SECTION II

CHAPTER 1

MANUFACTURE OF MIXED SALT BY SOLAR EVAPORATION OF BITTERNS

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MIXED SALT PRODUCTION FROM BITTERNS

Chemistry of the process

The main constituents in the bittern are water, sulphates and chlorides of sodium, potassium and magnesium. It is a five component system: $NaCl-KCl-MgCl_2-MgSO_4 - H_2O$. Van't Hoff and his co-workers have determined the solubility relations of the above system at 25 and 83°C and the data are given in the Tables 10 and 11. To represent all the components in a diagram will be considerably more complex and simplification will enable one to understand their relationships properly. The graphic representation of the above equilibria is simplified by expressing the sodium chloride and the salts of the reciprocal salt pair (K, Mg) - (Cl, SO_4) in terms of 1000 mols of water. It is further simplified by not representing the sodium chloride field in the diagram bearing in mind that all the equilibria represented are equilibria in the presence of solid sodium chloride. As a result, there is a loss of one degree of freedom. Owing to the predominance of sodium chloride, deposition of other salts always takes place in presence of sodium chloride. As the sodium chloride is not represented, the diagram reduces to the orthogonal projection of the Lowenherz tetragonal pyramid for the system (K, Mg) - $(Cl,SO_4)-H_2O$ as shown in figs. 9 and 10 for 25° and 83°C isotherms. This type of graphic construction is used by van't Hoff to describe the equilibria of the system. The equilibria represented in the diagrams, Figs. 9 and 10 are the stable equilibria. The double molecule K_2Cl_2 is used to put it on a basis equivalent to $MgCl_2$. In connection with this space model, potassium sulphate does not occur as such but in presence of excess of sodium chloride, it is deposited as glaserite. The presence of sodium chloride in the solution also permits the formation of other solids containing sodium sulphate such as sodium sulphate itself and astrakanite. Their fields exist at the low concentration of magnesium chloride and are fully illustrated in the diagram. On evaporation of a solution of sea-water, however, super-saturation occurs and in some cases, with great ease, the stable phases may be entirely missed. Figure 11 gives a picture of the relations between the different salts only at 25°C but during solar evaporation of sea-water, the temperature changes during the day and night. As the temperature is altered, the solubility relations also alter and the areas for the different salts change. Determined data of the solubilities at a number of different temperatures of this complicated system are not available. Yet, 25°C isotherm can be taken as a mean temperature, during the day and night and solar evaporation data for the isolation of mixed salt can be usefully interpreted from this diagrams.

In the manufacture of common salt by solar evaporation of sea-water, most of the salt separates between 24° and 29° Be.

From the phase rule point of view, the solution (brine) which contains 19 per cent NaCl has attained saturation with respect to sodium chloride at 24° Be and the sodium chloride continues to separate as solid phase till it attains 29° Be, which is now called bittern. It contains potassium chloride, magnesium sulphate, magnesium chloride, and unrecovered sodium chloride. The composition of the bittern at this density in mols for 1000 mols of water is 20 Na_2Cl_2, 32 $MgCl_2$, 12 $MgSO_4$ and 3 K_2Cl_2. Further solar evaporation of bittern results in progressive crystallisation of various salts as these salts attain saturation. The second salt that attains saturation in the brine during solar evaporation is magnesium sulphate. The composition of the solution at this stage in mols per 1000 mols of H_2O is 48 $MgCl_2$, 22 $MgSO_4$, 12 Na_2Cl_2 and 4 K_2Cl_2 and the bittern attains a density of 33/34° Be and is represented by a point A_1 (Fig. 11) and is situated on the epsom salt boundary line. Further evaporation will lead the boundary between the epsom salt field and kainite field. Separation of epsom salt with sodium chloride takes place as the course of crystallisation as shown by a thick line is situated in the field of epsom salt. A_2 corresponds to the composition of 52 $MgCl_2$, 20 $MgSO_4$, 11.0 Na_2Cl_2 4.7 K_2Cl_2 per 1000 mols of H_2O and corresponds to the density of 34.5° Be. Further concentration will lead to the point A_3 at the boundary between epsom salt field and kainite field. At A_3, the liquor measures a density 35° Be having a composition of

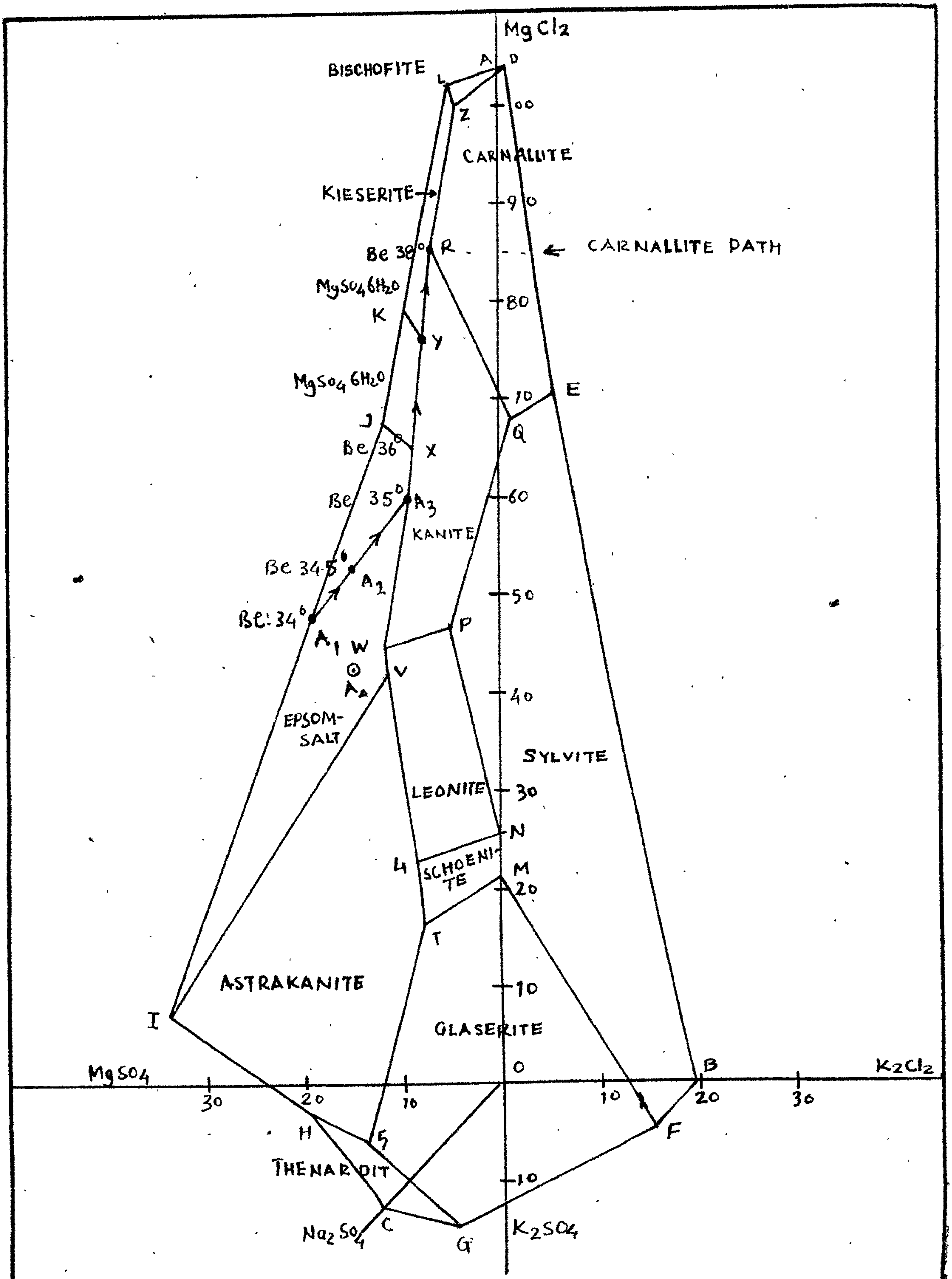


FIG. 11 SYSTEM: $NaCl-KCl-MgCl_2-MgSO_4-Na_2SO_4-H_2O$ at 25°C

60 $MgCl_2$, 16 $MgSO_4$, 9 Na_2Cl_2, 5.5 K_2Cl_2 per 1000 mols of H_2O. Between the point A_3 and X, kainite, epsom salt, and sodium chloride separate out. It is evident from the positions of A_1, A_2 and A_3, in the diagram Fig. 11 that epsom salt with sodium chloride will be crystallised out by the evaporation of bittern between 34 to 35° Be before kainite will begin to separate. It is reported that kainite shows a great tendency to supersaturation and epsom salt continues to separate somewhat further on the boundary line of epsom salt field and kainite field. Therefore, evaporation can be continued till the composition reaches the point X in the diagrams without the appreciable separation of KCl as kainite. The point X roughly corresponds to the density of 36° Be, having the composition 65.5 $MgCl_2$, 13 $MgSO_4$, 4.0 Na_2Cl_2, 3.5 K_2Cl_2 per 1000 mols of H_2O. Further solar evaporation will follow the boundary line between $MgSO_4 6H_2O$ and kainite field till it reaches the invariant point R, equilibria with kieserite ($MgSO_4 H_2O$), $MgSO_4 6H_2O$, kainite ($KCl, MgSO_4 3H_2O$), and carnallite saturated with sodium chloride. The point R corresponds to the density of 37.5 to 38.0° Be containing 85 $MgCl_2$, 8.0 $MgSO_4$, 1.0 Na_2Cl_2, 1.0 K_2Cl_2 per 1000 mols of H_2O. 'Mixed salt' fraction containing kainite, $MgSO_4 6H_2O$ and sodium chloride has separated out between 36° to 38° Be. By the time that the liquor composition reaches R, practically all the potassium chloride has separated out as kainite. This mixed salt fraction is rich in potassium chloride. Solar

evaporation beyond R, will result in the separation of mixed salt containing carnallite, kieserite and sodium chloride and continue to separate until it reaches a composition corresponding to the point Z, the end point of crystallisation. The composition is now saturated with magnesium chloride to such an extent that it separates out as bischofite $MgCl_2.6H_2O$. The point Z represents the invariant point of three fields kieserite, bischofite, ($MgCl_2 6H_2O$) and carnallite, saturated with sodium chloride. In practice, it is possible to reach the Z composition from R by artificial evaporation using coal etc. With favourable weather conditions such as high temperature, low humidity and wind, it has been found possible to reach 38° Be bittern, corresponding to the composition of the point R.

From the Fig. 11, it is evident that potassium chloride chiefly as kainite, has separated throughout the solar evaporation of bittern between 36 to 38° Be and distributed along with other marine salts. As sodium chloride and magnesium sulphate are predominately more and separated along with potassium chloride, the potassium chloride content in the whole salt fraction between 29 to 38° Be will be very low, being less than 8 - 10 per cent. In order to obtain a rich fraction of potassium chloride, the evaporation can be carried out in two or three stages so that in some stages, sodium chloride is removed predominately and in some stages, epsom salt predominately leaving a fraction rich in potassium chloride. As pointed out earlier, rich fraction of sodium chloride ranging between 80 - 85 per cent NaCl (dry basis) can be separated up to 34°Be. The second fraction between 34 to 36° Be consists principally sodium chloride and epsom salt, (sel's mixts) contaminated with a small amount of kainite as the crystallisation path has traversed from A_3 to X, boundary line of epsom salt and kainite fields. The loss of potassium chloride in this fraction will be less than 10 per cent. The third fraction beyond 36° Be consists principally kainite, $MgSO_4 \cdot 6H_2O$ and sodium chloride. The average composition of the "mixed salt" fraction between 36 -38° Be is 18 - 20 per cent KCl, 30 - 35 per cent $MgSO_4$, 15-20 per cent NaCl, and 6 - 8 per cent $MgCl_2$ (wet analysis). The presence of magnesium chloride is due to adherence of the mother liquor. If the composition goes beyond R composition, carnallite will also separate out. Therefore mixed salt occasionally shows a high content of 10 - 15 per cent $MgCl_2$ due to the separation of carnallite. The magnesium chloride drains out on storage and complete absence of magnesium chloride indicates that the mixed salt has been stored and exposed to high humid atmosphere.

It may be observed that the sea-bittern is not saturated with respect to magnesium chloride and will be saturated when the composition reaches the point R. It is also known that the solubilities of sodium chloride and potassium chloride decrease with increase in concentration of magnesium chloride due to common ion effect. If magnesium chloride concentration of the bittern is increased at some stage, it is possible to carry out effective separation of various fractions. As sodium chloride is predominately more in the bittern of 29/30°Be, large quantity of sodium chloride separates out first by the addition of magnesium chloride. Magnesium chloride may be added in the form of high density bittern of 36° Be/38° Be, which is the end liquor of the mixed salt production in such a proportion that there is an increase of 10 per cent $MgCl_2$ which seems to be optimum strength that can be raised. By adding 10 per cent $MgCl_2$, the 29°/30° Be bittern contains 42 mols $MgCl_2$ per 1000 mols of water and point A_4 lies in the field of epsom salt. As the composition lies in the field of epsom salt it attains saturation with respect to magnesium sulphate at lower density. Various fractions obtained in straight evaporation of sea-bittern separates at lower densities. Most of the sodium chloride separates out at 32° Be from the enriched sea-bittern. Between 32 to 34°Be, the solid fraction is rich in magnesium sulphate and sodium chloride similar to the fraction between 34 - 36° Be from virgin bittern. Between 34 to 36° Be from the enriched bittern, the fraction consists mainly of kainite, magnesium sulphate and sodium chloride. The composition of 36° Be contains 85 mols of $MgCl_2$ per 1000 mols of water, corresponds to the point R in the isotherm diagram, Fig. 11. The composition of the mixed salt is 18 - 20 per cent KCl, 30 - 35 per cent $MgSO_4$, 10 - 15 per cent NaCl and 8-10 per cent $MgCl_2$ similar in composition to previous mixed salt fraction between 36° - 38° Be.

The above principle has been verified in the laboratory and in the salt farms on large scale. Mixed salt, assaying between 18 to 20 per cent KCl has been produced at CSMCRI experimental salt farm at Bhavnagar, United Salt Works at Kandla, Salt Works at Tuticorin and Bhavnagar Salt Works at Bhavnagar.

LABORATORY EXPERIMENTS

A) Studies on direct solar evaporation of bitterns

Sea bittern of 29° Be was kept in mild steel trays painted with anticorrosive paint (epoxy paint). The trays were kept in open space to receive the solar radiation. The r~~a~~ise in density, the fall in height of bittern level and the raise in temperature of bittern were recorded daily. The salt fractions separated out at different densities were collected, centrifuged and analysed. The mother liquor obtained from centrifuge was added each time to the evaporating solution. The control of evaporation was done mainly by density change and ratio of potassium and sodium chloride concentrations by using a flame photometer. The concentration of potassium chloride and magnesium chloride was raising daily while the concentration of magnesium sulphate was raising only in the initial stages of evaporation, after which it also separated along with sodium chloride. During bittern evaporation it was observed that concentration of sodium chloride was falling daily. A stage was reached when the concentrations of sodium chloride and potassium chloride were nearly equal. On further evaporation of bittern potassium chloride separated along with other salts.

