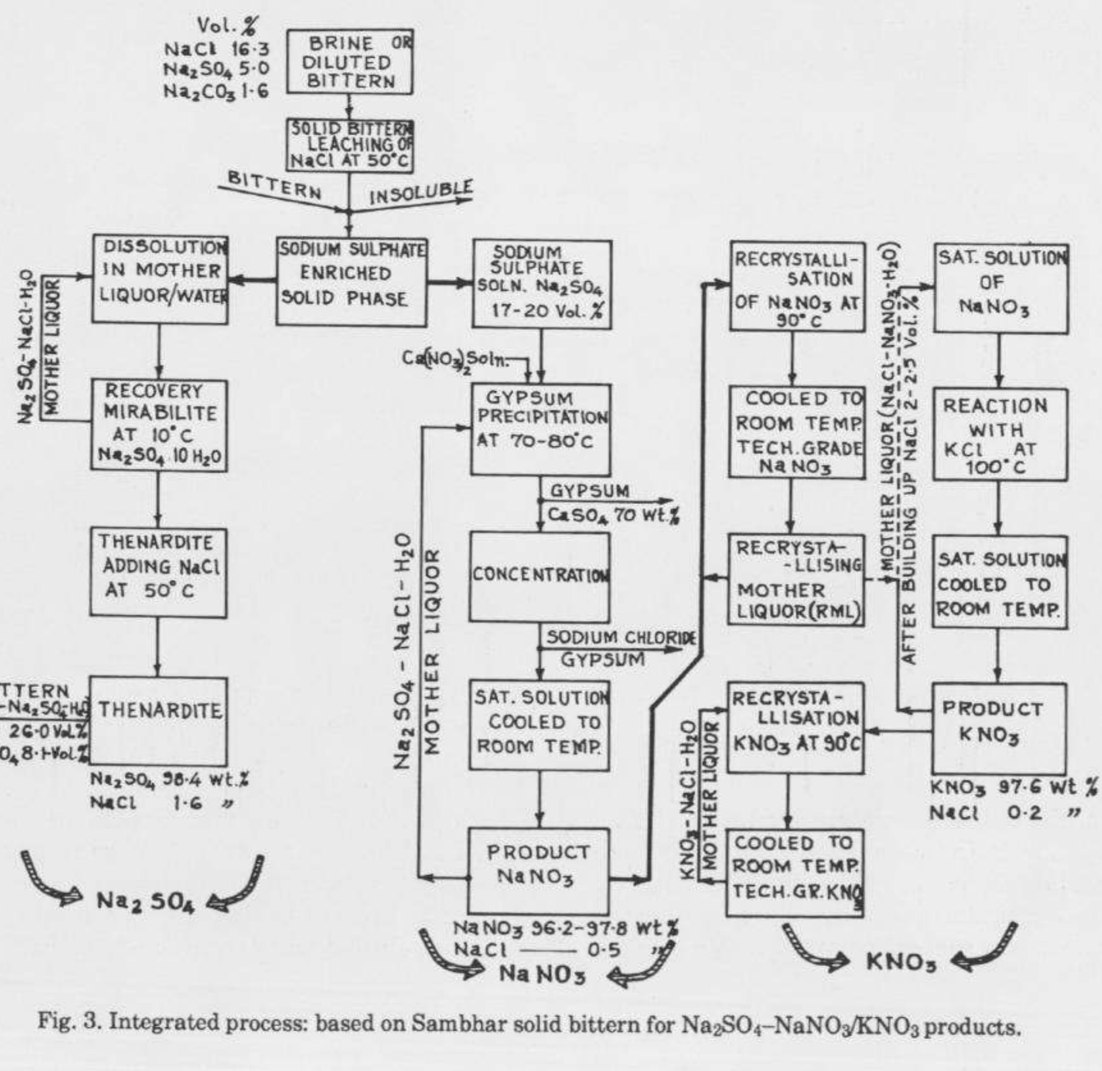

Fig. 3. Integrated process: based on Sambhar solid bittern for Na_2SO_4–$NaNO_3$/KNO_3 products.

greater demand and varied industrial uses. The flow diagram of the integrated process is presented in Fig. 3.

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