SECTION II

CHAPTER 2

UTILISATION OF MIXED SALT FOR THE RECOVERY OF POTASSIUM CHLORIDE AND BY-PRODUCTS,EPSOM SALT AND SODIUM SULPHATE

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UTILISATION OF MIXED SALT FOR THE RECOVERY OF POTASSIUM CHLORIDE AND BY-PRODUCTS,EPSOM SALT AND SODIUM SULPHATE

1) Chemistry of the process

The entire process is based on the phase relations of the oceanic salts. At every stage, the process is controlled by the solubility - temperature relationship of various systems. The first two steps, namely recovery of mixed salt a fraction rich in potassium chloride and extraction of carnallite from mixed salt are developed on the basis of van't Hoff's solubility relationship of oceanic salt system: $NaCl-KCl-MgCl_2-MgSO_4-Na_2SO_4-H_2O$ at 25° and 83°C (Tables 10, 11 and Figs. 9, 10). The decomposition of the carnallite to yield potassium chloride is based on the system: $KCl-MgCl_2-H_2O$ at 25°C whereas recrystallisation of impure potassium chloride is based on the $NaCl-KCl-H_2O$ at 30° and 110°C (Polytherm). The recovery of epsom salt ($MgSO_4 7H_2O$) and sodium sulphate from the "sel's mixts" is based on the reciprocal salt pair system $2NaCl + MgSO_4 \rightleftarrows MgCl_2 + Na_2SO_4$. Brief outline of the equilibrium conditions and application for isolation of individual salts by fractional crystallisation are described.

2) Potassium chloride from mixed salt

An examination of the Hildebrand's graphic representation of the oceanic system $NaCl - KCl - MgCl_2 - MgSO_4 - Na_2SO_4 - H_2O$ at 25°C and 83°C show that the carnallite field exists at a very high concentration of magnesium chloride and the solubility of potassium chloride has increased while the

~~while the~~ solubility of magnesium sulphate has decreased at 83°C. The solid phase of magnesium sulphate at 83°C is kieserite, $MgSO_4 \cdot H_2O$. The fact that the solubility of magnesium sulphate tends to decrease at high temperature while the solubilities of potassium chloride and magnesium chloride or in other words carnallite tend to increase has caused the kieserite field at 83°C to become larger at the expense of the fields of potassium chloride and carnallite. It is evident from the diagram, that most of the sulphate present in the bittern can be removed as kieserite by evaporating the bittern at higher temperatures until the composition reaches the carnallite boundary line. During the evaporation of bittern, the solids which separate will be a mixture of sodium chloride and kieserite, known as "sel's mixts". By removing the sel's mixts from the hot bittern, potassium chloride is left in the bittern; if the hot liquor is cooled to 25°C, the solid phase carnallite separates as the path of crystallisation lies in the carnallite field. The mother liquor in contact with carnallite at 25°C consists largely of magnesium chloride, corresponding to the point R of Fig. 9.

In the present process, the bittern is not evaporated to separate kieserite and sodium chloride at hot and obtain carnallite on cooling the clear hot liquor. On the other hand, the potassium chloride from the mixed salt is made to dissolve in the bittern of 36° Be at hot leaving behind sodium chloride and magnesium sulphate as sel's mixts in the residue as undissolved; carnallite is obtained on cooling the hot extracted bittern. The present extraction process is also based on the van't Hoff's solubility relationship of oceanic salts at 25 and 83°C. To understand properly the scientific basis of the process, van't Hoffs solubility data at 25°C and 83°C around carnallite field are given in Table No. 45. The data are calculated in grams per 100 grams of water from the original data.

Exploring around the carnallite field, potassium chloride can be extracted from the mixed salt and can be crystallised out as carnallite from the hot extracted bittern by cooling to room temperature. The three important points Z, R and Q around carnallite field of Figs. 9 and 10 are considered for working out the process. The solid phases corresponding to Z are carnallite, $MgCl_2 6H_2O$ and kieserite and this invariant point exists at very high concentration of the magnesium chloride. Corresponding to the point R, the solid phases are carnallite, kieserite and kainite and corresponding to Q, the phases are carnallite, kainite and potassium chloride. Table 45 indicates that the solubility of potassium chloride at 25° and 83°C corresponding to the point Z is very small whereas wide difference in solubility exists at R and Q points. The difference in solubility of potassium chloride at 25° and 83°C at R is 11.6 g per 100 g of water and magnesium sulphate is less soluble at 25°C than at 83°C. The above properties are favourable factors for extracting potassium chloride from mixed salt containing magnesium sulphate which does not dissolve in bittern and does not crystallise out while potassium chloride as carnallite crystallises out on cooling the