In collecting different salt fractions from the evaporating bitterns, the solution was separated from the rest of the separated fraction by decantation and the slurry was centrifuged. The mother liquor obtained was added to the siphoned solution and the evaporation was continued till the potassium chloride value in bittern at room temperature was nearly 1 to 1.5 per cent. The solid slurry of mixed salt was similarly centrifuged and the end liquor of 38° Be was separated out. The evaporation data are reported in tables 13, 14, 15. Some of the observations noted from these results were as follows.

(1) Volume of the original bittern of 29° Be was reduced to 48 per cent upto mixed salt stage (that is when bittern was saturated with reference to potassium chloride), while the volume was reduced to 33 per cent of the original 29° Be bittern after the mixed salt was separated out. (2) Area required for direct evaporation of bittern was 0.28 sq.meters (3 sq.ft) per 28.32 litres, or per hectare 1016 kilo litres (or 224 thousand gallons) of bittern. This was based on the basis of 15 cms height of bittern in crude salt and mixed salt pans.

(3) 29 litres of 29° Be bittern contained 11.4 kg of total salts, of which 5.13 kg separated out as crude salt and 2.91 kg separated as mixed salt, while 3.60 kg salts were retained in the end liquor of 38° Be. Separation of salts was 46.5 per cent

as crude salt 20.9 per cent as mixed salt and 32.6 per cent retained in the end liquor.

(4) Individual separation of salts in per cent of the original salt in different fractions was obtained as follows:

(Table 15)

	Per cent		
	Crude salt	Mixed salt	End liquor
Potassium chloride	21.17	68.06	10.77
Sodium chloride	89.04	8.52	2.45
Magnesium sulphate	55.98	24.57	19.45
Magnesium chloride	11.70	15.06	73.24

B) Studies on solar evaporation of mixed bitterns

The word mixed bittern means bittern obtained by mixing of 29° Be bittern with 36° Be bitterns. As direct evaporation of 29° Be bitterns required a longer period to reach 38° Be density which was required for the separation of potassium chloride as mixed salts, some of the laboratory experiments were (Table 17) conducted by addition of solid magnesium chloride ($MgCl_2 6H_2O$) in the ratio of 20 grams per 100 ml. of 29° Be bittern. The results showed that potassium chloride separation as mixed salts was achieved at lower densities namely between 34/34.5° Be to 36/36.5° Be instead of 35.5/36° Be to 37.5/38° Be as in the case of direct evaporation of bitterns.

As addition of solid magnesium chloride ($MgCl_2 6H_2O$)

Table 13 DIRECT SOLAR EVAPORATION OF BITTERNS

(Reduction in volume and raise in concentrations of salts)

Date	24-2-66	26-2-66	2-3-66	3-3-66	6-3-66	8-3-66	11-3-66
Ht.in cms	16	13.85	10.85	9.85	7.6	6.1	5.4
Volume(litres)	29.00	25.10	19.66	17.76	13.77	11.06	8.00
Density (°Be)	30.1	31.6	34.0	34.5	36.0	36.5	37.5
Total chloride g/100 ml	19.43	19.60	20.48	20.84	24.73	26.5	28.61
KCl (g/100 ml)	2.50	2.54	3.50	3.85	4.15	2.23	0.90
NaCl (")	13.00	9.50	6.50	4.50	3.00	2.30	1.15
$MgCl_2$(")	13.90	17.06	19.97	21.88	28.36	33.10	36.9
$MgSO_4$(")	8.65	9.77	12.20	10.78	8.02	6.17	6.10

Table 14 Salt fractions collected in direct evaporation of bittern

Salt separated between	30.1 to 32.6°Be		32.6 to 34.5° Be		34.5 to 36.0°Be		36 to 36.5° Be		36.5 to 37.6° Be	
amount in grams	1980		2020		2710		1150		1650	
Compo-sition	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)
KCl	0.62	12.27	2.40	48.48	3.53	95.60	17.03	195.84	18.01	297.16
NaCl	86.18	1706.00	51.40	1038.28	22.90	634.30	9.83	113.04	12.60	207.90
$MgCl_2$	2.50	49.50	2.55	51.51	2.86	79.23	6.35	81.93	8.30	137.00
$MgSO_4$	3.13	61.97	19.55	590.30	30.20	818.42	28.20	324.30	26.35	434.80
Total salts	~~92.~~ 92.43	kg 1.83	75.90	kg 1.53	59.49	kg 1.61	61.41	kg 0.71	65.26	kg 1.07
Per cent KCl sep-aration	... . 21.52% as crude salts						68% as mixed salt and 10.43% lost in end liquor.			

Table 15 DIRECT (SOLAR) EVAPORATION OF BITTERNS
(Composition of bitterns at various stages)

Date	24-2-66		26-2-66		2-3-66		3-3-66	
Density ° Be	30.1		32.6		34.0		34.5	
Volume (litres)	29.00		25.11		19.66		17.76	
g/100 ml	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)
KCl	2.50	724.9	2.80	703.1	3.50	688.2	3.85	683.9
NaCl	13.00	3770.0	9.50	2386.0	6.50	1277.0	4.5	799.3
$MgCl_2$	13.90	4031.0	16.05	4030.0	19.97	3926.0	21.88	388.7
$MgSO_4$	8.65	2508.0	9.77	2455.0	12.20	2399.0	10.78	1914.0
Total salts	38.05	11.04 kg	38.73	9.77 kg	42.17	8.29 kg	41.01	7.28 kg

Date	6-3-66		8-3-66		11-3-66	
Density ° Be	36		36.5		37.6	
Volume (litres)	13.77		11.06		8.00	
	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)
KCl	4.15	571.4	2.23	246.6	0.90	72.0
NaCl	3.00	413.0	2.30	254.3	1.15	92.0
$MgCl_2$	28.36	3904.0	33.10	3440.0	36.9	2952.0
$MgSO_4$	8.02	1104.0	6.17	682.3	6.1	487.9
Total salts	43.53	5.91 kg	43.80	4.85 kg	45.05	3.6 kg

Table 16 DIRECT EVAPORATION OF 30.5° Be to 38° Be

(Composition of salt fractions)

	Sea bitterns 30.5° Be 10 L		Salt I Fraction. 30.5 to 34.5°Be 1645 g		Salt II Fraction. 34.5°Be to 36° Be. 575 g		Bitterns 36° Be 4 L		Salt III Fraction. 36 to 38° Be 850 g		Bitterns 38° Be 2.6 L	
Constituents	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Percent	Total salts (g)	Per cent	Total salts (g)
KCl	2.50	250	2.03	34	3.49	20	4.92	197	20.27	172	0.90	24
NaCl	14.34	1434	62.62	1030	46.00	265	3.52	141	10.50	89	1.90	52
$MgCl_2$	13.05	1305	8.32	137	10.60	61	27.70	1107	12.12	103	37.20	1004
$MgSO_4$	8.18	818	14.22	234	27.97	161	10.57	424	30.00	240	6.80	184

A) <u>Separation of KCl</u> <u>Crude salts</u> (Fraction I + II) 21.36 per cent

<u>Mixed salt</u> (Fraction III) 68.93 per cent

End liquor (Loss) 9.72 per cent

B) Mixed salt obtained per litre of 30° Be bitterns 85 g
C) Crude salt obtained per litre of 30° Be bitterns 220 g
D) End liquor of 38° Be obtained per litre of 30° Be Bitterns 260 ml

was uneconomical due to its high cost, mixing of 29° Be bittern with 36° Be or 38° Be bittern containing 35 to 36 per cent magnesium chloride was contemplated. The addition of high density bittern to 29° Be bittern was such that the concentration of magnesium chloride in the mixed solution was raised to 21 per cent. Normally 1:1 ratio of addition was suitable. Some of the results obtained are tabulated in tables 17 to 21. The evaporation was controlled as in the previous case by noting the density readings and also by noting daily the concentration changes of potassium and sodium chloride by using a flame photometer. Some of the observations noted from these tables were as follows.

(1) Mixing of 29 and 36° Be bitterns in 1:1 ratio showed that the original volume of the bittern was reduced to only 75 per cent upto mixed salt stage (that is when bittern was saturated with reference to potassium chloride) while the volume was reduced to 67 per cent after the mixed salt was separated out.

(2) Mixing of 29 and 36° Be bitterns in 2:1 ratio showed that the original volume of bitterns was reduced to 58 per cent upto mixed salt stage (till bittern got saturated with potassium chloride) and the volume was reduced to 48 per cent by the end of the mixed salt separation.

(3) The highest concentration of potassium chloride was 4.5 to 5 per cent in direct evaporation while it was only 2.5 to 3.5 per cent in case of mixed bittern evaporation.

(4) Mixing of high and low density bitterns resulted in separation of sodium chloride in large quantities (30 to 40 per cent of the total NaCl separation). The separation

required a long time (overnight) and the salt obtained was fine powder, as it was a precipitated product. Magnesium sulphate separating with sodium chloride was 5 to 2.5 per cent depending on the ratio of mixing the bittern. It was more in case of 1:1 ratio of mixing. Similarly separation of magnesium chloride as adhering liquor was more in case of 1:1 ratio of mixing (4 per cent and 2.5 per cent) with the result the purity of precipitated crude salt was only 80 to 85 per cent sodium chloride.

(5) Area required for mixed bittern evaporation was double in case of 1:1 ratio of mixing while it was 1½ times in case of 2:1 ratio of mixing. Normally 1:1 ratio of mixing was suitable. In the case 29° Be bittern contained more concentration of magnesium chloride, as obtained by recycling of the 29° Be bittern with fresh brine during salt production or as obtained from subsoil brines, lesser addition or no addition of magnesium chloride (36° Be end liquor) was found necessary.

(6) Individual isolation of salts per cent from total salts in different fractions was as follows:

(A) Mixed bittern evaporation with 1:1 ratio ~~with 1:1 ratio~~ of mixing with normal sea bitterns (Table 18)

	Crude salt	Mixed salt	End liquor
Potassium chloride	11.1	75.3	13.6
Sodium chloride	68.9	27.1	3.9
Magnesium sulphate	8.3	49.8	42.0
Magnesium chloride	11.5	9.6	80.8

B) Mixed bittern evaporation with 2:1 ratio of mixing with normal sea bittern (Table 20)

	Crude salt	Mixed salt	End liquor
Potassium chloride	18.8	68.3	12.8
Sodium chloride	84.4	8.3	7.3
Magnesium sulphate	27.8	25.6	46.6
Magnesium chloride	10.0	10.0	80

C) Studies on improvement in the quality of mixed salt.

Studies were carried out in order to obtain mixed salt containing more than 18 to 20 per cent potassium chloride. The details of the laboratory experiments were as follows.

Exp. No.1: Mixed salt was treated with 30° Be bittern and the saturated solution containing 6.25 per cent potassium chloride 9.0 per cent sodium chloride 14.55 per cent magnesium chloride and 15.0 per cent magnesium sulphate was evaporated in open pans. Bittern of 30° Be was selected in order to suppress the reaction between potassium chloride and magnesium sulphate and to obtain potassium chloride either as KCl-NaCl mixture or as kainite or as carnallite. Collected fractions were analysed. The compositions are reported in table 22. The results showed that magnesium sulphate separated in almost equal concentrations in all the fractions. As concentrations of potassium chloride and sodium chloride remained practically constant, no fractions were collected wherein potassium chloride was more than 20 per cent.

Expt. 2 Mixed salt was dissolved in water and the saturated solution was allowed to evaporate in open pans.

Table 17 SOLAR EVAPORATION OF SEA BITTERN (4 LITRES) WITH 200 grams $MgCl_2.6H_2O$ ADDITION PER LITRE (RAISE OF 10 g $MgCl_2$ per 100 ml BITTERN)

Constituents	Salt Fraction 30.5 to 32.5° Be 450 g		Bittern 32.5°Be 3.28 litres		Salt Fraction 32.5 to 34.5° Be 100 g		Bittern 34.5° Be 2.65 litres		Salt Fraction 34.5 to 36°Be 340 g		Bittern 36° Be 1.9 litres	
	Per cent	Total salts (g)	Per cent (w/v)	Total salts (g)	Per cent	Total salts (g)	Per cent (w/v)	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)
KCl	2.11	9.50	3.16	103.60	2.92	2.92	3.80	100.70	21.14	71.88	1.50	28.50
NaCl	90.17	405.70	5.13	168.30	74.82	74.82	3.57	94.61	18.00	61.20	2.02	38.38
$MgCl_2$	2.15	9.60	22.30	731.40	6.72	6.72	27.86	738.10	13.87	47.18	34.42	655.00
$MgSO_4$	2.87	12.92	8.88	291.30	3.24	3.24	10.81	286.40	37.72	128.20	8.31	158.00
	CRUDE SALT		INTERMEDIATE SOLUTION		CRUDE SALT		INTERMEDIATE SOLUTION		MIXED SALT		END LIQUOR	

Table 18 EVAPORATION OF MIXED BITTERN (RATIO OF ADDITION 1:1 by Vol. at 30° Be).

Date	24-2-66		24-2-66		26-2-66		28-2-66	
Composition (g/100 ml)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)
KCl	2.50	362	0.70	102	1.68	457	1.75	414
NaCl	13.00	1885	1.15	167	7.57	2058	2.70	638
$MgCl_2$	13.90	2016	36.34	5270	26.88	7286	29.43	6955
$MgSO_4$	8.65	1254	6.10	885	7.89	2159	8.30	1962
Total salts	38.05	5.52 kg	44.24	6.42 kg	44.02	11.93 kg	42-18	9.97 kg
Description	Original bittern		Mixing Bittern ...		Mixed bittern.....			
Ht.in cms		8.0		8.00		14.95		13.05
Vol.in litres		14.5		14.50		27.10		23.64
Density in°Be		30.1		36.1		33.5		34.00
Total chloride g/100 ml		19.4		28.78		-		24.38
Total magnesium "		5.28		10.77		-		9.18

Date	2-3-66		6-3-66		8-3-66	
Composition (g/100 ml)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)
KCl	1.87	413	0.60	118	0.38	61
NaCl	1.63	358	0.90	176	0.50	82
MgCl	33.00	7260	37.0	7252	40.60	6620
$MgSO^2_4$	7.10	1562	6.15	1205	5.50	897
Total salts	45.07	9.92 kg	46.15	8.70 kg	47.05	7.66 kg
Description				Mixed bittern		
Ht.in cms		12.00		10.80		9.00
Vol.in litres		22.00		19.60		16.30
Density in°Be		34.5		35.5		36.5
Total chloride g/100 ml			27.55	29.49		30.73
Total magnesium "			10.05	11.07		11.48

Table 19 SALT FRACTIONS (EVAPORATION OF MIXED BITTERN 1:1 RATIO)

Separation of salts	Immediately on mixing the bitterns at 31°Be		32 to 33.5°Be		33.5 to 34.5°Be		34.5 to 35.5°Be		35.2 to 36.5 °Be	
Quantity in g	1150		565		1700		1300		670	
Composition	Per cent	Total salts (g)	per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)
KCl	0.62	7.13	2.55	14.41	1.25	21.25	19.04	247.5	17.90	120.0
NaCl	79.50	914.5	69.20	390.90	22.50	382.50	14.74	191.62	15.90	106.5
$MgCl_2$	4.43	50.95	4.23	23.90	1.31	22.27	6.95	90.35	11.95	80.10
$MgSO_4$	4.66	53.60	9.92	56.04	35.30	600.10	28.40	369.2	26.50	177.5
Total salts	89.21	1.03 kg	85.90	0.49 kg	60.36	1.03 kg	69.13	0.90 kg	72.25	0.48 kg
KCl separation	----....	....	....	9.4%	...	...	.. ..	77.3%	(13.3% End liquor)	

