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Recovery of Potassium Chloride from Subsoil Brine of Kharaghoda (India) by Solar Evaporation

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ABSTRACT

By and large, salt is manufactured in India by solar evaporation. Salt is also manufactured to some extent from subsoil brine obtained by digging wells at Kharaghoda in the Little Rann of Kutch (India). After separation of salt, the resulting liquid — bittern — is obtained containing potassium and magnesium in addition to sodium chloride and very little or no sulphate. The typical analysis of 29.5°Be' bittern was as follows: NaCl 6.2%, KCl 1.8%, $MgSO_4$ 0.85% and $MgCl_2$ 24.5%. When bittern of similar composition was evaporated by solar energy, the evaporite obtained was carnallite along with sodium chloride. Potassium present in the bittern was recovered as carnallite which is a double salt of potassium and magnesium. Phase equilibrium study of the quaternary system K–Mg–Cl–H_2O, saturated with sodium chloride was carried out. It was concluded from the study that the evaporite obtained by solar evaporation of this bittern was carnallite. The system has been found to be similar to that of Dead Sea brine.

From the carnallite obtained by solar evaporation of subsoil bittern potassium chloride was recovered by decomposition with water, as a mixture of potassium chloride and sodium chloride. Fertilizer grade potassium chloride was obtained by cooling the filtered solution. Phase equilibrium study of the ternary system NaCl–KCl–H_2O was carried out. The same solution of sodium chloride and potassium chloride was recycled.

INTRODUCTION

Kharaghoda is an area situated in the Little Rann of Kutch (India). The Rann of Kutch lies between 24°40′ to 26°6′N and 68°48′ to 71°47′E of Greenwich. Aggarwal (1976) has reported that the Rann covers an area of about 23,000 km^2 and is divided into two sections, Greater Rann and Little Rann. There are many salt works in this area, the biggest being at Kharaghoda, situated in Surendranagar district of Gujarat State, India. It is a vast flat, sandy and salty tract only just above sea level, marshy in portions dry in others and covered during dry months with saline efflorescent deposits. During the rains it is covered partly with sea water of high tides and partly with waters discharged by rivers. The Rann is completely flooded in August and September up to 1–1.2 m near the coastline and 2–3 m in the centre of the Rann. An enormous quantity of salt and sand is brought by the rivers. Successive layers of these are found in the sections of wells dug into the Rann. Salt is manufactured from subsoil brine drawn by digging wells in the Rann. The wells are about 6–10 m deep and about 3 m in diameter. The density of the brines varies from 11° to 21°Bé (1.083 to 1.170 S.G.).

TABLE 1

Analysis of bittern from different areas in Kharaghoda

Density °Bé	Composition in g/100 ml			
	KCl	NaCl	$MgCl_2$	$MgSO_4$
29.5	1.80	6.12	24.50	0.85
30.0	1.90	7.12	25.20	0.64
30.2	1.92	6.65	25.35	0.90
29.6	1.89	5.75	25.20	0.22
29.8	1.88	6.13	24.85	0.32
30.0	1.93	6.75	25.40	1.14
30.5	2.02	7.30	24.15	5.60
30.2	1.95	7.00	23.24	5.27

The brine lifted from wells by pump is led by gravity through channels into reservoir-cum-condensers. The brine is led from the reservoir by gravity to crystalliser laid parallel to the reservoir. After the manufacture of common salt, the mother liquor that remains is called 'bittern'. Table 1 shows the analysis of bittern from different areas in Kharaghoda.

This bittern contains 1.8–2% (g/100 ml) potassium chloride and is the raw material for obtaining potassium chloride. As the bittern is a poor source, it was concentrated by solar evaporation to obtain evaporates rich in potassium chloride. Some laboratory and field scale experiments were carried out.

EXPERIMENTAL DESCRIPTION

A 29°Be′ subsoil bittern was kept for solar evaporation. When the density was nearly 32°Bé, the concentrations of NaCl and KCl were determined and, if found to be similar, the solid was removed and bittern was allowed to evaporate further. When the density of bittern was nearly 36°Bé and the concentration of KCl was about 0.5%, the crystallized solid was removed. The experimental results are shown in Tables 2 and 3.