Table 45 INVARIANT COMPOSITIONS CORRESPONDING TO THE BOUNDARY OF CARNALLITE AT 25° AND 83°C

($NaCl - KCl - MgCl_2 - MgSO_4 - Na_2SO_4 - H_2O$)

Point	Solid phase	Temp. °C	Mols per 1000 mols of H_2O				gms per 100 gms of H_2O			
			Na_2Cl_2	K_2Cl_2	$MgCl_2$	$MgSO_4$	NaCl	KCl	$MgCl_2$	$MgSO_4$
Z	Carnallite, $MgCl_2.6H_2O$, kieserite ($MgSO_4.H_2O$)	25	0.0	0.5	100.0	5.0	0.0	0.41	52.9	3.34
		83	1.0	2.0	116.0	1.0	0.65	1.65	61.36	0.668
R	Carnallite, kieserite, kainite ($MgSO_4.KCl.3H_2O$)	25	0.5	1.0	85.5	8.0	0.32	0.83	45.22	5.34
	KCl, carnallite, kieserite, langebenite	83	11.0	15.0	76.0	5.0	7.14	12.41	40.22	3.34
Q	KCl, kainite, carnallite	25	2.5	6.0	68.0	5.0	1.62	4.96	35.97	3.34
	-do-	83	2.0	12.0	86.5	5.0	1.30	9.93	47.75	3.34

As the magnesium sulphate is present in the fraction collected between 34° to 36° Be, Point E is not considered.

hot bittern. The composition of the liquor at R corresponds to 36° Be bittern, end liquor in the production of mixed salt. This will be available in large quantity and can be employed as a solvent without adjusting the liquor's composition. Solubility of sodium chloride is higher at 83°C than at 25°C and therefore, some sodium chloride separates along with carnallite, resulting impure carnallite of 75 - 80 per cent purity. On the other hand, if Q point is chosen for extraction, the carnallite will not be contaminated with sodium chloride and will be a mixture of carnallite and potassium chloride. This composition is not favourable for extraction since the concentration of magnesium chloride in equilibria at 83°C is higher than at 25°C which requires evaporation to attain the equilibrium at 83°C. In view of this difficulty, the invariant composition corresponding to R has been chosen for working out the process since there is advantage that concentration of magnesium chloride increases when carnallite crystallises out with 6 molecules of water as water of crystallisation. The concentration of magnesium chloride at R is less at 83°C than at 25°C and can be achieved easily in the operation by various factors. Employing the composition of R at 25°C, the concentration of magnesium chloride falls to equilibrium concentration at 83°C caused by dehydration of epsom salt to kieserite and volume increase with rise in temperatures. Therefore, equilibrium state is well maintained at 25° and 83°C during the process operation if the composition of bittern corresponds to R of 25° isotherm (Fig. 9, Table 10) employed for extraction.

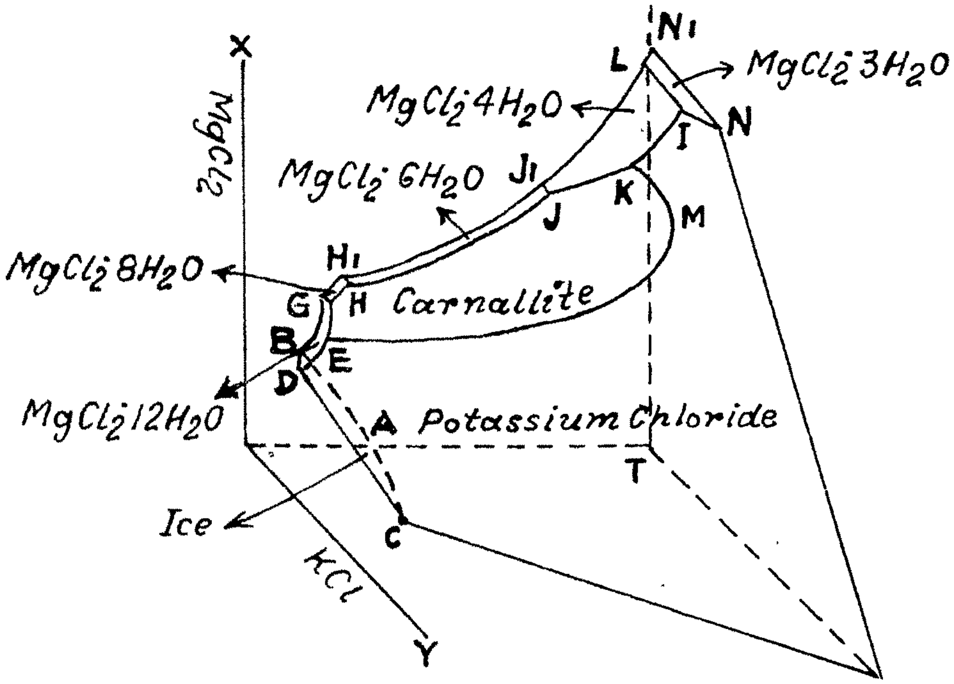
The above deductions have been verified in the laboratory and in the pilot plant scale and the results are given as laboratory and pilot plant experiments.