Table 20 EVAPORATION OF MIXED BITTERN (Ratio of addition 2:1 by vol.at 30°Be)

Date	17-3-66		17-3-66		17-3-66		19-3-66		24-3-66		28-3-66	
Composition	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)
KCl	2.23	446	0.65	65	1.80	518	1.85	507	2.4	415	0.8	116
NaCl	14.50	2900	0.85	85	7.00	2016	5.25	1440	2.70	467	1.5	219
$MgCl_2$	12.61	2522	38.0	3800	22.04	6348 ~~3648~~	23.60	6468	30.18	5220	35.05	5118
$MgSO_4$	8.66	1732	6.2	620	7.85	2261	7.71	2113	9.82	1698	7.50	1095
Total salts	38	7.6 kg	45.6	4.56 kg	38.74	11.14 ~~12.16~~ kg	38.21	10.44 kg	45.10	7.80 kg	45.70	6.67 kg
Description			Original bittern		Mixed bittern		Mixed bittern ..	..	.. ..	.. ..	..	..
Ht.in cms			11.0			5.0	15.5	14.6		9.2	7.8	
Vol.in litres			20			10	28.8	27.4		17.3	14.6	
Density in °Be			30			36	30.7	31.5		34.5	36	
Total chloride(g/100 ml)			19.25			-	21.54	21.54		25.25	27.9	
Total magnesium(" ")			4.95			-	7.20	7.57		9.66	10.65	

Table 21 Salt fractions (EVAPORATION OF MIXED BITTERN 2:1 RATIO)

Separation of salts between densities	After mixing and keeping overnight at 30.7°Be		30.7 to 34.5° Be		34.5 to 36° Be	
Quantity in (g)	1200		2100		2000	
Composition	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)
KCl	0.66	7.92	0.73	15.33	18.50	370.00
NaCl	85.23	1023.00	60.02	1260.42	23.90	478.00
$MgCl_2$	2.30	27.60	2.96	62.16	8.08	161.60
$MgSO_4$	2.50	30.00	13.35	280.35	30.35	607.00
Total salts	90.69	1.1 kg	77.06	1.62 kg	80.83	1.62 kg
KCl separation	1.55%		3%		72.4%	

(22.9% lost in end liquor)

Salt fractions collected were analysed (reported in table 23 and 24). The results indicated that (1) Recovery of potassium chloride as schoenite was 46 per cent (and fraction contained 80 per cent schoenite). (2) The second fraction gave 32 per cent of potassium chloride which was available as kainite and schoenite mixture. While 22 per cent of potassium chloride was obtained again back as mixed salt. Fractions 1 and 2 (in table 24) if collected together could have given 78 per cent recovery of potassium chloride which would have been a mixture of schoenite, kainite and sodium chloride 46.1, 22.8 and 28 per cent respectively. However the above fraction contains higher concentration of sodium chloride which needs further treatment

Exp. No.3: Fractionation of precipitating mixed salt in normal process was studied to find out the possibility of getting a fraction rich in potassium chloride. In direct solar evaporation of 29° Be bittern when the concentrations of potassium chloride and sodium chloride were nearly equal the bittern was decanted to other trough for separation of mixed salt which was collected in three fractions. Compositions of fractions removed and the bittern at various respective stages were studied. The results are reported in table 25 A & B. The data showed that the sodium chloride in the first fraction had separated more than potassium chloride upto 35.05° Be and in later fraction, it was less than potassium chloride. If the first fraction was not mixed up with the subsequent fractions, mixed salt obtained between 35.05 - 36.10° Be, would have contained less amount of sodium chloride. The yield was decreased from 70 per cent to 60 per cent

Table 22 Evaporation of bittern treated with mixed salt

Composition	Fractions			End liquor
	I	II	III	
Per cent	W/W	W/W	W/W	W/V
KCl	8.80	18.80	19.95	1.00
NaCl	42.26	22.15	15.60	1.50
$MgCl_2$	1.05	1.21	6.95	36.50
$MgSO_4$	30.90	31.84	32.30	7.71
Recovery of KCl per cent	15.60	32.13	47.00	5.00 (loss)

Table 23 EVAPORATION OF MIXED SALT SOLUTION IN WATER

(Mixed salt was dissolved in water 1 kg per litre (1:1 ratio) to obtain a solution saturated with potassium chloride.)

Vol. in litres	4.33	-	2.73	-	1.22	-	-	-	0.6 End liquor
Density °Be	31.7	32.1	33	33.4	-	-	-	-	38
Total chloride	(g/100 ml)	14.76	18.98	20.38	-	22.14	-	-	-
Total magnesium	"	4.17	5.14	6.25	-	7.7	-	-	-
Composition	"								
KCl	Not taken	9.30	7.0	6.25	5.0	5.0	4.5	3.3	1.0
NaCl	"	12.5	14.5	8.0	5.0	5.0	4.3	3.2	2.1
$MgCl_2$	"	3.7	9.2	16.65	-	22.6	-	-	36.2
$MgSO_4$	"	16.1	13.9	10.0	-	9.5	-	-	7.0

Table 24 SALT FRACTIONS COLLECTED BY EVAPORATION OF MIXED SALT SOLUTION

Salt fraction	A		B		C		End liquor	
Quantity	620 (g)		720 (g)		250 (g)		600 (ml)	
Composition	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent w/v	Total salts (g)
KCl	(29.7)	(184.0)	13.84	132.62	17.93	44.82	1.00	6.00
K_2SO_4	34.62	(215)	5.35	38.32	nil	nil	nil	nil
NaCl	17.34	107.5	38.5	277.2	17.0	42.50	2.1	12.60
$MgCl_2$	nil	nil	nil	nil	8.26	20.65	36.2	217.20
$MgSO_4$	28.3	175.5	26.18	188.5	28.82	72.05	7.00	42.0
Recovery of potassium chloride	45%		32%		22%		-	

Table 25 A SEPARATION OF MIXED SALT IN THREE FRACTIONS

Composition	Fractions per cent (wet basis)		
	I (34.50 to 35.05)	II (35.05 to 35.55)	III (35.55to36.1)
KCl	7.33	20.71	19.96
NaCl	29.60	18.64	11.45
$MgCl_2$	6.50	8.10	10.57
$MgSO_4$	32.20	38.20	28.36
Recovery of potassium chloride	15%	25%	60%

Table 25 B BITTERN COMPOSITIONS AT VARIOUS STAGES (Per cent wt. by volume)

Composition	I	II	III	IV
°Be	34.50	35.05	35.55	36.10
KCl	3.60	4.05	2.40	1.15
NaCl	4.00	2.86	1.80	1.25
Mg''	8.20	8.89	9.70	10.50
Cl'_2	23.60	25.54	27.22	27.70

D) Studies in acceleration of evaporation

Salt is made by evaporating the sea water or subsoil saline water and at the end of salt production copious bittern of 28/29° Be is discharged; bittern in its turn produces two fractions crude salt and mixed salt leaving 36° Be bittern which is a rich source of magnesium chloride. All this is done with the aid of sun rays. Evaporation process depends mainly on the intensity of the sun rays, temperature, vapour pressure and wind velocity. All these are natural forces which we can use to our advantage but we have no control on them. Sun rays are not completely absorbed as most of it are reflected back to the open space, and the sheet of colourless liquid acts as a mirror; the reflection is much more worst in crystallisers where the shining crystals reflect the received solar radiation. Absorption of solar energy in brines and bitterns is improved to a great extent in presence of green or red colouring matter. The process of evaporation can be quickened by using suitable dyes which are very soluble in brines and bitterns and which are fast to sun light. The effectiveness of dyes for absorption, non-toxicity, low cost and availability are some of the other considerations that determine the suitability of a dye for the acceleration in the rate of evaporation by solar radiation.

Earlier work of Bloch[29], Kane[30], Neelakanthan[31] showed the use of different dyes for the evaporation of brines to obtain more production of sodium chloride. Some of the useful dyes such as solivap green, B.A.S.F green PLX, Atul vaporaid green PXC were used in carrying out the following laboratory experiments. Figures 12 and 13 showed the transmittance data of solivap green and other two dyes in presence of water at various wave lengths. The figures (12 and 13) showed that absorption of solar radiation was higher at 400 and between 700 to 750 millimicrons. The Fig. 12 showed that 100 milligrams of solivap green dye was required to obtain complete absorption when the cell diameter was one centimeter. The dye concentration required for complete absorption was in agreement with the I.C.I published data (Tables 26). The Fig. 13 showed that the other two dyes were more pure and showed complete absorption with little less concentration. Evaporation of water with and without addition of solivap green dye showed that for the same exposed area and depth the average difference in evaporation due to dye addition was 150 ml per day (Table 27). It was also observed that concentration of dye above a certain limit was not useful and the decomposition of dye was increased in case of high concentration of dye in the solution. Dye colour changed from green to yellow after exposure to solar radiation for a long time. It was also observed that the solivap green and B.A.S.F. green dyes were changed to yellow when the pH of the solution was changed to 5 or below. It was possible to restore the hue by increasing the pH to near about 7. The dyes obey Beer and Lambert's law and it was observed that addition of 7 milligrams of dye per litre was sufficient

Table 26 SOLIVAP GREEN DYE REQUIREMENT (I.C.I. data)

Depth of bitterns (cms)	Concentration of dye required for complete absorption of solar radiation (mg per litre)	Requirement of dye kg per hectare
5	20	11.21
10	10	5.61
15	7	3.92
20	5	2.80
25	4	2.24
30	3.3	1.80
40	2.5	1.40
45	2.2	1.23
50	2.0	1.12

Table 26 B ATUL VAPORAID GREEN PXC REQUIREMENT
(Atul Bros. Manf. data)

Depth of bitterns (cms)	Concentration of dye required. (mg per litre)	Requirement of dye kg for pans 90x30 meters (kg)
2.5	8	1.70
5.0	8	1.70
7.5	8	1.70

Table 27 EVAPORATION OF WATER WITH AND WITHOUT SOLIVAP GREEN

(Addition 20 mg of per litre)

(15 cms depth and uniform area of exposure)

	Initial vol.	Evaporation period	Remaining vol.	Reduction in vol. per day per 100 ml	Dye concentration.		Decomposition of dye	Total decomposition	Average difference in evaporation
					Expected as per depth	Actual			
	(L)	(days)	(L)	(ml)	(mg per litre)		mg/L	%	(ml/day)
A) Water	10	4	6.70	8.25	-	-	-	-	-
B) Water + dye	10	4	6.05	9.88	33.06	28	5.06	15.31	162.5
A) Water	10	6	5.33	7.8	-	-	-	-	-
B) Water+ dye	10	6	4.40	9.33	45.45	33.7	12.28	27.0	155
A) Water	10	9	3.80	6.9	-	-	-	-	-
B) Water + dye	10	9	2.38	8.47	52.64	32.24	20.40	23.80	157.5
A) Water	10	11	2.75	6.6	-	-	-	-	-
B) Water + dye	10	11	1.54	7.7	130	97	33.0	25.41	110

1) Decomposition of dye increased with concentration.
2) Difference in rate of evaporation is about 150 ml/day.
3) Dye colour changed from green to yellowish green.

Fig. 12 *Percent transmission of Solivap green in water with different dye concentration*

Cell diameter 1 Cm.
Instrument – "Spectronic 20"

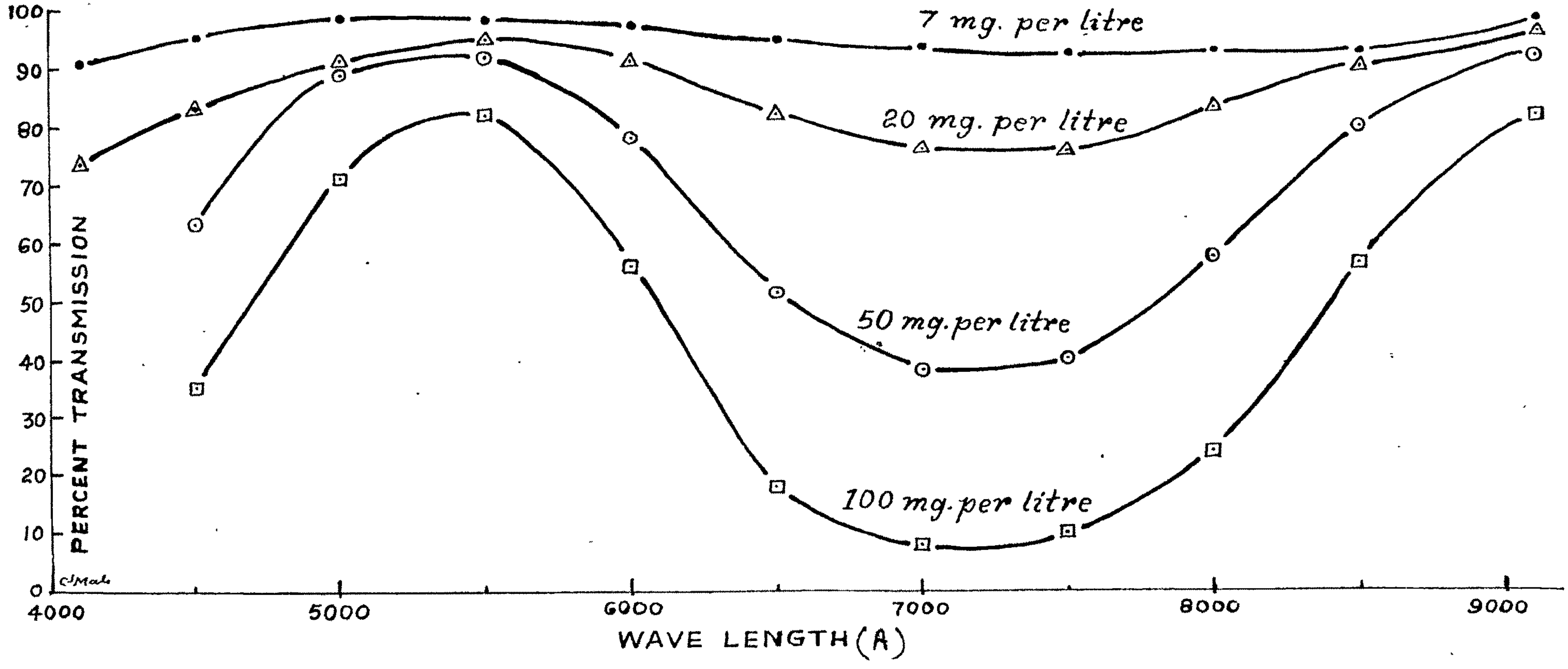
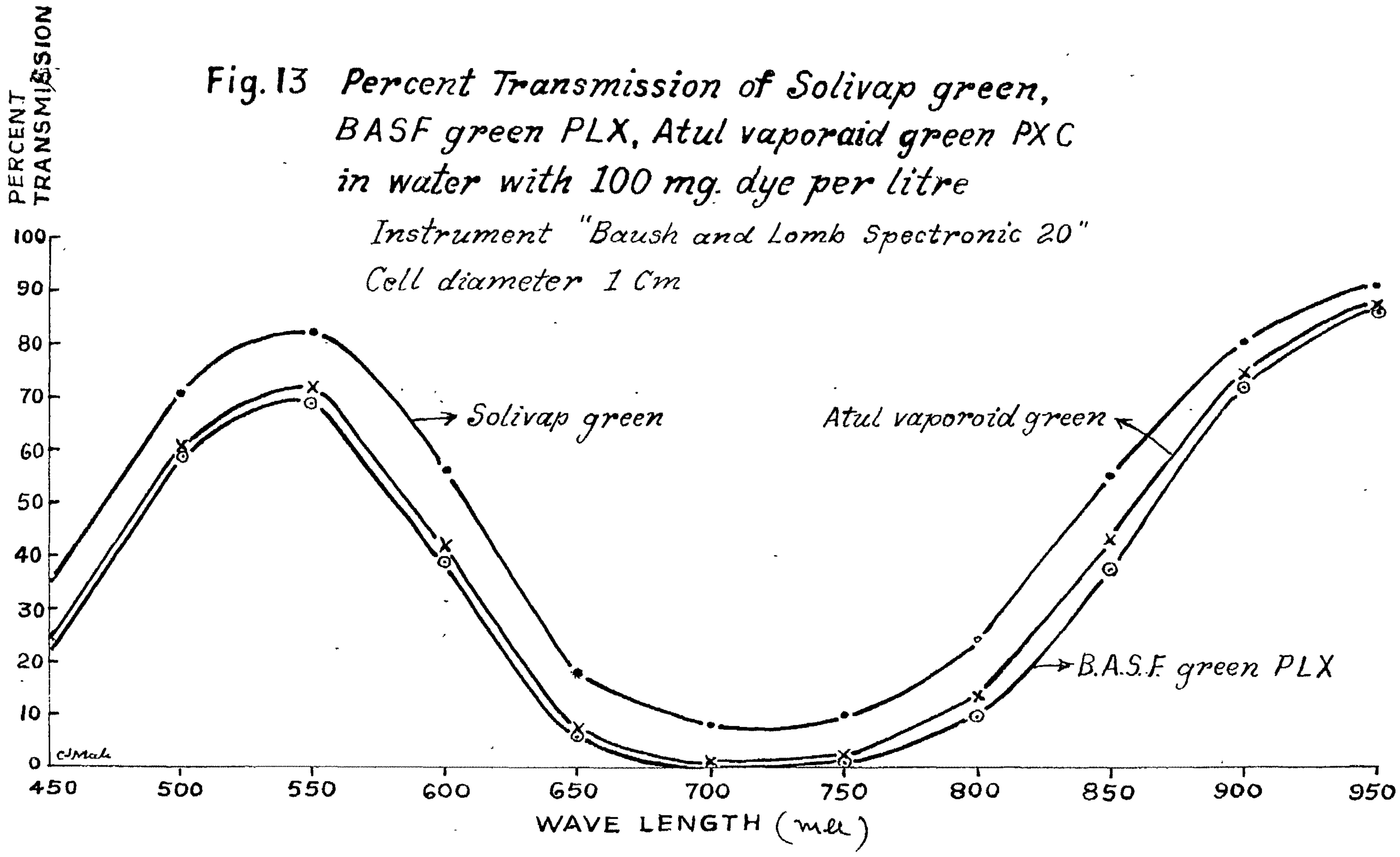