From these experiments it had been found that the solid separated at between 32 and 36°Bé was carnallite containing the impurity of sodium chloride. Based on the result of laboratory experiments, field-scale experiments were carried out on solar evaporation of subsoil bittern at Kharaghoda.

DISCUSSION AND RESULTS

The phase diagram of oceanic salt system NaCl–KCl–$MgCl_2$–H_2O prepared by Jänecke's method as described by Findlay (1951) has been applied for predicting the course of crystallization of salts during solar evaporation of subsoil bittern. As shown in Fig. 1, the concentration of 29/30°Bé falls into the sodium chloride zone shown by point A and, on evaporation, sodium chloride separates. Sodium chloride separation continues until it reaches 32°Bé density. This point is shown by point B which touches the carnallite field. On further evaporation of bittern of 32°Bé, the crystallization path travels on the boundary between the carnallite and NaCl fields and thus carnallite is crystallized with sodium chloride until it reaches point C at the density 37°Bé. The evaporation is discontinued at this point. However, carnallite can separate up to point R but further evaporation would impart bischofite impurity to the carnallite. Thus by solar evaporation of subsoil bittern, potassium chloride was recovered as carnallite with sodium chloride, i.e. mixed salt. This mixed salt is a raw material for recovering potassium chloride.

Mixed salt was decomposed by water to obtain a mixture of potassium chloride and sodium chloride. Carnallite at all temperatures is incongruently saturated because all points on its surface of saturation have a ratio of magnesium chloride to potassium chloride greater than that in the double salt. Therefore when water is added to solid carnallite, magnesium chloride goes into solution leaving behind

TABLE 2

Solar evaporation of bittern

	Bittern 29.5°Bé 10 l		Crude salt 430 g		Bittern 32.2°Bé 7.6 l		Mixed salt 850 g		Bittern 37°Bé 5.15 l	
	%	Total (g)	%	Total (g)	%	Total (g)	%	Total (g)	%	Total (g)
KCl	1.90	190	0.50	2.15	2.50	190	18.10	154.0	0.70	36.1
NaCl	5.20	520	72.20	311.00	2.76	210	19.05	162.0	0.93	46.8
$MgSO_4$	0.92	92	1.60	6.90	1.15	87.4	1.20	10.0	1.52	77.8
$MgCl_2$	24.55	2455	12.42	53.50	31.60	2402	30.50	260.0	40.50	2086.0

Recovery of KCl: 81.0%.

TABLE 3

Solar evaporation of bittern

	Bittern 29.5°Bé 100 l		Crude salt 4.4 kg		Bittern 32°Bé 76.5 l		Mixed salt 8.4 kg		Bittern 36.8°Bé 52.5 l	
	%	Total (kg)	%	Total (kg)	%	Total (kg)	%	Total (kg)	%	Total (kg)
KCl	1.87	1.87	1.87	0.023	2.45	1.87	18.55	1.56	0.67	0.35
NaCl	5.35	5.35	73.80	3.23	2.62	2.00	19.20	1.61	0.80	0.42
$MgSO_4$	0.85	0.85	1.56	0.68	1.05	0.80	1.15	0.09	0.48	0.25
$MgCl_2$	25.30	25.30	13.20	0.58	32.10	24.55	30.80	2.58	41.20	21.63

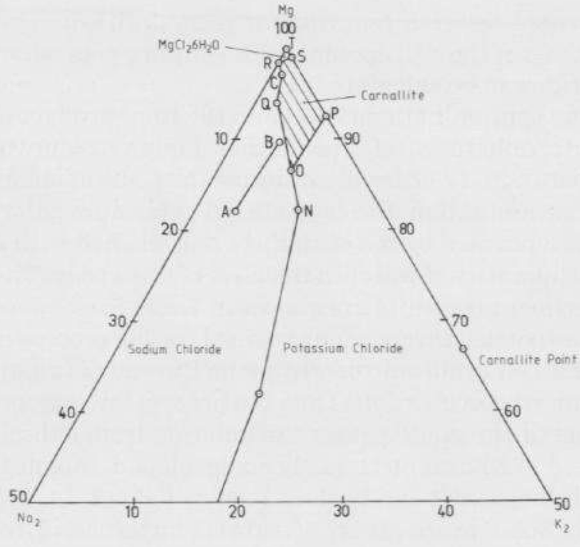

Fig. 1. Janecke's diagram: The system NaCl–KCl–$MgCl_2$–H_2O at 25°C.