3. Recovery of potassium chloride from carnallite

The carnallite obtained from mixed salt is decomposed with water to obtain potassium chloride and the principle is based on the system $KCl-MgCl_2-H_2O$. The system has been studied in detail because carnallite represents the major potash mineral processed in Germany (Stassfurt) and is the basis for the production of magnesium chloride which led to the establishment of magnesium industry.

Fig. 23 (Table 46) is a diagrammatic sketch of the model for carnallite and denotes the polytherm of the system. "X" axis represents the concentration of magnesium chloride in the solution; "Y" axis represents the concentration of potassium chloride; while "T" axis represents the temperature. The various saturation surfaces marked in space model are according to the solid phases present. Most of the features are evident from the diagram drawn from the published data[32]. Carnallite is, at all temperatures, incongruently saturated because all points on its surface of saturation have a ratio of magnesium chloride to potassium chloride greater than that in the double salt. Therefore when water is added to solid carnallite, magnesium chloride goes into solution leaving behind potassium chloride as solid phase as they attain saturation at various temperatures.

Fig. 23



Space model for Carnallite

Table 46 SOLUBILITY DATA FOR THE SYSTEM: $KCl-MgCl_2-H_2O$

Pt.	Solid phases	Temp. °C	Composition of solution g mols of salt per 1000 g mols water
E	$MgCl_2.12H_2O$, KCl, carnallite	- 21°	66.1 $MgCl_2$, 4.9 KCl
F	$MgCl_2.12H_2O$, carnallite	- 16.6°	83.33 $MgCl_2$ with small amount of KCl
G	$MgCl_2.12H_2O$, $MgCl_2.8H_2O$, carnallite	- 16.9°	87.5 $MgCl_2$ with small quantity of KCl
H	$MgCl_2.8H_2O$, $MgCl_2.6H_2O$, carnallite	- 3.4°	99 $MgCl_2$ with small quantity of KCl
J	$MgCl_2.6H_2O$, $MgCl_2.4H_2O$ carnallite	115.7°	162 $MgCl_2$, 4 KCl
K	$MgCl_2.4H_2O$, KCl, carnallite	152.5°	200 $MgCl_2$, 24 KCl
M	Carnallite, KCl	167.5	166.7 $MgCl_2$, 41.7 KCl

The important point is whether the decomposition of carnallite at hot or cold should be used for this purpose. The polytherm diagram shows that the proportion of potassium chloride to magnesium chloride in the solution at equilibrium with potassium chloride and carnallite is much less at 25° than at 83°C. This makes it obvious that a much smaller proportion of potassium chloride goes into solution at the lower temperatures. Therefore, there is no advantage in carrying out the decomposition of carnallite with water at higher temperatures. For the industrial application, decomposition at room temperature is most suitable and the amount of water to be used has to be adjusted with an example cited for 25°C isotherm.

The 25°C isotherm is shown in the (Table7, Fig.7). Solubilities are expressed as moles $MgCl_2$ and moles K_2Cl_2 in 1000 moles of water. Similar to earlier diagrams, the double molecule K_2Cl_2 is used to put it on a basis equivalent to $MgCl_2$. The significant points are A,B, E and F.