Fig. 13 *Percent Transmission of Solivap green, BASF green PLX, Atul vaporaid green PXC in water with 100 mg. dye per litre*



Instrument "Baush and Lomb Spectronic 20"

Cell diameter 1 Cm

for a depth of 15 centimeters. The variation in concentration of dye with similar depth of brine was helpful in getting more yields of sodium chloride (Table 28, 31). The effect of addition of solivap green to water and brine showed that increase in evaporation was more for brine solutions. Thus by addition of dye the yields were increased by 15 to 20 per cent during the same period of exposure; or in other words more brine could be evaporated in the same area and during same period of exposure. In Table 32 it was seen clearly how the stage of 38° Be bitterns was reached earlier by the use of the dye. The effect of addition of Atul vaporaid green PXC in bittern evaporation are reported in Tables 34, 35, 36. Tables 35 and 37 showed how the number of days required for evaporation of bittern to obtain mixed salt could be saved by using dye and method of recycling the bitterns. It was also observed that the temperature of the bittern whrein dye was added, reached 5° to 10°C higher than without dye addition. The recording of daily temperatures indicated that the temperature of bittern was maximum at 1 to 3 p.m., while it was minimum during morning hours (6 to 8 p.m.). Heat was retained for a long time by bitterns and even at 8 p.m. bittern remained quite hot, as compared to water of similar depth. There was usually 1 to 1.5° C temperature gradient between the top and bottom layers, which was reversed during night hours.

It was also observed that in ~~regarding~~ recycling of high density bitterns (mixed bitterns evaporation) the concentration of dye left over was almost half; hence in fresh cycle one fourth quantity of dye was less required to obtain the same dye concentration. After repeated cycles of solar evaporation the green blue colour slightly changed to yellow green. Even though the colour was completely changed to yellow, the absorption of solar radiation was better than the blank bitterns (bitterns without dye).

The time required for evaporation of bitterns to mixed salt stage varied with meteorological conditions. The period required also changed with the initial density of the bittern used. The time required in winter for evaporation of 29° Be bitterns to 38° Be (direct evaporation) was as high as 30 days, while it was reduced to 15 to 17 days during end of April and May. Normally 20 to 21 days were required for direct evaporation of bitterns. The period was effectively reduced to 14 days by addition of dye, 7 mg per litre for 15 cms depth of bitterns. The period was further reduced to 9 days (Table 37) by mixing end liquor of 36° Be bittern with fresh bittern of 29° Be. Thus addition of dye and magnesium chloride (as 36° Be bittern) gave more production of mixed salt; as the mixed salt was produced at earlier densities and more evaporation cycles could be carried out during the season.

Table 28 EFFECT OF CONCENTRATION OF DYE ON YIELD OF SALT AND EVAPORATION IN SIMILAR DEPTH OF BRINES (15 cms)

Solivap green concentration mg per litre	10	16	20	25
Per cent vol.reduction	24	26	34	34
Yield of salt (g)	20	22	31	30

Table 29 EFFECT OF ADDITION OF DYE (SOLIVAP GREEN) ON WATER AND BRINE EVAPORATION

Description	Water 0° Be	Water+Dye 20 mg/l	Brine 26° Be	Brine with dye 20 mg/l
Total evaporation(litres)	2.900	3.385	1.100	1.330
Evaporation per 100 ml of original solution	72.5	84.6	27.5	33.25
Increase in evaporation due to dye addition,per cent		17		20

Table 30 DECOMPOSITION OF THE DYE (IN TWO WEEKS) DUE TO EXPOSURE TO SOLAR RADIATION.

Concentration of dye,mg/litre	20	25	28	35	95
Per cent decomposition	5.0	25.0	27.5	above 30	above 30
				Not comparable	

Table 31 EFFECT OF SOLIVAP GREEN ON EVAPORATION OF BRINE
(7 mg per litre, height of brine 15 cms)

Brine 26° Be	Days	Unevaporated volume (L)	Density (°Be)	Average temp. and relative humidity			Evaporation per 100 ml (ml)	Salt removed (g)
				Max. (T)	Min. (T)	R.H.		
A) Brine without dye	2	3.72	26	103	80	47.5	7.25	a
B) Brine + dye	2	3.67	26	-	-	-	8.25	a
A) Brine without dye	4	3.50	27	103	79	34	12.5	a
B) Brine + dye	4	3.39	27	-	-	-	15.25	a
A) Brine without dye	6	3.28	26	98.5	70	37	18	a
B) Brine + dye	6	3.13	26	-	-	-	21.75	a
A) Brine without dye	8	3.08	25.8	96	100	34	23	a
B) Brine + dye	8	2.89	25.8	-	-	-	28.95	a
A) Brine without dye	10	2.90	26.0	105	80	29	27.5	a
B) Brine + dye	10	2.67	26.0	-	-	-	35	a
A) Brine without dye	13	2.60	26.0	-	-	-	35	425
B) Brine + dye	13	2.31	26.0	-	-	-	42.5	500

a = not collected

Table 32 SOLAR EVAPORATION OF 26° Be BRINE TO 38° Be BITTERN STAGE WITH AND WITHOUT DYE ADDITION

	26° Be brine without dye (solution A)		26° Be brine with 20 mg/l dye (solivap green) (solution B)	
	°Be(density)	g(salt removed)	°Be(density)	g(salt removed)
After six days	27.5	245	29	340
After ten days	29.0	100	34.5	120
After fourteen days	33.0	65	38	55
After nineteen days	38.0	115	-	-
Total salt obtained	-	525	-	515

Period required (days)

Rise in density	With dye	Without dye
26° to 29° Be	6	10
29° to 34° Be	4	8
34° to 38° Be	4	9
Total days	14	27

Table 33 EVAPORATION OF BITTERN(BLANK) WITHOUT DYE OR MAGNESIUM CHLORIDE ADDITION DURING AND MIDDLE OF MAY 1966

Date	26/4	27/4	28/4	29/4	30/4	1/5	2/5	3/5
Description								
Ht.in cms	15.2	15.1	14.3	13.65	13.2	-	12	11.3
Vol.in litres	30	-	-	-	-	-	-	-
Density(°Be')	29.5	30	30.3	30.6	31.4	-	-	33.4
Temperature (Top/bottom)	44/44	44.5/45	47/47.5	46/46.5	-/-	-/-	-/-	42.5/43
KCl	2.5	2.65	-	2.8	-	-	3.2	3.3
NaCl	18	14.0	-	14.5	-	-	5.8	5.4

Date	4/5	5/5	6/5	8/5	10/5	11/5	12/5
Description							
Ht.in cms	-	-	-	-	-	-	-
Vol.in litres	-	-	-	-	-	-	8.9
Density(°Be')	35.8	-	36.5	-	37.0	37.5	37.8
Temperature (Top/bottom)	-/-	58/59	58/59	57/58	56/57	58/59	58/59
KCl	4.5	-	4.3	-	3.1	1.6	1.1
NaCl	4.8	-	4.5	-	2.6	1.2	1.2

Table 34 EVAPORATION OF BITTERN(BLANK) WITHOUT MIXING MAGNESIUM CHLORIDE BUT WITH ADDITION OF DYE ATUL VAPORID GREEN PXC (10mg/L) DURING APRIL AND MIDDLE OF MAY 1966

Date	26/4	27/4	28/4	29/4	30/4	1/5	2/5	3/5	4/5	5/5	6/5	7/5
Ht.in cms	12.2	15.2	14.4	13.5	12.6	-	-	7.6	-	-	5.2	5.0
Vol.in litres	30	30	-	-	24.9	-	-	15.0	-	-	-	10.15
Density ° Be	29.5	30	30.2	31	32	-	33.8	35.3	-	36.0	37.0	37.8
Temper-ature(°C) Top/bottom	41/42	42/43	43/44	44/44.5	-	44/45	-	43/44	-	53/54	53/55	52/54
KCl	2.50	2.65	-	3.0	-	3.5	3.8	4.4	-	-	2.1	1.0
NaCl	12.5	8.3	-	7.0	-	6.1	5.8	3.4	-	-	1.6	1.5

Table 35 EVAPORATION OF MIXED BITTERN (30° + 36° Be in 1:1 RATIO) WITH ADDITION OF DYE (ATUL VAPORID GREEN PXC) (10 mg/LITRE) IN END OF APRIL AND MIDDLE OF MAY 1966

Date	26/4	27/4	28/4	29/4	30/4	1/5	2/5	3/5
Ht.in cms	15.2	15.2	14.8	14.4	13.7	12.2	11.5	11.2
Vol. in litres	15+15	30	-	-	27	26	-	22.1
Density °Be	-	31.0	32.5	34.0	35.5	35.8	36.0	36.2
Temperature (°C) Top/bottom	43/44	45/46	45/46	46/48	48/49.5	48/49.5	48/49.5	48/49
KCl	1.42	1.45	2.48	2.5	1.45	1.0	0.8	0.5
NaCl	5.2	2.8	2.6	2.0	1.6	2.2	1.8	0.8

Table 36 EVAPORATION OF MIXED BITTERN (30° + 36° Be IN 2:1 RATIO) WITH ADDITION OF DYE ATUL VAPORID GREEN PXC (10 mg/ litre) DURING APRIL AND MIDDLE OF MAY 1966

Date	26/4	27/4	28/4	29/4	30/4	1/5	2/5	3/5
Ht.in cms	15.2	14.57	14.40	13.80	13.15	-	-	9.90
Vol.in litres	20+10=30	30	28.5	27.2	26.0	-	-	19.5
Density (°Be)	31.5	31.9	32.7	33.5	34.5	35.8	36	36.5
Temperature (°C) Top/bottom	43/44	45/45	45/46	50/52	50/51	52/53	52/54	52/53.5
KCl	1.8	1.9	2.6	2.9	3.1	2.0	1.56	1.1
NaCl	7.8	6.5	-	5.0	3.5	2.3	2.3	2.2

Table 37 EFFECT OF SOLIVAP GREEN AND MAGNESIUM CHLORIDE ADDITION ON BITTERN EVAPORATION

Density rise	Depth of bittern cms	Volume gallons	Days required	Conditions
1)29.5° Be to 36°Be	17.5	175	9	$MgCl_2 \cdot 6H_2O$, 20 per cent on volume + 7 mg dye/litre
2)29.5°Be to 37.5°Be	17.5	176	14	Direct evaporation with 7 mg dye/litre
3)29.5°Be to 37.5°Be	17.5	175	21	Direct evaporation without dye or $MgCl_2$
4)29.5°Be to 36° Be	17.5	175	16	Addition of 20 per cent $MgCl_2 \cdot 6H_2O$ on volume
5)29.5°Be to 36°Be	17.6	178	17	Addition of 36°Be bittern (1:1 ratio) with 29.5° Be bitterns
6)29.5°Be to 36°Be	17.6	178	9	Addition of 36°Be bitterns (1:1 ratio) with 29° Be bitterns + 7 mg /dye per litre

1) Precipitation of potassium chloride is complete at lower densities by addition of magnesium chloride 20 per cent as solid $MgCl_2 \cdot 6H_2O$ or as 36° Be bitterns in 1:1 ratio containing 35 to 36 per cent magnesium chloride.

