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Recovery of sodium chloride, sodium sulphate and sodium carbonate from Sambhar Lake brine–A theoretical study

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Abstract. Sambhar Lake brine contains predominantly sodium chloride, sodium sulphate and sodium carbonate. The mutual solubility relationships existing in the system NaCl–Na_2SO_4–Na_2CO_3–H_2O have been projected isothermally at 0°, 20°, 35° and 100°C, indicating various solid phases formed. The theoretical recoveries have been calculated by plotting the course of change in brine and bittern compositions on the respective phase diagrams. Various steps to recover each of the constituents have been worked out using these diagrams.

Keywords. Burkeite; Glauber's salt; phase diagrams.

1. Introduction

Sodium chloride, sodium sulphate and sodium carbonate are the major salts contained in the brine of Sambhar Lake in India. For an efficient recovery of these salts, knowledge of the phase equilibria existing in the system NaCl–Na_2SO_4–Na_2CO_3–H_2O at different temperatures is essential. The four isothermal projections of the system NaCl–Na_2SO_4–Na_2CO_3–H_2O at 0°, 20°, 35° and 100°C (Teeple 1929; Kobe 1953; Seshadri and Lobo 1957) have been shown in figures 1–4. From these projections, it can be seen that sodium sulphate decahydrate occupies a greater area at lower temperatures and its area reduces as the temperature increases. The sodium sulphate which occurs as the decahydrate ($Na_2SO_4 \cdot 10H_2O$) at 0°C gets converted to anhydrous salt in the presence of sodium chloride as the temperature rises above 17·5°C and hence its area also reduces. Sodium carbonate occurs as the decahydrate ($Na_2CO_3 \cdot 10H_2O$) up to 20°C. It gets converted to monohydrate ($Na_2CO_3 \cdot H_2O$) at higher temperatures. A double salt of sodium sulphate and sodium carbonate called Burkeite (Teeple 1929; Seshadri and Lobo 1957) ($2Na_2SO_4 \cdot Na_2CO_3$) is formed at 20°C and the Burkeite field increases with rise in temperature.

* For correspondence

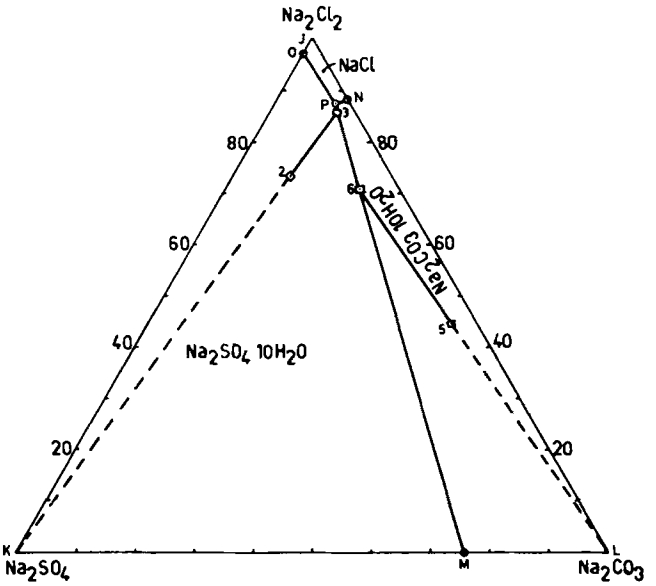

Figure 1. The system NaCl–Na_2SO_4–Na_2CO_3–H_2O at 0°C.

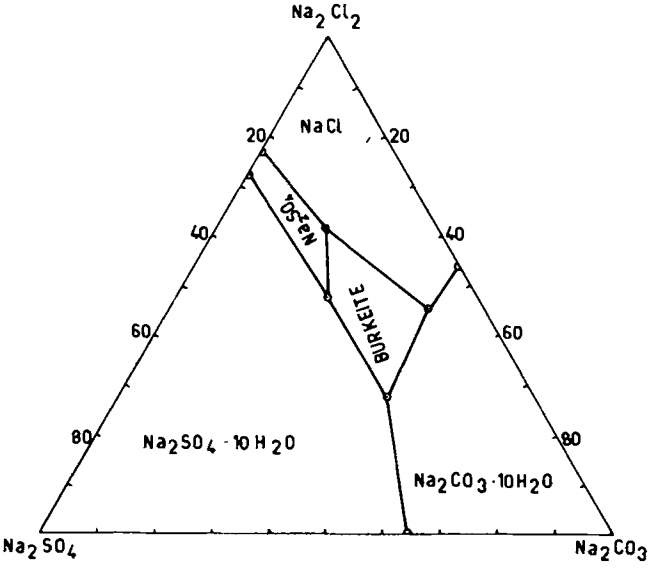

Figure 2. The system NaCl–Na_2SO_4–Na_2CO_3–H_2O at 20°C.