With the boundary line AEFB, all solutions are saturated and outside the line, solutions are heterogeneous mixtures of salts and solutions. If a solution of composition X is evaporated isothermally at 25°C, the concentration of the solution increases until line AE is reached. Further evaporation deposits potassium chloride until the composition of the solution reaches E, where carnallite forms. If the deposited potassium chloride is not removed, it will be dissolved and redeposited as carnallite; the solution at E is termed incongruently saturated. Carnallite is deposited until F is reached, where magnesium chloride hexahydrate also is deposited with the carnallite; the solution at F is termed congruently saturated. The above features are made use of in the separation of potassium chloride from solid carnallite by adding sufficient water to dissolve all the magnesium chloride and form a solution of composition E. The composition of the solution E is in equilibrium with potassium chloride and carnallite at 25° and is as follows: 1000 H_2O, 5.5 K_2Cl_2, 72.5 $MgCl_2$. From this, it is possible to calculate the water to be used in extracting the magnesium chloride from the carnallite at this temperature. By calculations, one mole of carnallite (277.5 g) requires 7.8 moles or 140.4 g of water or the weight of the water required is approximately half the weight of the carnallite. It means that one kg of carnallite requires 500 ml of water for decomposition; 7.5 per cent of the potassium chloride present in the carnallite is retained in the solution and the other 92.5 per cent remains behind as a solid which can be separated. The polytherm diagram shows that somewhat more water will be required at lower temperatures, but relatively less potassium chloride will be dissolved. It is, obvious, therefore that it is not difficult to obtain potassium chloride from carnallite, a point of importance in the present process.

The liquor after the separation of potassium chloride may then be evaporated and cooled, whereupon another crop of carnallite crystals can be obtained. In order to obtain the maximum amount of carnallite, but no magnesium chloride, the solution must be evaporated to such an extent that on cooling carnallite separates. Solution composition will correspond to point R, in 25°C isotherm which is 1000 H_2O, 105 $MgCl_2$. The amount of evaporation necessary is calculated from the following equation 1000 H_2O + 72.5 $MgCl_2$ + 5.5 K_2Cl_2 = XH_2O+Y $MgCl_2.6H_2O$ + Z (1000 H_2O + 105 $MgCl_2$ + K_2Cl_2). This gives X = 340; Y = 9.8, Z = 0.6; hence 25720 g of solution shall lose 6120 g of water, giving 2720 g of carnallite on cooling or one ton of decomposed liquor shall lose 0.238 ton of water and deposits 0.107 ton of carnallite. On volume basis, approximately one fourth reduction in volume by evaporation is necessary to attain equilibrium corresponding to point F. The second crop carnallite can be treated with water, leaving solid potassium chloride. The mother liquor after the separation of carnallite has the same composition as that of 36° Be bittern, used in the extraction of potassium chloride from mixed salt. This mother liquor is recycled in the present process with the advantage that loss of 36° Be bittern from the main crop of carnallite is made up by the recycled mother liquor, obtained by evaporation. These features are incorporated in the present process.

4. Recrystallisation of impure potassium chloride

It was discussed earlier that the carnallite obtained by this process contains 6 to 10 per cent sodium chloride and decomposition of carnallite by water yields impure potassium chloride due to the fact sodium chloride cannot go into solution, containing high strength of magnesium chloride. The result is that the decomposed product, potassium chloride contains sodium chloride as impurity and the average composition is 65 per cent KCl and 28 per cent NaCl, 2.5 per cent $MgCl_2$ and 3.5 per cent moisture. Purification is carried out by recrystallisation of impure potassium chloride based on the solubility - temperature relationship of the ternary system NaCl + KCl + H_2O.

This ternary system is one in which one ion is common to the two salts. Hence, the solubility of one salt will be decreased in the presence of the other. Solubility data of NaCl + KCl and at boiling points and at various temperatures are given in Table 6. As a basis for crystallisation calculations, Fig. 24, Table 47 is more useful where 30°C isotherm