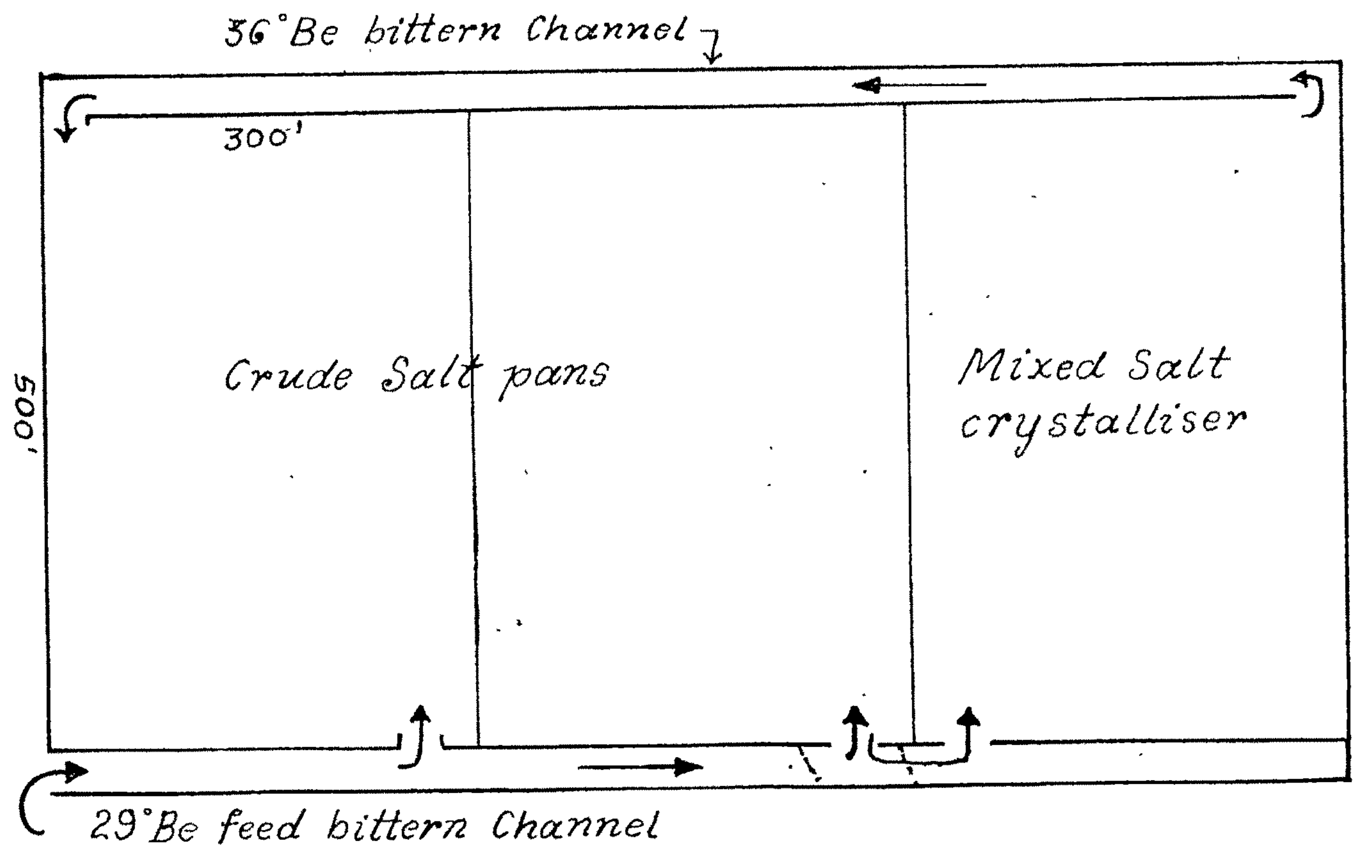
2) Addition of both $MgCl_2$ and dye complete evaporation in 9 days instead of 21 days.

3-A Yield and quality of mixed salt produced on field scale trials

Depending on the laboratory studies, mixed salt production on field scale was undertaken at Kamdar Salt Works and at experimental salt farm,Bhavnagar. the Size of pans at Kamdar Salt Works was 500 x 300 feet while at the experimental salt farm, it was 300 x 100 feet. The work was undertaken in order to satisfy the party regarding the quality and quantity of raw material (mixed salt for setting up potassium chloride plant) that could be obtained at his salt works. During the first season only three salt crystallising pans were given for mixed salt production. Pans were already brick lined which gave additional advantage to produce good quality mixed salt. The crystallisers were first cleaned and all the salt was removed. Two channels on both the sides of the pans were prepared, with a gradient in reverse directions. Gradient of 3 to 4 inches per 500 feet was sufficient for the channels. Channels were prepared in such a way as to facilitate the feeding of bittern to pans and recycling of 36° Be bittern from mixed salt crystallising pan mostly by gravity flow. Two similar size pans were used as crude salt pans and the third pan was used as mixed salt crystallising pan (Fig. 14). 29° Be bittern was taken in the first two pans with an average height of 15 cms. in the pans. Regular analysis of bittern samples was conducted in the laboratory. Some of the results are as follows.

FIG. 14

FIELD SCALE EXPERIMENTS AT KAMDAR SALT WORKS
A DRAWING SHOWING CRUDE SALT AND MIXED SALT PANS
AND ARRANGEMENT OF CHANNELS.



cJMali

(g per 100 ml)

Density	29° Be	34° Be	36°Be	39°Be
Composition				
KCl	2.00	4.30	1.10	0.15
NaCl	16.50	4.75	2.20	0.42
$MgCl_2$	13.67	22.14	35.44	43.92
$MgSO_4$	7.17	11.24	6.86	2.83

In the initial stages only direct evaporation of bitterns was carried out. The samples of bittern were taken daily and analysed in the institute to find out the concentration of different salts. Instructions were given to the party for feeding mixed salt crystallisers as soon as potassium and sodium chloride values were nearly equal. Most of the bittern was fed to mixed salt pans by gravity alone and a very little quantity of bittern was fed to mixed salt pans from the bittern channel by manual labour. It was observed that by the time bittern was saturated with reference to potassium chloride the volume was reduced to half and the bittern from both the crude salt pans was accommodated in mixed salt crystallising pan. Thus calculations based on laboratory data agreed well with the field scale experimental results. Mixed salt pan ~~was containing~~ contained bittern 15 cms depth which was allowed to crystallise. The precipitation of mixed salt was complete which was indicated by 1.5 per cent potassium chloride value per 100 ml in 36° Be bittern. The end bittern or mother liquor containing 35 to 36 per cent magnesium chloride was discharged through the other channel on the other side of the pans from where it was taken to crude salt pans for mixing with fresh bittern. The mixing of bittern was carried out by noting the average heights before and after mixing the bittern. The density of mixed bittern rose immediately by 1° Be and the solution became turbid. The fraction of sodium chloride was collected next day (after overnight settling) morning. Similarly, fractions of crude salt and mixed salt were collected and analysed. Three crops of mixed salt were collected during the season. The analysis of mixed salt was good and showed 18 to 20 per cent potassium chloride content. Test experiments were simultaneously carried out by using Kamdar bittern of 34° Be and following results obtained in the laboratory agreed well with the field scale results (Table 38).

Table 38 <u>TEST EXPERIMENTS RESULTS</u> (KAMDAR BITTERNS)

Contents	34° 30 litres		Separated mixed salt 6215 g		End bittern 36° Be	
	% w/v	Total salts	% w/w	Total salts	% w/v	Total salts
KCl	4.35	1305	18.28	1136	1.1	166
NaCl	4.75	1425	17.97	1116	2.2	332
$MgSO_4$	11.24	3372	29.97	1862	9.07	1510
$MgCl_2$	22.14	6642	10.80	661	35.44	5900

Total mixed salt collected during the season was 150 tonnes. It was observed that during March when the days were hot and nights were cool magnesium sulphate separated out in large quantity as needle shaped crystals. The crystals were collected and analysed showed almost pure epsom salt with 5 to 10 per cent sodium chloride as impurity. It was possible to collect large quantity of epsom salt crystals and sodium chloride was removed by mechanical wet seiving with bittern. The other observations were

(1) Quality of mixed salt produced was uniform and contained 15 to 20 per cent sodium chloride with 18 to 20 per cent potassium chloride

(2) Lot of bittern remained with crude salt which needs removal from the pan atleast once in a season

(3) Crude salt contained on an average 2 per cent potassium chloride and the quantity of crude salt produced was roughly double that of mixed salt produced. Analysis of crude salt samples (Ist fraction) was KCl 0.44; NaCl 78.54; $MgCl_2$ 2.76; $MgSO_4$ 2.63 per cent and IInd fraction was KCl 3.18; NaCl 60.54; $MgCl_2$ 9.70; $MgSO_4$ 20.2 per cent.

(4) Roughly 100 tonnes of mixed salt were produced per acre (of mixed salt crystallising pan per season.).

(5) Deep charging of bittern was favourable to obtain crystalline and easily collectable mixed salt. In case of shallow feeding (1 to 3 inches), the precipitation of mixed salt was almost like a slurry which was difficult to heap.

(6) Multiple irrigation system was favourable from the point of collection and purity of mixed salt.

(7) It was necessary to use a small pump to collect all the 36° Be bittern from the channel for recycling operation

(8) Mixed salt was collected by scraping with pavda and collection was done by mild steel baskets (Tagara). In the next season 1000 tonnes of mixed salt was produced.

In experimental salt farm, the pans were of mud alone. Proper consolidation of the earth was carried out by usual methods of pagali and then one ton roller was slowly used for preparing impervious solid surface. Thick crust of mixed salt was exposed to sun light for one day after draining all the supernatant mother liquor. The crust automatically breaks and number of cracks were seen on the surface. The crust was broken with crackers (iron drill type instrument with wooden handle) and was then collected by pavada and Tagara. Two reservoirs (size 500 x 100) were also constructed to store bitterns of 29 and 36° Be density. Portable pumps were used for transfer of bitterns where gravity flow was not possible. Control of mixed salt operation was carried out by flame photometric analysis of bittern for sodium and potassium chloride values. The quality of mixed salt produced was good. The average analysis of mixed salt was KCl 18.51; NaCl 16.66; $MgSO_4$ 31.59; $MgCl_2$ 4.41 per cent. It was difficult to assess exactly the yield of mixed salt to the total bittern used. Roughly 60 per cent of potassium chloride content in the 29° Be bittern was recovered as mixed salt.

3-B) Studies on storage of mixed salt in pits

Mixed salt was stored in a pit of the following size in experimental salt farm.

Size of pit	2' x 2' x 2'
Total cubic feet	8 cu ft
Total mixed salt stored	208 kg.

Mixed salt was stored in a pit under the earth, about six inches (15 cms) from the ground level. Mixed salt was stored in the pit by the end of May and the pit was opened after the rains were over (7 Nov.67). Comparison of the analysis of the stored mixed salt before and after the rainy season showed that very little or no change in composition had taken place even though the total rainfall during the season was 40 inches (100 cms). Appearance of mixed salt was clear white. Magnesium chloride content was slightly reduced. The experiment showed that in case of difficulties of getting a suitable shed, mixed salt could be preserved in pits atleast for a period of one year. The results of the analysis are reported in the table 39.

Table 39 ANALYSIS OF MIXED SALT STORED IN PIT, SIX INCHES BELOW THE GROUND LEVEL

(Per cent by wt. on wet basis)

	Mixed salt as collected from pan	Top layer	15 cms below top layer	30 cms below top layer	40 cms below top layer	45 cms below top layer	From bottom layer
KCl	19.01	21.43	21.57	21.95	21.79	20.39	18.06
NaCl	14.47	19.64	19.91	19.23	18.69	18.54	12.64
$MgCl_2$	10.59	1.03	1.32	1.87	1.87	2.08	2.09
$MgSO_4$	26.24	33.92	33.06	32.13	32.87	31.87	30.35
Free & combined moisture	29.69	23.98	24.14	24.82	24.73	27.13	28.95

Use of tarpaulin in mixed salt storage

Mixed salt was heaped in two heaps, one at the Institute and the other at Experimental Salt Farm. The heaps were covered with tarpaulin during the entire rainy season. On examination of the stored mixed salt after the rains it was observed that only the top layers of 1 to 2 inches thickness were found changed in composition. Rest of the layers were in good condition with no change in composition; except that it was slightly dehydrated and magnesium chloride content was reduced. The top layers of 1 to 2 inches thickness however showed that part of the potassium chloride was converted to potassium sulphate. The top layers of 1 to 2 inches thickness were very dry and the magnesium sulphate was also slightly dehydrated. Results are reported in table 40.

Table 40 MIXED SALT STORED UNDER TARPAULIN COVER

(Per cent by wt. (on wet basis)

No	0	1	2	3	4	5	6
Description of samples Composition	Analysis before storing	Top layer upto 1" deep	Top layer upto 2" deep	Layer 6" deep from the top	Layer 12" deep from the top	Layer 24" deep from the top	Central portion of the heap
KCl	18.50	16.92	19.32	24.98	25.42	23.95	18.51
K_2SO_4	nil	16.93	11.44	-	-	-	-
NaCl	16.66	22.84	22.25	20.47	19.06	19.69	17.05
$MgCl_2$	4.41	nil	nil	2.02	2.88	2.3	4.3
$MgSO_4$	31.60	34.02	35.16	35.25	35.09	35.70	30.80
Free and combined water	28.83	9.29	11.83	17.28	17.55	18.38	29.34

3-C) Studies in storage of bitterns

Laboratory experiments were carried out on small scale (in plastic buckets) to find out the dilution of the bittern and free height above the bittern level necessary to accommodate all the rain water during the monsoon. As evaporation was simultaneously going on, it was observed that bittern of the same density could be obtained after the monsoon, say by the end of August or within 15 days from the last shower. (2) Bittern losses were 10 to 15 per cent due to dilution and overflowing of the diluted bittern. (3) Highest rainfall was recorded in July which was roughly 309 cms. The details of rainfall in other months were as follows (Figures 15, 16).

May	-	Nil......	
June	76 cms	76 cms	Total rainfall
July	309.3	385.3	"
August	139.1	524.4	"
September	102.4	626.6	"
October	6.35	632.95	"

Maximum rainfall on a single day was 102 mm. (4) Lower layers of bittern remained undiluted and surface (diluted) layers evaporated faster. (5) Rate of evaporation was 4.4 to 5 mm per day on clear sky days while it was 2 to 3 mm. during the cloudy days. Density of the top layers usually remained between 20 to 22° Be during the entire monsoon season, even though the top layers were showing 0°Be as soon as the rain ~~was~~ started. (6) It was ascertained that minimum 6 inches or 15 cms. free height of the reservoir above the bittern level was essential to stop overflow of the bittern from tank or reservoir by dilution with rain water. (7) Experiments conducted to store bittern under cover in cement tanks showed that (1) cracks at various places were developed and often repairing was necessary (2) the top layers upto 1 to 2 feet deep got diluted by absorption of moisture from air particularly when 36° Be bittern was stored. The density fall was upto 30° Be while the bottom layers below 2 feet were 36° Be. (3) absorption of moisture by 30° Be stored bittern was not observed.

Field scale experiments were conducted to store high density bitterns in reservoirs (500' x 100') (Fig. 17) during the monsoon in experimental salt farm. Losses of bittern (30° Be) due to percolation were as high as 25 per cent. Erosion of bunds due to severe wave action and rain showers was severe. Reinforcement of bunds by wooden planks, stone lining (pitching) or brick lining was found necessary. Storing of 36° Be bittern was also carried out in United Salt Works, Kandla where the sides of the reservoir (200' x 200') was reinforced by gypsum lumps from the salt works which showed better protection of bunds. The experiments showed that bittern could be stored in bittern ponds and 4 to 6 ft. deep bittern could be stored during monsoon. The same density of bittern obtained from bottom while the top layers concentrated to the original density within a fortnight after the last showers.