2. Theoretical deductions

All the three constituents, sodium chloride, sodium sulphate and sodium carbonate in Sambhar Lake brine can be recovered in pure form by making use of phase diagrams as explained below.

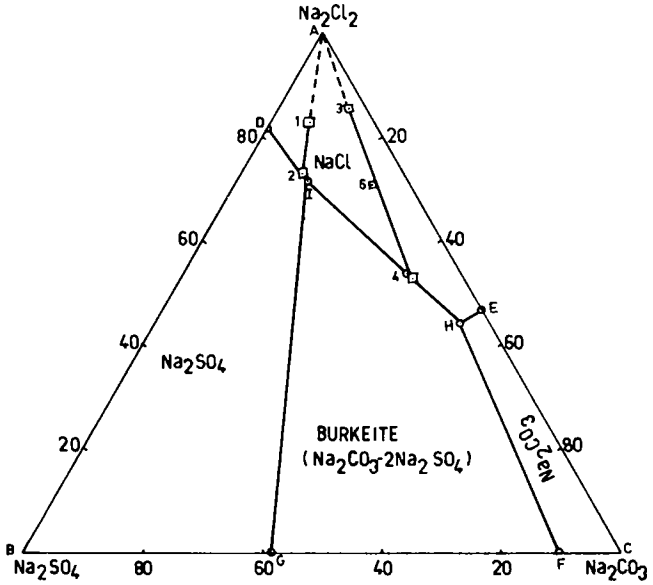

Figure 3. The system $NaCl–Na_2SO_4–Na_2CO_3–H_2O$ at 35°C.

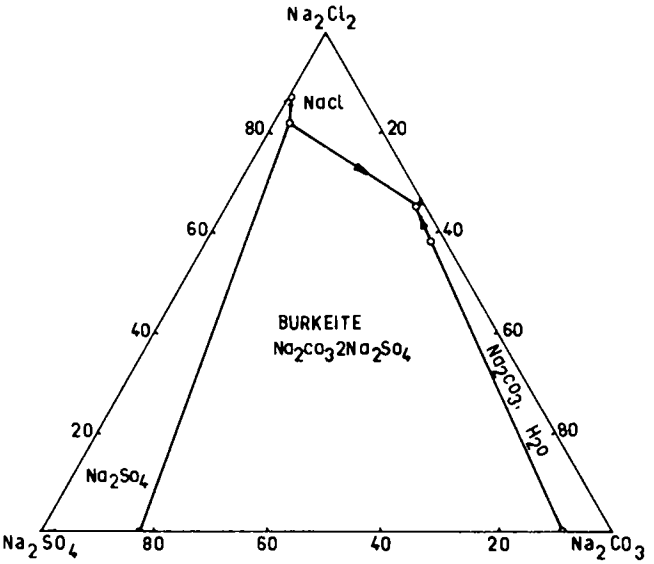

Fig.4. The system $NaCl - Na_2SO_4 - Na_2CO_3 - H_2O$ at 100 °C

Figure 4. The system $NaCl–Na_2SO_4–Na_2CO_3–H_2O$ at 100°C.

Stage 1: Composition of Sambhar brine (given in table 1), falls at point 1 in the sodium chloride field at 35°C, figure 3. On isothermal evaporation at 35°C, the composition of the brine moves along the line drawn by extending the line connecting the NaCl apex and point 1 and the salt separating out is sodium chloride alone till the solution composition reaches the point 2 on the line separating the NaCl and

Table 1. Composition of Sambhar brine.
Degree Baume = 25·6.
Density = 1·214.

Contents	g/100 ml salt soln.	g/100 g salt soln.	g/100 g H_2O	Contents	Mol/ 1000 mol H_2O	Mol% of salts
NaCl	26·32	21·68	29·56	Na_2Cl_2	45·50	82·78
Na_2SO_4	4·21	3·47	4·73	Na_2SO_4	6·00	10·91
Na_2CO_3	1·82	1·50	2·05	Na_2CO_3	3·47	6·31

Table 2. Evaporation of Sambhar brine at ambient temperature.

	Input brine (Point 1) 6070 kg			On evaporation till solution temperature composition reaches point 2 Mother liquor-2	
Contents	In g/100 g solution	Quantity	Quantity separated out	Quantity 3411 kg	In g/100 g
NaCl	21·68	1316	577	739	21·67
Na_2SO_4	3·47	211	—	211	6·18
Na_2CO_3	1·50	91	—	91	2·67
Water	—	4452	2082*	2370	—
Total	—	6070	2659	3411	—

*Water evaporated
Percent recovery of NaCl = (577 × 100)/1316 = 43·84

Na_2SO_4 fields. The calculated composition and the quantity of brine at point 2 and the quantity of sodium chloride separated out are given in (table 2) (Hildebrand 1918; Chemtab *et al* 1966) of sodium chloride is 43·84 per cent that of the input.