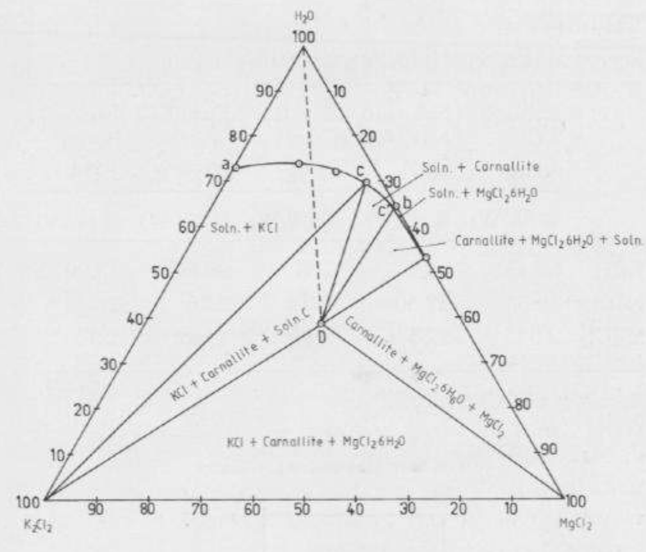

Fig. 2. The system KCl–$MgCl_2$–H_2O at 25°C.

TABLE 4

Bench scale experiment. Decomposition of mixed salt (carnallite) by water

	Mixed salt (Carnallite)	Water	Filtrate	Impure pot. chloride
	50 kg	25 l	45 l	15.5 kg
	% (g/100 g)		% (g/100 ml)	% (g/100 g)
KCl	19.45		3.22	54.44
NaCl	18.53		6.63	40.23
$MgCl_2$	29.48		31.85	2.03
$MgSO_4$	1.10		1.12	Trace

Recovery of KCl: 86.7%.

potassium chloride as solid phase.

The system KCl–$MgCl_2$–H_2O at 25°C is represented in Fig. 2. This diagram was used to calculate water required to decompose carnallite completely. The diagram was also used to calculate the amount of potassium chloride which can be obtained as solid, and the quantity of solution by addition of a calculated quantity of water to the carnallite. Some laboratory experiments with 1 kg and bench-scale experiments with 50 kg mixed salt were carried out. Result of the bench scale experiment is given in Table 4.

Recrystallization of the impure product obtained by decomposition was carried out, based on the ternary system NaCl–KCl–H_2O at 30°C and at boiling point as per the solubilities reported by Seidell (1953). As a basis for crystallization calculation, 30°C isotherm and boiling point isobars were drawn on rectangular co-ordinates as shown in Fig. 3. If impure potassium chloride is mixed with calculated quantity of NaCl–KCl saturated solution at 30°C, the diagram indicates that the solubility of sodium chloride in the NaCl–KCl–H_2O system does not alter with temperature, whereas the solubility of potassium chloride increases with temperature. On boiling the impure potassium chloride with the saturated solution of NaCl–KCl, the composition of NaCl–KCl solution — which is represented by point C at 30°C — in the presence of a sufficient quantity of both the salts, will move on a straight line joining point C and D. The slope of the line C–D increases from 30°C to boiling point, the sodium chloride is

Fig. 3. Polytherm diagram NaCl–KCl–H_2O system at 30°C and boililng point isobar.

TABLE 5

Recrystallization of impure potassium chloride

	Impure KCl 50 kg	Sat. soln. NaCl+KCl 195 l	Residue 22 kg	Pure KCl 26.5 kg	End liquor 193 l
	% (W/W)	% (W/V)	% (W/W)	% (W/W)	% (W/V)
KCl	55.45	13.75	9.63	96.50	13.90
NaCl	40.53	22.50	88.52	2.75	22.75
$MgCl_2$	2.03	1.35	Trace	Trace	1.92

Recovery of KCl: 92.20%.