3-D) Layout of mixed salt pans

It is found out by experience that a salt farm producing 1 lakh tonnes of salt per year has a potentiality of producing 6000 tonnes of mixed salt or in other words for every hundred tonnes of salt production hundred tonnes or 176 hundred gallons of 29° Be bittern is ~~required~~ produced. As mentioned in the cost estimate

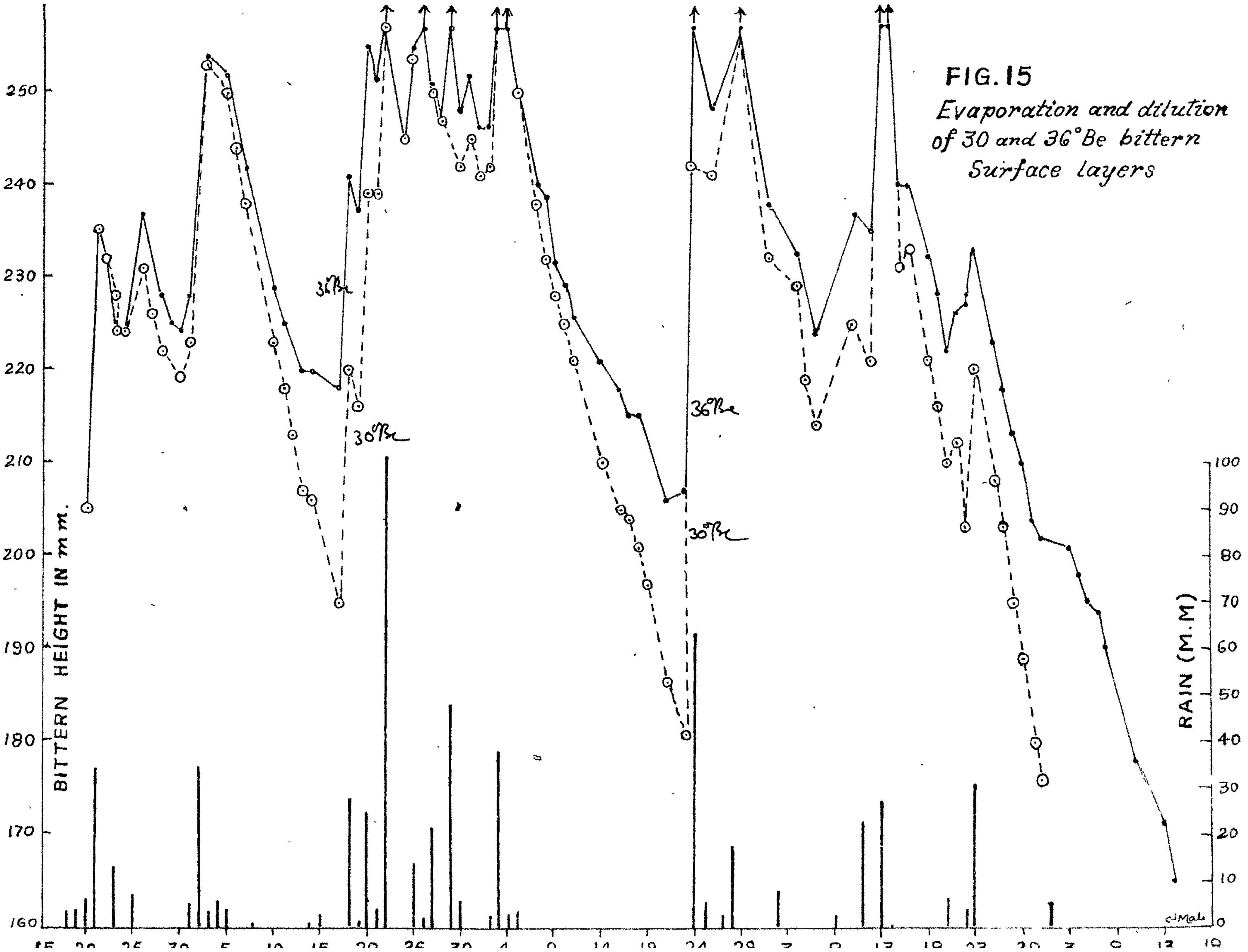


FIG. 15

Evaporation and dilution of 30 and 36°Be bittern Surface layers for 600 tonnes of mixed salt production roughly 29 hectares or 72 acres of area are required. The total area is further divided into crude salt pan area (16 hectares), mixed salt pans or crystallisers (8 hectares) and area for construction of bittern reservoirs storage yards pathways channels etc (5 hectares). The plan for layout of mixed salt pans, (Fig. 18) shows mixing pan for high and low density bitterns. The bittern of 29 and 36° Be density is first taken in this pan mixed in 1:1 ratio and kept overnight to separate most of the precipitating sodium chloride. The mixed bittern is then fed by gravity to crude salt pans. It is necessary to have atleast 30 cms. deep pans except the mixing pan which is required to be 40 to 50 cms deep. The individual size of pans may vary according to local conditions. However, 100' x 300' size pans may be economical and suitable.

Lay out of mixed salt pans are~~a~~ such that it is possible to arrange most of the bittern flow by gravity. Lay out of mixed salt pans is similar to salt crystallisers with feeding and discharge channels on both the sides with suitable gradients. Total area required for mixed salt pans will vary depending on the period available for bittern evaporation and the total number of discharges available per season. The following table 41 gives some idea how the acreage varies with the number of bittern discharges available during the ~~mens~~ season.

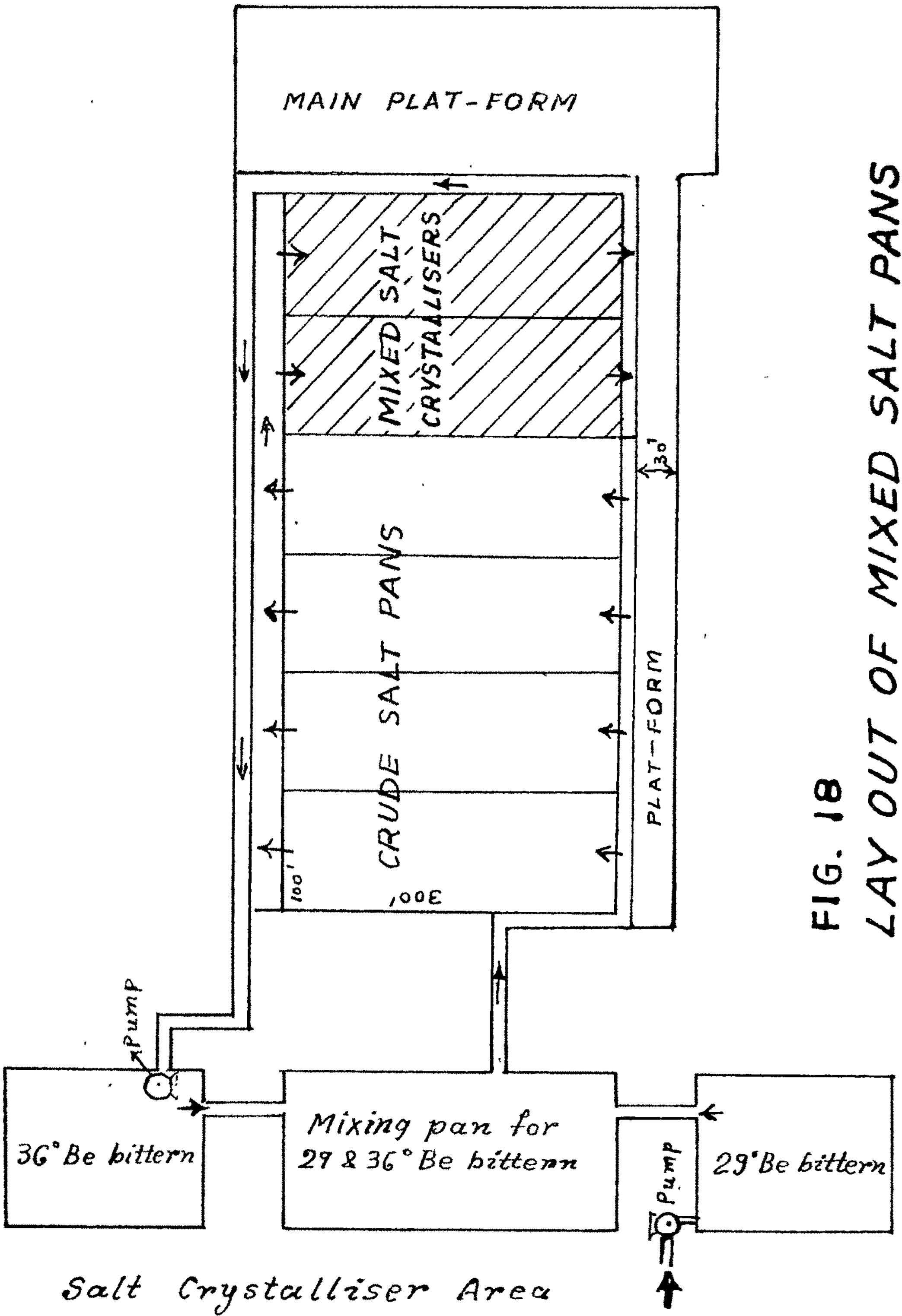


FIG. 18
LAY OUT OF MIXED SALT PANS

PHOTOGRAPHS (Fig. 19)

MIXED SALT PRODUCTION AT TUTICORIN

A) Mixed salt pan bed after the removal of 36° Be bitterns

B) Collection of mixed salt and general layout of crystallisers

C) Mixed salt heaps

D) Covering of mixed salt heaps with palm leaves

Fig. 19

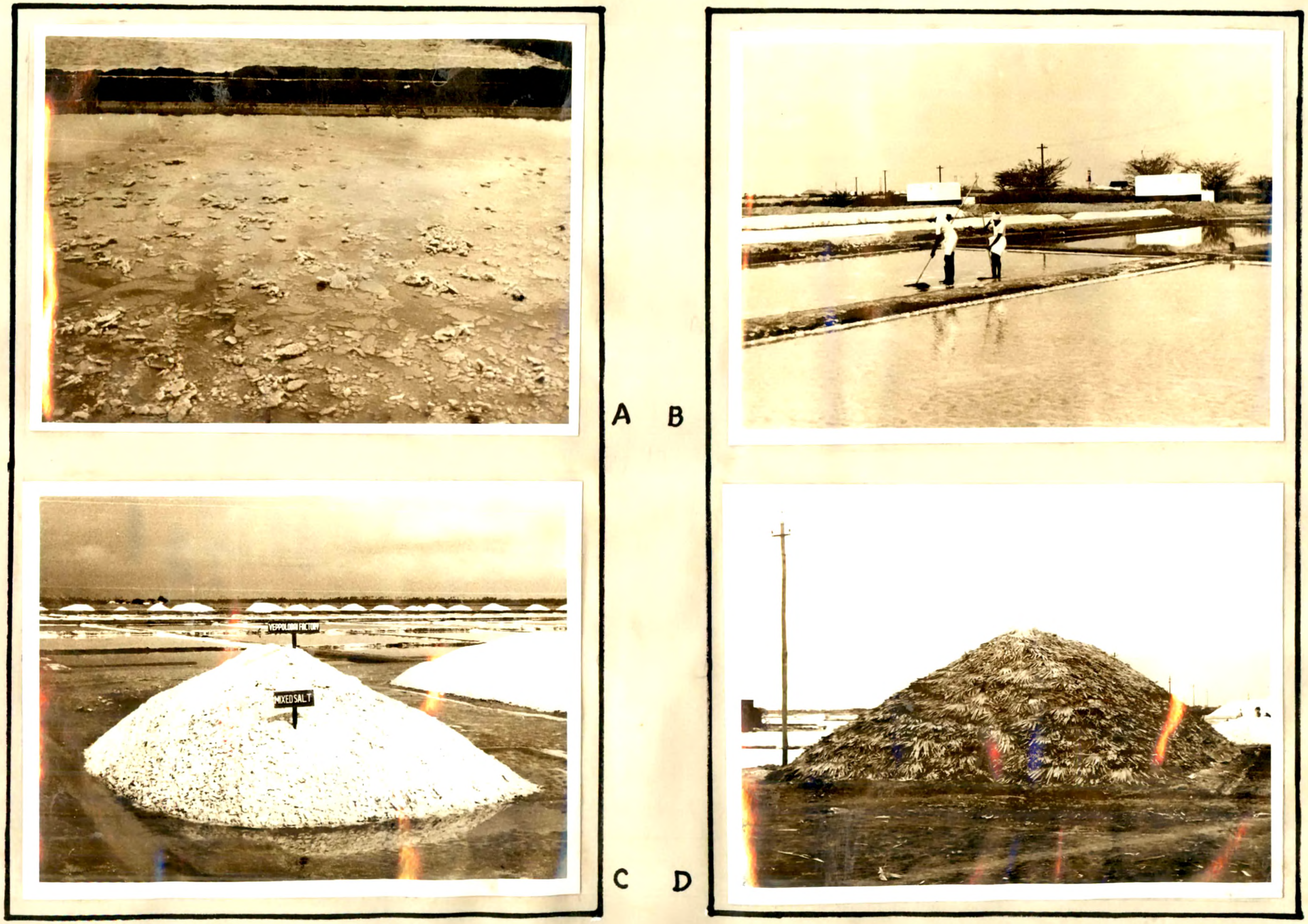


Table 41 Area required for 1000 tonnes mixed salt production

(Area in acres)

No.of charges	Crude salt	Mixed salt	Total area required
3 charges	7.11	4.44	11.55
4 charges	6.40	3.82	10.22
5 charges	4.44	2.66	7.10

The above calculations do not include area for platforms channels or reservoirs for bittern tanks.

3-E) Preparation of mixed salt crystallisers

Mixed salt crystallisers are prepared similar to salt crystallisers. The object is to avoid percolation and contamination of mud and clay particles with mixed salt; secondly to have sufficiently hard bed which will not be spoiled by workers when removing mixed salt from pans.

The percolation losses of high density bittern are less compared to brine of lower densities. Due to high concentration of magnesium chloride in bittern, clay becomes very slimy. In order to facilitate collection of mixed salt it is found by experience better to spread a layer of sand on the beds of mixed salt pans. The usual methods of consolidation of soil are followed. The soil is kept wet during the consolidation process by spraying bittern. It is observed that rolling the soil with half, one and two tonne rollers one after the other with little sand on the surface gives very hard surface. Rolling is carried out on sufficiently moist bed which is not very dry but at the same time does not stick to the roller.

It is better to have tipani first and then roller. The first crop of mixed salt half an inch layer or so may be used for making the bed by putting once more roller. While the subsequent crops are lifted after draining the bittern and cracking 3 to 4 inch thick bed of mixed salt. The last layer of mixed salt is kept undisturbed to avoid contamination from mud. Usually bed cracks when it is exposed to sun light after the bitterns are drained off and the cakes of crystallised mixed salt are easily removed.

PROCESS OF MIXED SALT PRODUCTION

Sea bittern or bittern from certain inland brines like those of the Rann of Kutch or Kharaghoda bittern can be used for mixed salt production. Bittern of 29/30° Be is mixed with equal volume of 36° Be bittern e.g. 454.6 litres (100 gallons) of 30° Be bittern with 454.6 litres (100 gallons) of 36° Be, obtained at the end of the solar evaporation of bittern. The mixed or treated bittern shows 1° Be rise in density and is now led into the salt pans by gravity, where it is concentrated by solar evaporation to 34/34.5° Be. Most of the sodium chloride separates as crude salt along with a little of the magnesium sulphate and calcium sulphate. The crude salt is collected periodically by scraping and heaped up at a place to drain off the adhering mother liquor.

The 34/34.5° Be which then contains nearly equal amounts of potassium chloride and sodium chloride is ready for mixed salt crystallisation. The concentration of sodium chloride and potassium chloride can be quickly and accurately determined by using a flame photometer. This checking is essential as it avoids precipitation of sodium chloride along with mixed salt which will otherwise vary from 15 to 30 per cent. Bittern is then lead to the mixed salt crystallisation pans preferably by gravity. The mixed salt crystallisation pans are to be specially prepared similar to salt crystallisers.