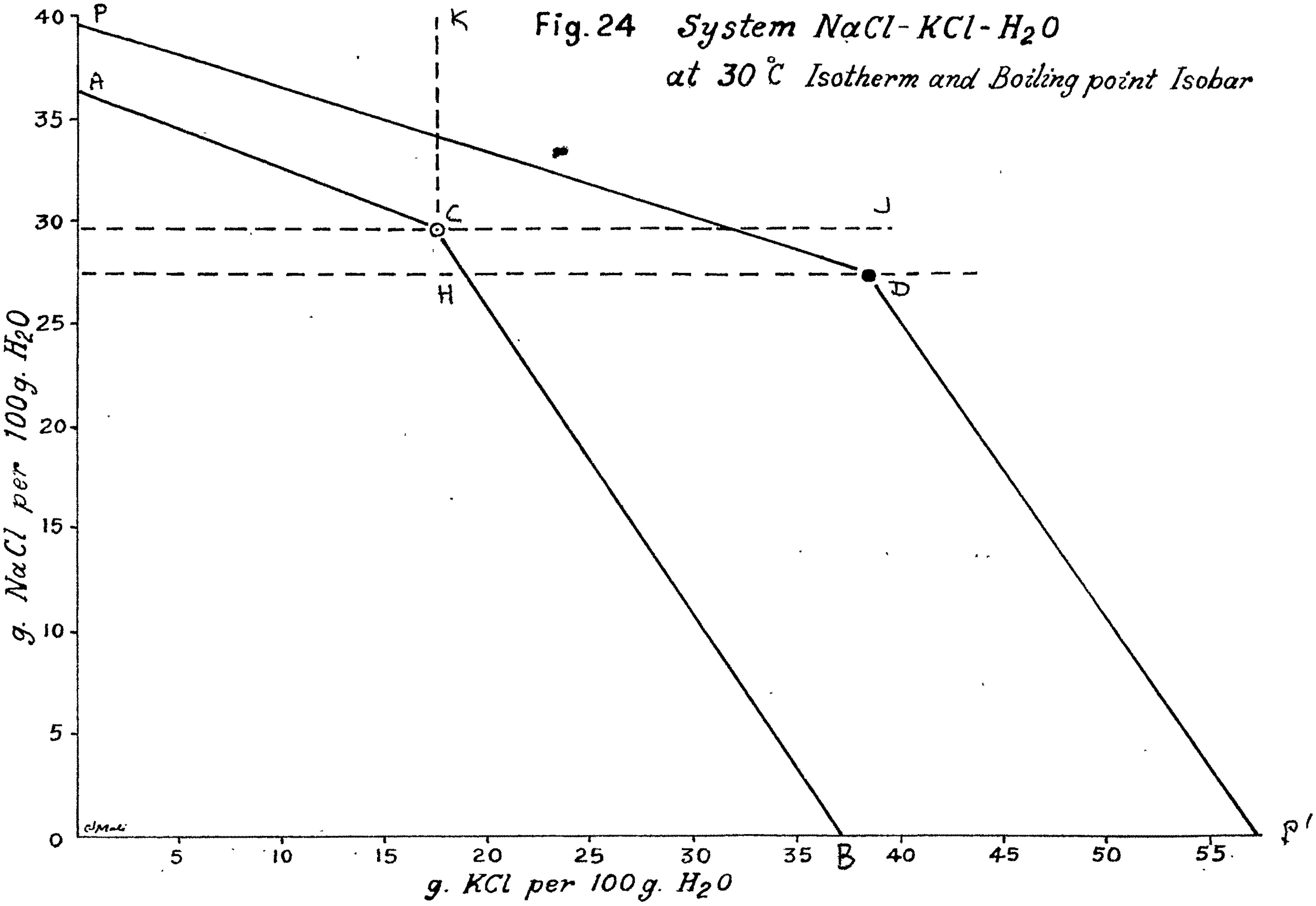


Fig. 24 System NaCl-KCl-H_2O at 30°C Isotherm and Boiling point Isobar

and boiling point isobars 'PDP' are shown. ACB represents the boundary between homogeneous solution below and a heterogeneous mixture outside the lines; within the area ACK, sodium chloride is the solid phase in equilibrium with the saturated solution. Within BCJ, the solid phase is potassium chloride. Within KCJ, the solid phase is a mixture of both salts, in equilibrium with a solution saturated with respect to both. Invariant point is represented by C. Similar relationships exist along the isobar 'PDP'.

If impure potassium chloride (solid) is mixed with calculated quantity of NaCl-KCl saturated solution at 30°C, the diagrams indicate that the solubility of sodium chloride in $NaCl-KCl-H_2O$ system does not alter with temperature whereas the solubility of potassium chloride increases with temperature. On boiling the impure potassium chloride with the saturated solution of NaCl-KCl, potassium chloride goes into solution. Sodium chloride is left in the residue. By hot filtration of the solution, the undissolved sodium chloride is removed as residue and on cooling the filtered hot solution to room temperature, the dissolved potassium chloride crystallises out as pure potassium chloride from the solution.

The invariant compositions of $NaCl-KCl-H_2O$ at 30°C and boiling point (111.9°C) show clear difference in potassium chloride solubility and further indicate that 11.5 g of potassium chloride per 100 g of solution can be separated in each batch and NaCl-KCl saturated solution can be recycled for the extraction of potassium chloride from the residue in the next batches. It is possible to calculate the amount of saturated solution required for recrystallisation on the basis of potassium chloride content in the impure potassium chloride. For 66 per cent KCl, the requirement of NaCl-KCl saturated solution is 5.8 kg per kg impure potassium chloride or 7.2 litres of NaCl-KCl saturated solution per kg impure potassium chloride.