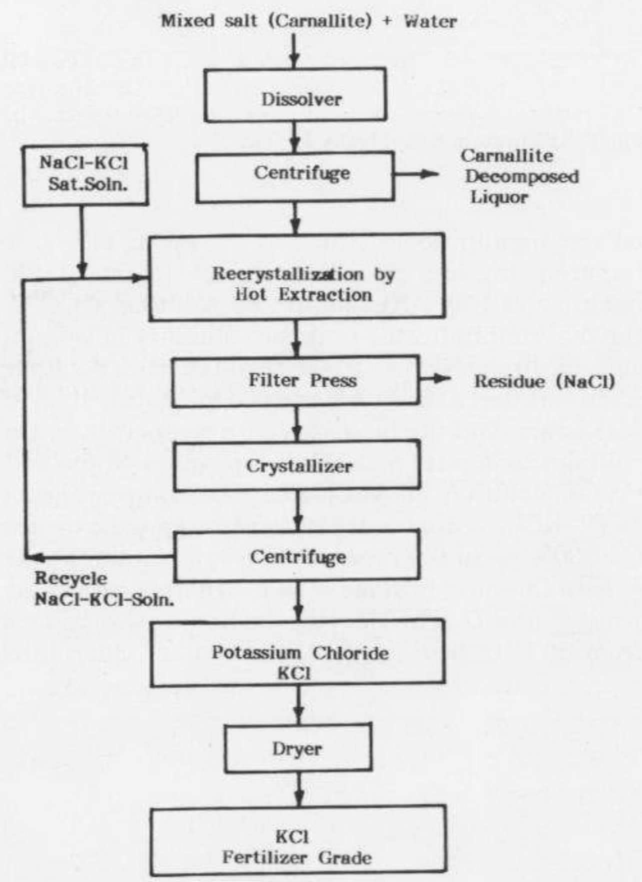

Fig. 4. Flow sheet diagram of the process for the manufacture of potassium chloride.

saturated at lower concentration than at the point C. Hence, potassium chloride will go into solution and sodium chloride is left as residue. Thus, by hot filtration of the solution, the undissolved sodium chloride is removed as filter cake and, on cooling the filtered hot solution to 30°C, the composition of D falls into the KCl field at the lower temperature. Hence, the dissolved potassium chloride crystallizes out as pure potassium chloride from the solution. The amount of saturated solution required for recrystallization on the basis of the KCl content in the impure potassium chloride can be calculated.

Any contamination of NaCl in the final product is due to adherence of the mother liquor or due to evaporation. In order to minimize the sodium chloride contamination, the crystallized potassium chloride is separated by the centrifuge and washed with a small quantity of water in the form of fine spray. The experimental results are shown in Table 5.

The potassium chloride obtained by this process is of fertilizer grade and confirms the Bureau of Indian Standard specification. Thus the process for recovering fertilizer-grade potassium chloride from subsoil bittern of Kharaghoda has been developed. In a nutshell the process can be described as follows:

(1) Solar evaporation of subsoil bittern and recovery of potassium as carnallite.

(2) Decomposition of carnallite with water to obtain impure potassium chloride.

(3) Recrystallization of potassium chloride by heating impure potassium chloride with a saturated NaCl–KCl solution. A flow-sheet diagram of the process indicating the process steps is shown in Fig. 4.

CONCLUSIONS

A process has been developed to prepare fertilizer-grade potassium chloride from mixed salt obtained by solar evaporation of subsoil bittern of Kharaghoda. The process involves preparation of good quality mixed salt from subsoil bittern of Kharaghoda by solar evaporation. The mixed salt obtained is decomposed at 30°C by the addition of half the quantity of water. The contents are stirred to obtain impure potassium chloride. It is then recrystallized using a NaCl–KCl saturated solution. The hot slurry is filtered and the filtrate is cooled to crystallize potassium chloride.

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