The bittern is further concentrated by solar evaporation to reach 36/36.5° Be (The composition of 36.5° Be bittern is approximately 34.7% $MgCl_2$, 7.1 % $MgSO_4$, 1.5% KCl, 2.5% NaCl). Seventy per cent of the total potassium chloride present in the original 29/30° Be bittern separates as mixed salt (Table 19). The final checking of the bittern at 36° Be is also essential as otherwise bittern will be recycled for mixing with fresh bittern without precipitation of potassium chloride. The normal composition of mixed salt is 30-35% $MgSO_4$ 6.8% $MgCl_2$, 15-20% NaCl and 18-20% KCl (wet analysis). Yield of mixed salt per 454.6 litres (100 gallons) of bittern is approximately 39 to 40 kg. (Tables 13 to 21).

At the beginning of the season when 36° Be bittern is not available for addition, direct evaporation of sea bittern from 30 to 38° Be is to be carried out only during the first month. This is also carried out in two steps; first 30 to 35.5/36° Be wherein the most of the sodium chloride separates as crude salt which is heaped periodically to drain the adhering mother liquor. Bittern of 35.5/36° Be is ready for mixed salt crystallisation only when concentrations of both sodium chloride and potassium chloride are nearly equal. At this stage it is led to mixed salt crystallising pans and allowed to evaporate to 38° Be when most of the potassium chloride separates out as mixed salt. The concentration of potassium chloride in the end liquor (36° Be) should be 1.5 to 1 per cent. After one or two direct evaporation cycles it is preferable to recycle the bittern as discussed above.

Crude salt which will be approximately double the mixed salt production can be washed in a washery unit to obtain common salt or alternatively it can be dumped in low density brine to increase the concentration of sodium chloride, resulting in increased production of salt during the subsequent year. It is advantageous to fractionate crude salt into two fractions. Salt separating between 30 to 32° Be bittern evaporation and that separating between 32 to 34° Be bittern evaporation. First fraction is rich in sodium chloride which is easily washed to obtain common salt while the second fraction contains 18 to 22 per cent magnesium sulphate which can be used to obtain a saturated solution of magnesium sulphate to produce epsom salt. It is estimated that a salt farm producing one lakh tonnes of salt per annum can produce 6000 to 7000 tonnes of mixed salt (see cost estimates for mixed salt) which when processed can give 1000 tonnes of potassium chloride 1800 tonnes of epsom salt and 900 tonnes of sodium sulphate. Epsom salt and sodium sulphate obtained by treatment of second crude salt fraction will yield once again the additional quantity of 1800 tonnes of epsom salt and 900 tonnes of sodium sulphate, This shows that it is necessary to fractionate crude salt and recover epsom salt and sodium sulphate. The end liquor of 36° Be bittern available at the end of the season will be approximately 24/25 thousand kilolitres containing high concentration (35 per cent) of magnesium chloride. This can be either easily concentrated to produce solid magnesium chloride or it can be used for manufacture of other magnesium chemicals.

4 (A) <u>Systems of irrigation</u> The changing of bitterns or brine into crystallizers is spoken of as irrigation. Irrigation is suitable where there is a threat of interruption by rain. Field scale trials at Experimental Salt Farm and Kamdar Salt Works and also experience at United Salt Works, Kandla show that it is preferable to follow multiple irrigation

system. In this method, bittern for mixed salt crystallisation (34° Be in mixed bittern and 36° Be in direct evaporation of bittern) is fed three to five times in mixed salt crystallization pans. When the crust of the separated mixed salt is two to three inches thick, the end liquor is discharged for recycling and the top layers are scrapped and collected. It is necessary to ensure that before discharging, the bittern contains only 1 to 1.5 per cent potassium chloride. The main advantage of multiple irrigation system is that it helps in collection of white mixed salt free from mud which facilitates ~~in~~ further processing of mixed salt.

4-B) <u>Quality control of mixed salt</u>

Sea bitterns of 29/30° Be density contains 2 to 2.5 per cent by volume potassium chloride. In evaporation of bitterns it is very essential to minimise precipitation of sodium chloride along with potassium chloride in mixed salt, and at the same time the losses of potassium chloride in the earlier crude salt fractions.

In any chemical process industry, the importance of the constant composition and good raw material can not be over emphasized. Variations in the components effect purity and yields of the final product. The concentrations of impurities in the raw materials play a deciding role on the final results. This is so very true in case of mixed salt, a raw material for marine by-product recoveries such as potassium and magnesium chemicals. The insoluble matter or clay adhering to mixed salt crop due to improper consolidation of beds and lack of supervision during lifting of mixed salt from the pan is a dead loss in many ways as cess, transport, storage, collection and processing charges are to be paid on it. More-over the fine clay particles chokes up filter cloth which gives enormous trouble during filteration and centrifuging operations. Insoluble matter comes from a number of souces. Some of it comes from loose soil in crystalliser pans as mentioned earlier while other comes from the atmosphere as a fine dust due to dust storms before the rains. Stacked mixed salt heap also gets coated with a lot of fine dust. Proper consolidation of crystalliser beds, strict supervision while collection, multiple irrigation system, sprinkling of sea water in surrounding area and removal of the top mud layers from stack mixed salt heaps are some of the useful methods to combat this problem. The entire operation is controlled only by finding out when the bittern is saturated with reference to potassium chloride. This is done easily by using flame photometer or by gravimetric methods. In gravimetric estimations the reagents are costly and determination requires more time and trained personal. Moreover when a number of pans are ready simultaneously, it is difficult to cope up with the work.

During solar evaporation of sea bittern for the production of mixed salt, the density of bittern goes on ~~on~~ rising from 29 to 38° Be in case of direct evaporation and between 29 to 36° Be in case of mixed bitterns evaporation. The separation of mixed salt is between 36 to 38° Be while in the second case it is 34 to 36° Be. Hydrometer gives density of the solution and indicates very roughly the composition of the brine or bittern to an experienced salt manufacturer. The type of hydrometers used in the salt industry are Baume hydrometers and are available in various ranges; such as 0° to 10° Be, 10° to 20° Be, 20° to 30° Be, 30 to 40° Be or 0 to 40° Be and 0 to 70° Be. It is desirable to have narrow range hydrometers to have proper control. The range 30 to 40° Be is suitable for mixed salt manufacture. It is necessary to select hydrometers of the above range with each degree divided into ten equal parts so as to read accurately fraction of a degree. Baume meters are generally graduated at 20°C or 27.5°C. However for better accuracy it is always desirable to use hydrometers calibrated at 29°C (84°F) which is considered as standard atmospheric temperature in India. It is equally necessary that bitterns is cooled to room temperature (29°C) before such density reading are taken. It is preferable to take daily readings during morning hours.

As seen earlier bittern is saturated with reference to potassium chloride at 34/34.5° Be during mixed bittern evaporation but at 355/36° Be during direct evaporation of bittern. At the beginning of the season when 36° Be bittern is not available for addition, direct evaporation of sea bittern from 30 to 38° Be is to be carried out. After one or two direct evaporation cycles, it is possible to recycle the bittern for mixed bittern evaporation. Similarly precipitation of mixed salt is complete at 36° Be in mixed bittern evaporation while it is complete at 38° Be in case of direct evaporation. Thus density control alone cannot be entirely relied upon.

It is observed during field scale experiments that mixed salt quality and quantity can be better obtained if potassium chloride and sodium chloride values are checked by analysis. Bittern is ready for feeding in mixed salt crystallisers as soon as KCl, NaCl values are nearly equal and bittern is ready for discharge from mixed salt pans as soon as potassium chloride value is nearly 1 to 1.5 per cent. In case of direct evaporation of bittern, the maximum concentration of potassium chloride reached are 4.5 to 5 grams per 100 ml of the solution while in the mixed bittern evaporation, the maximum concentration of potassium chloride reached are 2.5 to 3.5 per cent depending on the amounts of 36° Be bittern mixed with 29° Be bittern.

Chloride content

During evaporation of bittern, the total chloride content of bittern slowly rises from 17 to 29 per cent by volume. It is seen from the graph (Fig. 21) that when the total chloride content reaches approximately 21 per cent by volume, the bittern is saturated with respect to potassium chloride and is ready for mixed salt precipitation. Similarly precipitation of potassium chloride is complete when the total chloride is nearly 29.0 to 29.5 per cent by volume. As the source is constant, the control based upon density and chloride content are accurate and fairly reliable.

Total magnesium value

Similar to estimations of chloride, total magnesium can be easily estimated by compleximetric methods. It is observed in bittern evaporation that the total magnesium value changes from 4.5 to 10.5 or 11 per cent by volume.

The bittern is ready for mixed salt separation as soon as total magnesium reaches to 7.5 to 8.0 per cent by volume and it is ready for discharge when it shows 11 per cent magnesium by volume.

Limitations Flame photometric control is the simplest, easiest and quickest to carry out but in absence of the above instrument, the other methods mentioned above are found fairly reliable and are suitable for producing good quality mixed salt. Results are summarised in Tables 42, 43 and Figs. 20,21 and 22.

4-C) Operational difficulties in mixed salt production

(1) Availability of constant supply of bittern:

It is a common practice in most of the salt works that bittern is not regularly discharged. Most of them discharge large quantities of bittern by the end of May which simply dries up in bittern pits and channels or washed off back to the sea by the rains. This practice is mainly due to inadequate supply of brine, which depends on tidal levels and availability of pumps. Some of the salt works discharge bittern regularly while in others it is only discharged twice or thrice in the whole season. In places like Kharaghoda, bittern is discharged only two times in January and May in a season of nine months. The January discharge of bittern is less as the salt production during winter is less and very large quantities of bittern remains with the separated salt. May discharge of bittern can not be utilised directly for the production of mixed salt as rainy season starts by the time the salt is removed from the pans. It is necessary that bittern is regularly discharged in bittern channels and bittern channels are kept clean so that all the available bittern is utilised for mixed salt

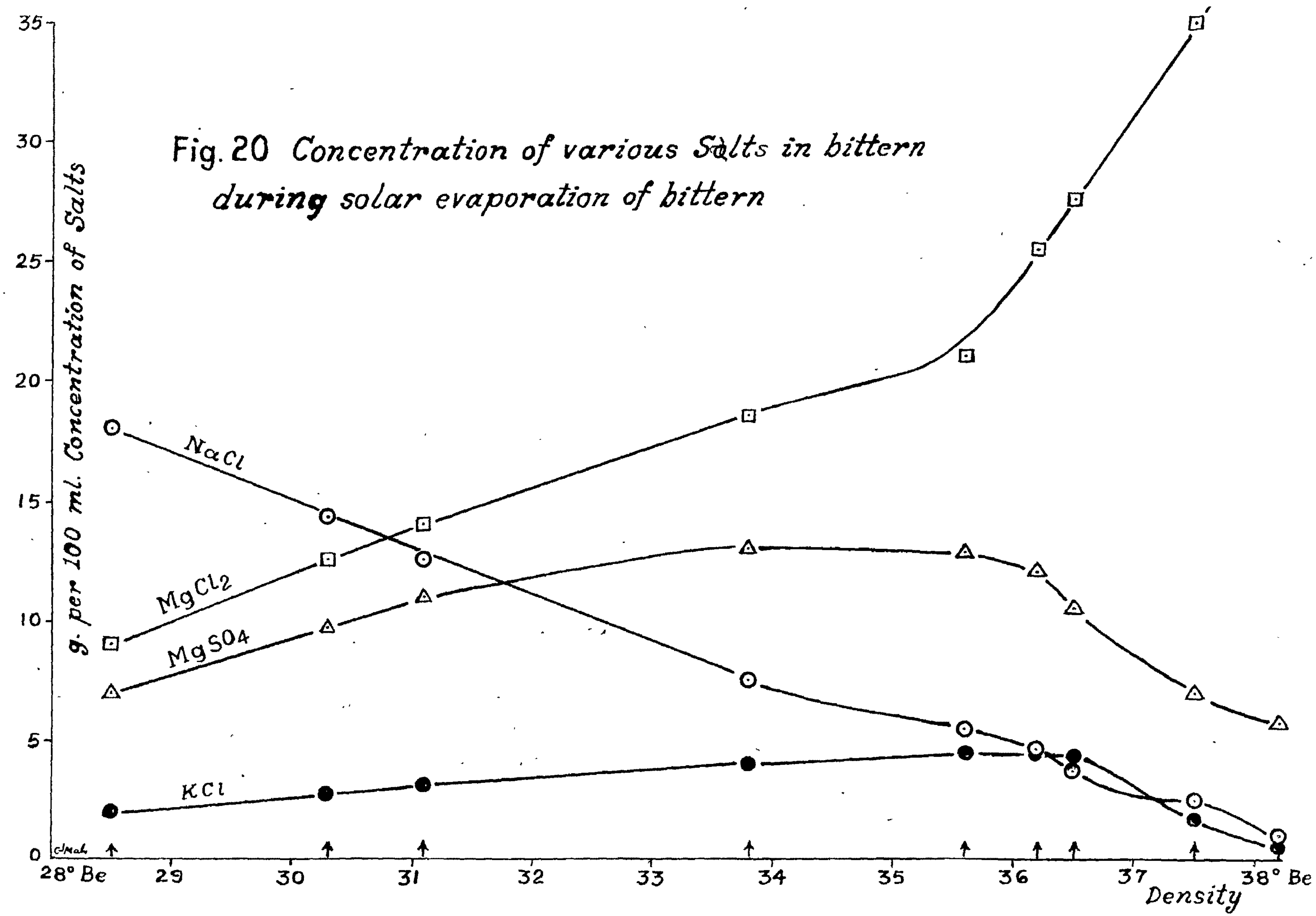


Fig. 20 Concentration of various Salts in bittern during solar evaporation of bittern

Table 42 EVAPORATION OF SEA BITTERN

Evaporation of bittern density readings (°Be)	Approximate chloride value percentage (g/100 ml)	Approximate magnesium value (g/100 ml)	Approximate concentrations of KCl (g/100 ml)	NaCl	Remarks
a) 29/30° Be to 35.5/36° (direct evaporation)	21	7.5 to 8.0	3.5 to 4.5	4 to5	Crude salt separation is complete bittern is ready for charging mixed salt pans.
b) 30°/31° Be to 34°/34.5° Be (mixed bittern)	21	7.5 to 8.0	3 to 3.5	4 to5	
a) 35.5/36°Be to 37.5/38° Be (direct evaporation)	29	10.5 to11.0	1 to 1.5	2 to 2.5	Precipitation of mixed salt is complete
b) 34/34.5°Be to 36/36.5° Be mixed bittern	29	10.5 to11.0	"	"	Bittern is ready for recycling

Table 43 BITTERN COMPOSITIONS AT VARIOUS DENSITIES (Direct evaporation of bittern)

Sr. No.	Density	Chloride content g/100 ml	Composition of Bittern g/100 ml KCl	NaCl	$MgSO_4$	$MgCl_2$
1	28.5	18.9	2.0	18.5	7.1	9.1
2	30.3	19.1	2.8	14.2	9.8	12.3
3	31.1	19.2	3.1	12.6	10.9	13.6
4	33.8	20.2	4.0	7.6	13.3	18.3
5	35.6	21.1	4.6	5.6	12.9	20.9
6	36.2	23.6	4.3	4.8	12.2	26.1
7	36.5	26.7	4.4	3.8	10.3	29.9
8	37.5	28,6	1.5	2.5	7.0	34.5
9	38.2	30.2	0.42	0.8	5.7	40.1

production. The problem can be solved effectively by construction of large bittern ponds where bittern is collected to a height of 4 to 5 feet and preserved throughout the monsoon season. The capacity of these reservoirs must accommodate all the bittern produced during April and May, which is easily calculated from the salt production figures during these months. The problem of storing bittern in places like Kharaghoda is somewhat difficult as the whole area is inundated with sea water and preservation of bittern needs careful planning.