Stage 2: Recovery of sodium sulphate decahydrate (Glauber's salt–$Na_2SO_4 \cdot 10H_2O$) by chilling is as follows. The brine of composition 2 falls in the $Na_2SO_4 \cdot 10H_2O$ field at 0°C, figure 1. When this brine is chilled to 0°C, $Na_2SO_4 \cdot 10H_2O$ will separate out and the composition of brine will move along a line drawn by extending the line connecting the Na_2SO_4 apex and point 2 till the composition reaches point 3 on the line separating $Na_2SO_4 \cdot 10H_2O$ and $Na_2CO_3 \cdot 10H_2O$ fields. The calculated composition and the quantity of brine remaining at point 3 and the quantity of sodium sulphate decahydrate formed are given in (table 3) (Hildebrand 1918; Chemtab *et al* 1966). The recovery efficiency of Na_2SO_4 as $Na_2SO_4 \cdot 10H_2O$ is 83·9%. This can be further processed by conventional processes for getting anhydrous sodium sulphate.

Stage 3: Recovery of NaCl by evaporating brine of composition 3 is as follows. The brine of composition 3 falls in the NaCl field at 35°C, figure 3. On the isothermal evaporation at 35°C, the composition of the brine at 3 will move along the line drawn

Table 3. Recovery of $Na_2SO_4 \cdot 10H_2O$ by chilling ML (2) (mother liquor at point 2) at 0°C.

	Input in 3411 kg ML (2)			On chilling to 0°C ML (2)	
Contents	In g/100 g solution	Quantity	Quantity separated	Quantity 3262 kg	In g/100 g solution
NaCl	21·69	739	—	739	22·66
Na_2SO_4	6·18	211	177	34	1·04
Na_2CO_3	2·67	91	—	91	2·79
Water	—	2370	224	2398	
Total	—	3411	401	3262	—
			252*		

*Water condensed.

Input ML (2)	3411 kg
Salt seprated ($Na_2SO_4 \cdot 10H_2O$)	401
	3010
Water condensed	252
	3262

Recovery efficiency of Na_2SO_4 as $(117 \times 100)/211 = 83{\cdot}9\%$

by extending the line joining NaCl and point 3. The salt separating out is pure NaCl till the composition reaches the point 4 on the line separating NaCl and Burkeite field. The calculated composition and the quantity of brine at point 4 and the quantity of NaCl separating out are given in table 4. The recovery efficiency of NaCl in stage 3 is 80·92% and overall efficiency of recovery of NaCl comes to 89·29%.

Stage 4: Recovery of mixture of burkeite, NaCl and sodium carbonate is as follows. The composition at point 4 falls in a triangle NaCl–burkeite–Na_2CO_3 at 35°C, figure 3. When this brine is evaporated, composition will move from point 4 towards the invariant point H where all the three salts co-exist and will dry up completely on evaporation at the invariant point giving the composition of the solid as it was at point 4. Table 4 gives the composition and quantity of this dried-up mixture called solid bittern. This composition comes as NaCl 17·19, Na_2SO_4 4·15 and Na_2CO_3 11·09 g/100 g solution. This differs from that of solid bittern available at Sambhar Lake because of its low Na_2SO_4 content which has been already recovered as Glauber's salt fraction in stage 2. This solid bittern can be further processed for the recovery of Na_2CO_3, Na_2SO_4 and NaCl as given in the stage 5.

Stage 5: A solution saturated with Na_2CO_3 from solid bittern is prepared and Na_2CO_3 is recovered as $Na_2CO_3 \cdot 10H_2O$ by chilling as follows. At invariant point where NaCl, Burkeite and Na_2CO_3 are in equilibrium, the solution composition is 23·2 NaCl, 2·7 Na_2SO_4 and 24·2 Na_2CO_3(g/100 g H_2O). The solid bittern obtained at the end of stage 4 has 141·0 g NaCl, 34·0 g Na_2SO_4 and 91·0 g Na_2CO_3 (table 5). On the basis of 100 g water per 24·2 g of Na_2CO_3, 376 g of water will be required to prepare a saturated solution of Na_2CO_3. The composition of this solution will fall

Table 4. Recovery of NaCl on evaporation of ML (3) at ambient temperature.

Contents	Input ML (3) in 3262 kg		Quantity separated out	On evaportion of ML (3) to ML (4)–output	
	In g/100 g solution	Quantity		Quantity 820 kg	In g/100 g solution
NaCl	22·65	739	598	141	17·19
Na_2SO_4	1·04	34	—	34	4·15
Na_2CO_3	2·79	91	—	91	11·09
Water	—	2398	1844	554	—
Total	—	3262	2442	820	—

Recovery efficiency of NaCl = (598 × 100)/739 = 80·92%
Overall recovery efficiency of NaCl = [(577 + 598) × 100]/(1316) = (1175 × 100)/1316 = 89·29%.

Table 5. Dissolution of solid bittern obtained from ML (4) for getting saturated solution of sodium carbonate to ML (5).

Contents	Input salt	Water added	After stirring and filtering	Composition of the solution (filtrate)		Residual (solid) salt
				Quantity 564 kg	In g/100 g solution	
NaCl	141·0	—		87·0	15·43	54
Na_2SO_4	34·0	—		10·0	1·77	24
Na_2CO_3	91·0	—		91·0	16·13	—
Water	—	376		376·0	—	—
Total	266·0	376		564·0	—	—

at point 5 in figure 1. The residual mixture will be that of NaCl and sodium sulphate (table 5) which can be treated separately (please see stage 6) for recovery of NaCl and Na_2SO_4. The solution composition at point 5, when chilled to 0°C, will move from point 6, figure 1, along the line obtained by extending the line joining Na_2CO_3 apex and point 5. $Na_2CO_3 \cdot 10H_2O$ separates out till the composition reaches from point 5 to point 6 on the boundary line between Na_2CO_3 and $Na_2SO_4 \cdot 10H_2O$. The recovery efficiency as Na_2CO_3 is 72·38% (table 6).

Stage 6: Recovery of sodium chloride from solution at point 6 in stage 5 is as follows. The composition of the solution at point 6 falls in the NaCl field at 35°C diagram, figure 3. If this solution is evaporated, the sodium chloride will be thrown out. This mother liquor 6 together with the residual mixture of NaCl and Na_2SO_4 obtained in table 5 should be recycled with the original Sambhar brine mother liquor 1 for recovery of salts as given in stage 1 to 5. This will improve the recovery efficiency. The anhydrous salts sodium sulphate and sodium carbonate can be obtained by conventional methods.

Table 6. Recovery of $Na_2CO_3 \cdot 10H_2O$ by chilling solution at point 5 to point 6 at 0°C.

Contents	Composition of solution 5 (Input 564 kg)		Quantity separated out	Composition of solution on chilling to 0°C–ML (6)	
	Quantity in kg	In g/100 g solution		Quantity 459 kg	In g/100 g solution
NaCl	87	15·43	—	87	18·95
Na_2SO_4	10	1·77	—	10	2·18
Na_2CO_3	91	16·13	66	25	5·44
Water	376	—	111	—	—
Total	564	—	177	—	—
Water			72*		

*Condensed water 72 kg. Quantity of $Na_2CO_3 \cdot 10H_2O$ separating out 177 kg.

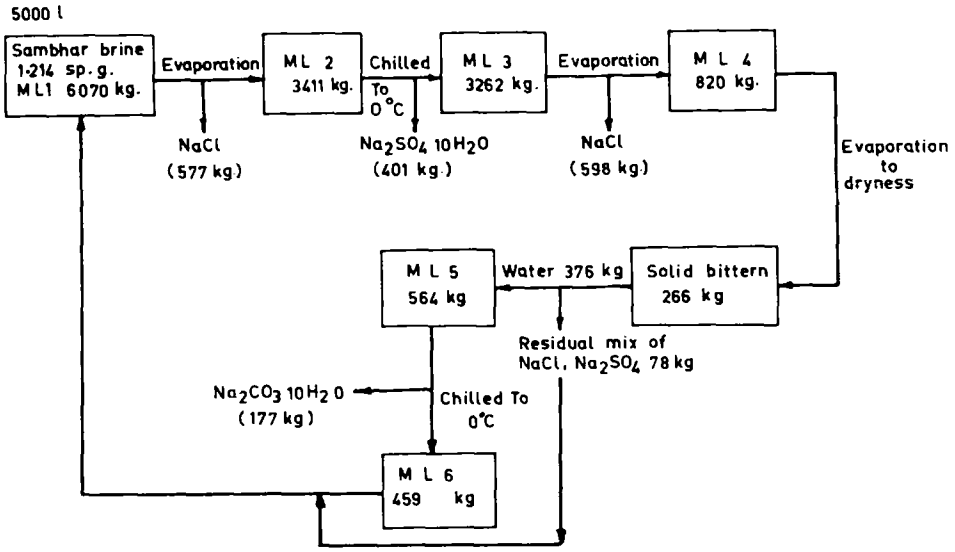

Figure 5. Flow sheet diagram for processing Sambhar Lake brine.

3. Conclusion

From the calculations worked out, to get 100 tonnes of salt 517 tonnes of Sambhar Lake brine will be required and about 7 tonnes of anhydrous sodium sulphate and 5 tonnes of anhydrous sodium carbonate can be obtained. Process diagram is given in figure 5.

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