(2) Seapage and dilution with low density brines

Normally due to high density and large concentration of magnesium chloride, the percolation losses of bittern are less compared to brine at lower densities. It is observed that due to high concentration of magnesium and sodium ions in bittern, the clay bed remains very slimy and the trouble of soil boring insects is also minimum. But the close proximity of salt crystallisers or condensor area with low lying mixed salt pans often causes dilution of bittern with low density brines. It is observed that in such cases it is necessary to have a ring channel to the entire mixed salt area.

(3) Difficulties of quality control, transport and immediate use

Instruments such as flame photometer and facilities of laboratory are not available with most of salt manufacturers. Similarly most of the salt works do not possess even matriculate staff to look after mixed salt production. The quality of the produce suffers and mixed salt containing large amounts of sodium chloride is produced. As mixed salt is a cheap raw material and is also corrosive, the cost of transportation for longer distances is prohibitive. Mixed salt contains four salts which react on long storage. The cost of storage is high and mixed salt cannot be stored indefinitely (4) Due to unavailability of bitterns at times, mixed salt pans are fed only 2 to 3 inches. This causes rapid evaporation resulting in slurry which is hard to heap and collect good mixed salt. (5) Lastly as salt and mixed salt production are simultaneously carried out with the same persons, mixed salt production such as feeding the pans, removal of mixed salt are often overlooked. This results in poor quality and less yields of mixed salt.

4 D) Meteorological conditions

The causes which influence the rapidity of evaporation of water in open surface are the causes for solar evaporation of brines and bitterns. Some of the main causes are (1) temperature which increases the molecular activity of water (2) quantity of water vapour in the surrounding atmosphere and the rapidity of removal of this atmosphere (3) extent of the surface of the evaporation. If evaporation is to be accelerated, it is necessary that the molecular activity of water or temperature should be high. Temperature of bittern or brine will depend on the temperature of the air and completeness of absorption of solar radiation. The temperature of the air depends on latitude of the sun, latitude elevation, distance from sea, character of winds and on the amount of rainfall and clouds in the sky. The variation in temperature in the country is very wide; in interiors it varies from -1°C (30 °F) to 44.4°C (112°F) while on the costal regions it varies from 20°C (68°F) in winter to 44.4°C (112°F) in summer. During November to February, the temperature of the air decreases with the increase of latitude and hence from south to north the isotherms run across nearly parallel to the parallels of the latitude. Dry continental or land winds prevail in coastal regions while dry land winds are flowing over the interior parts. During the next three months, March, April and May, the interior part is more heated than the coastal regions while during June to September, the evaporation comes to a standstill or is minimum as the south west monsoon or rainy season prevails. The rainfall and number of rainy days are obtained from nearby meteorological departments. Rainy day is calculated when there is at least 1/10 inch or 0.25 cms of rainfall during the twentyfour hours.

The moisture in the air is usually determined with wet and dry bulb thermometer. It is important to know the relative humidity of the place before we assess the suitability of the place for mixed salt or common salt production. Relative humidity is the ratio of the pressure of the aqueous vapour actually present at a particular temperature to the pressure of the vapour which is saturated with moisture at that temperature. Assuming the baro-metric pressure as constant, the relative humidity is determined by the formula.

$$\text{Relative humidity} = \frac{P_2}{P_1}$$

Where P_1 is the pressure of aqueous vapour when saturated at T_1
P_2 is pressure of aqueous vapour when saturated ~~degree~~ at T_2
T_1, the observation temperature of air in degree centigrade and
T_2 is dew point at that temperature. Other formulae which also gives accurate results is

$$\text{Relative humidity} = \frac{\text{Mass of water vapour per unit volume of air at observed temperature}}{\text{Mass of water vapour per unit volume of saturated air at the same temperature}}$$

In preparing relative humidity tables August's formula as modified by Renault is used. The formula is based on the principle that the difference of temperature of dry and wet bulb is proportional to the difference between the actual vapour pressure and the saturation vapour pressure at the same temperature.

where T and t are observed temperature on dry and wet bulb thermometer, E and C saturation and actual aqueous vapour pressure at temperature T in degree centigrade. Measurement of humidity in the air is carried out by numerous methods such as Dew point method, wet bulb method and various instruments such as sling psychrometers, Assmann psychrometers, mechanical hydrometers, relative hygrometers are available. Just as vapour pressure of water is fixed by its temperature so the vapour pressure of any solution is fixed by its temperature at an amount somewhat lower than the vapour pressure of water at that temperature. If the saturated solution is brought into contact with air in which partial pressure of water is less than the vapour pressure of the solution, the solution will evaporate; on the other hand, moisture will be absorbed by the solution if the air contains more moisture than its limiting amount. Both the phenomenon are observed during bittern evaporation.

The general average evaporation during the year is roughly taken 5 feet or 150 centimeters. Buckley has shown that loss on evaporation rarely exceeds 0.4 inches (1 cm.) per day even on hottest and driest day. Strange has determined following averages.

Condition	Evaporation per month	Total months	Total evaporation
Cold weather	3"	4	12"
Hot weather	8"	4	32"
Raining	4"	4	16"
		Total	60" (or 150 cms)

It is estimated that average evaporation in Bombay region is 0.42 to 0.45 cms (0.17 to 0.18 inches), except during October, end of March, April and May when it varies between 0.6 to 1 centimeter (0.25 to 0.4 inches) per day. Experiments carried out in Bombay have conclusively proved that it is possible to produce mixed salt during March, April and May in Bombay, when the relative humidities are between 55 to 65. Thus mixed salt production is possible during the months where relative humidities are below 70. Evaporation in Rann area and Kutch is very high and 217 to 225 centimeters (7.25 to 7.5 feet) total evaporation is reported per year. The relative humidities are often as low as 30, naturally these regions are very favourable for bittern and brine evaporation. Rate of evaporation and percolation is very rapid at lower densities but as concentration of salts increases, the rate of both is appreciably lowered. It is observed that for bittern evaporation of six inches (15 cms) depth, the average loss of water or evaporation varies slightly during different months.

January and February	0.33 cms per day
March and April	0.50 cms per day
May	0.60 cms per day

The temperature of bittern is highest between 1 to 2 PM. while it is minimum at sun rise. It is noted that the temperature of bittern increases from 25°C to 50°C (for 15 cms deep bittern) during summer. The addition of dyes such as solivap green helps to increase the temperature by about 5°C above the blank bittern temperature (without addition of dye). Wind velocity in Saurashtra is high but generally ranges from 2 to 10 miles per hour in most of the coastal regions and the direction of the wind is north-east in Gujarat upto middle of May which changes to south-west before the rainy season.

In solar evaporation, the surface exposed is to be as large as possible. If, instead of the present method of static condition the bittern is kept moving in thin layers, a very large surface will be available for rapid evaporation. Wind is considered the greatest factor in the removal of saturated water vapours from the evaporating surfaces. Wind also increases area exposed by creating waves and ripples. In French salterns, wind is considered of greater importance than the sun. In tropical and subtropical countries if local conditions such as supply of brines, soil level and transport are favourable, solar evaporation is the cheapest and far more advantageous than by any other means for brine and bittern evaporation.

4-E Storage of mixed salt

In mixed salt manufacture, it is essential to guard from three things, namely contamination by crude salt separating along with mixed salt, contamination with mud while collection of mixed salt and possible reaction of mixed salt with water from rain or other sources. While contamination by crude salt or mud is avoided by taking proper precautions during its manufacture and collection, the storage and care of the produced raw material is generally overlooked considering mixed salt as similar to salt. Salt is generally stored in open space with probably little or no damage, but the same is not true with mixed salt. As mixed salt consists of four salts namely potassium chloride (18 to 20 per cent), sodium chloride (15 to 20 per cent) magnesium sulphate (25 to 35 per cent) and magnesium chloride (5 to 8 per cent). Presence of magnesium chloride is mainly due to adherence of mother liquor. The probable variations in mixed salt compositions arise out of (1) contamination of crude salt precipitating along with mixed salt due to improper control and (2) deficiencies in magnesium sulphate because of earlier separation of magnesium sulphate as epsom salt ($MgSO_4 7H_2O$) during cold winter nights. Mixed salts containing no magnesium sulphate or very negligible magnesium sulphate are produced from subsoil bitterns in certain places in Kuda and Kharaghoda area, which have lower magnesium sulphate content in the original brine.

All the four salts present in mixed salt are reactive. Main reactions are taking place between chlorides of potassium and sodium and magnesium sulphate. It is observed that as long as potassium chloride exists reaction is mainly with potassium chloride and magnesium sulphate to produce less soluble double salt schoenite. Reactions with sodium chloride and magnesium sulphate take place only if potassium chloride is absent or completely converted to potassium sulphate. The product of reaction is usually magnesium chloride and a less soluble double salt schoenite. Water is essential for the reactions and the rate and direction of the reaction is controlled by concentration of the reaction product, magnesium chloride in the reaction mixture. Drainage of concentrated solution of magnesium chloride also carries as high density bittern fairly good amounts of other salts (KCl, NaCl, $MgSO_4$) in solution. In case of rain and intermittent shower, the reactions are fast enough and go to completion within a few days. In case of very humid atmosphere or flowing of humid winds either due to wave action or spray ponds in the vicinity, the reactions progress but slowly. Mixed salt as a rule, therefore, cannot be stored in open space. It should be stored under shed and should be protected from shower and water sprays of any kind even during transportation. It is essential that both mixed salt producer and purchaser have suitable storage arrangements. In case of carnallite type mixed salt (crude carnallite) containing a mixture of sodium chloride and carnallite with very much less or no magnesium sulphate, storage difficulties are much more enhanced. Such mixtures cannot be stored in open sheds similar to mixed salt produced from sea bitterns. As magnesium chloride content is very high (28 to 30 per cent) such mixtures absorb moisture in humid atmosphere and are decomposed.

The slurry is difficult to heap and storing of such mixtures is possible only in closed cement tanks or more preferably the crude carnallite or carnallite type mixed salts is to be decomposed either by water or low density brine and the resulting unreactive mixture of sodium and potassium chlorides is to be stored in open sheds.

Mixed salt storage sheds

Completely enclosed structure is ideal but a costly proposition. Experience has shown that open sheds with corrugated cement or galvanized iron sheets or prefabricated structures are suitable. As mixed salt is corrosive, aluminium sheets or other structures such as brackets are unsuitable. Wooden structure or mild steel structure with anticorrosive paint is cheap and suitable. Storage sheds are to be erected preferably on raised platforms, one metre high from the surrounding ground level. The object is to avoid contact of accumulated water during heavy rains. In the Little Rann and in Kharaghoda area this point is more important as the whole area gets submerged under sea water during monsoon.

Height of mixed salt stored is 3.5 metres and suitable height of shed is 5 metres. Suitable size heaps of mixed salt are prepared in open sheds employing human labour or mechanical devices such as belt conveyors or screw conveyors or a combination of both. The heaps are required to be protected from westerly winds during monsoon either by periodic covering with tarpaulin or by loose cement sheets. Bulk density of mixed salt is 980 kg per cubic metre and the angle of repose varies between 40 and 45 degrees depending on crystal size.

The cost calculations based on the basis of Rs. 10 per sq.foot for open shed and Rs. 12 per sq.foot for an open shed with two side walls show very heavy capital expenditure for mixed salt storage (Table 44). The other methods of protection namely covering the heaps with tarpaulin or polythene sheets show that considering tarpaulin at Rs. 0.50 per sq. foot and polythene sheet at Rs. 1.00 per sq.foot, the heavy capital expenditure for storage sheds can be avoided. Tarpaulin and polythene sheets of any suitable size are available and average life can be safely considered as five years. The only precautions necessary are against leakage of rain water at joints and theft.

Storage of mixed salt in pits

Field experiments conducted to store mixed salt proved that mixed salt can be cheaply stored under earth without any damage at least for a year. The effect of monsoon is avoided by storing mixed salt 15 to 30 centimeters below the earth in large square or rectangular pits. The main precautions necessary are, it has to be stored in high level lands where water logging is avoided by proper precautions. During heavy rains it is essential to remove accumulated water to other low lying area by suitable channels (Table 39)

Table 44 CAPITAL EXPENDITURE FOR STORAGE OF MIXED SALT

Mixed salt to be stored in tonnes	Capital expenditure for storage in rupees per tonne of mixed salt			
	Open shed	Open shed with two side walls	Covering heap with tarpaulin	Covering heap with polythene sheets
1,000	50	60	3.6	7.1
2,000	42	51	2.8	5.5
5,000	36	43	2.4	4.7
10,000	35	42	1.2	2.5

5) COST ESTIMATE FOR 6000 TONNES MIXED SALT PRODUCTION PER SEASON

Total salt production, tonnes	1,00,000
Total mixed salt expected, tonnes	6,000
Total 29/30°Be bitterns available per season, kilolitres	80,000
Total 36°Be end liquor available per season, kilolitres	24,000
Area for mixed salt manufacture	Hectares
a) Area for crude salt pans	16
b) Area for mixed salt pans	8
c) Area for bittern ponds (for storing 30° and 36° Be bittern) storage yards pathways etc.	5
Total area	29

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Capital expenditure	Rs
a) Layout of crude salt and mixed salt pans at Rs. 3700 per hectare	88,800
b) Construction of bittern ponds	13,500
(i) Storage of 30° Be bittern capacity 48000 kilolitres (at Rs.9,000)	
(ii) Storage of 36° Be bittern capacity 24000 kilolitres (Rs.4,500.) (Considering 6' height of bittern stored)	
c) Storage shed for mixed salt capacity 6000 tonnes	1,50,000
d) Pumping sets (two)	20,000
e) Implements	2,000
f) Earthernware pipelines for bittern channels etc.	5,000
g) Contingencies	5,000
Total	2,84,300

Recurring expenditure	Rs.
1) Renovation of pans channels at Rs. 1235 per hectare	15,000
2) Labour for lifting 6000 tonnes mixed salt. Rate Rs. 2.50 per labour per day of eight hours; lifting 3 tonnes of mixed salt	5,000
3) Fuel or power for pumps at Re. 1 per 4500 litres	10,000
4) Attendants for pumps (two) at Rs. 150 per month for six months	1,800
5) Supervision and overhead charges at Re. 1 per tonne of mixed salt	6,000
6) Depreciation charges 10% on mixed salt shed and pumps	17,000
7) Maintenance 3% on capital investment	5,500
Total	60,300
Cost of production per tonne of mixed salt	Rs. 10.05

1) Capital expenditure for mixed salt storage shed can be reduced by using tarpaulin for covering mixed salt heaps or by storing in pits.

2) Crude salt (12,000 tonnes) and 36° Be bittern (24,000 kilolitres) which are available as byproducts are not considered in above cost estimates.