Table 47 DIFFERENCES IN SOLUBILITIES OF NaCl,KCl AT 30 and 111.9°C (B.P.)

Temperature °C	g per 100 g water			g per 100 g solution		
	KCl		NaCl	KCl		NaCl
30	17.2	-	29.7	11.7	-	20.2
B.P. 111.9	38.6	-	27.5	23.2	-	16.5
Difference	21.4		-	11.5		-
	Solubility at boiling points					
KCl(108.5°C)	57.6		0	36.5		0
NaCl(118.7°C)	0		39.4	0		28.2

As stated earlier, the crystallised product obtained on cooling does not contain sodium chloride, because no sodium chloride is crystallised out due to increased solubility of sodium chloride at lower temperatures at the invariant compositions. Any contamination of sodium chloride in the product is due to the adherence of the mother liquor. In order to minimise the sodium chloride contamination, the crystallised potassium chloride is separated by centrifuging and washed with a small quantity of saturated potassium chloride.

Although the above cycle of operation is shown between the temperature 30°C and 111°C, it may also be carried out between any other two temperatures e.g. 20, 25 and 35° and 100°C. By means of quantitative calculations as shown here, the conditions under which the cycle of operation may be most economically conducted may readily be decided in any given case.

These basic principles are incorporated in the recrystallisation process of impure potassium chloride.

5. Recovery of epsom salt and sodium sulphate from the sel's mixts.

The sel's mixts obtained as a residue in the potassium chloride extraction process from the mixed salt contains 30 - 35 per cent magnesium sulphate and 16 - 24 per cent sodium chloride with 8 per cent magnesium chloride and 1.5 to 2.0 per cent undissolved potassium chloride. If dissolved in water, the solution will be saturated with epsom salt in presence of sodium chloride and the ratio of epsom salt to that of sodium chloride remains practically the same as that of sel's mixts. The separation of epsom salt from sodium chloride is complicated by the possibility of forming astrakanite, $Na_2SO_4.MgSO_4.4H_2O$ at ordinary temperatures and of loeweite, $2Na_2SO_4.MgSO_4.5H_2O$ or vanthoffite, $2Na_2SO_4.MgSO_4$ at higher temperatures. The solubility relationship of the chlorides and sulphates of these two salts are used to separate epsom salt and sodium sulphate. The Reciprocal salt pair system 2NaCl + $MgSO_4$ = Na_2SO_4 + $MgCl_2$ forms the basis for the separation of epsom salt and sodium sulphate.

The solution prepared from sel's mixts lies in the astrakanite field in the van't Hoff~~s~~ diagram, Fig. 9 which will prevent the separation of epsom salt from sodium chloride. A little magnesium chloride (about 4 to 6 per cent), however, if present, raises the solution away from the astrakanite field so that we may have only sodium chloride and magnesium sulphate to deal with. The solubilities of these two salts and solid phases are affected so differently by the temperature that it is possible to separate epsom salt and sodium sulphate from the solution by cooling. The solubility data of the system ha~~s~~ve shown that it is possible to separate epsom salt in pure form from the solution by cooling to 10°C and the recovery of epsom salt from the solution is about 50 per cent.

The stable salt pair at lower temperatures is sodium sulphate and magnesium chloride. The transition temperature is about 3°C and below this temperature, the remaining magnesium sulphate reacts with sodium chloride to form sodium sulphate and magnesium chloride. The solid phase of sodium sulphate at lower temperatures is Glauber's salt ($Na_2SO_4.10H_2O$). By chilling the solution to 0°C, preferably -5°C, separation of Glauber's salt can be affected. As the solubility of sodium sulphate decreases with increase in concentration of sodium chloride, 80 per cent of sodium sulphate formed, can be separated from the solution saturated with sodium chloride at -5°C. The Glauber's salt melts at 32°C and changes to anhydrous sodium sulphate. By adding sodium chloride to the melt liquor, the sodium sulphate retained in the liquor is also precipitated out. Thus anhydrous sodium sulphate is obtained.

These are the bas~~i~~es for the separation of epsom salt and sodium sulphate from sel's mixts.

DESCRIPTION OF THE PROCESS

The process mainly consists of five steps which can be broadly divided as (1) Hot extraction of potassium chloride from mixed salt (2) Decomposition of carnallite (3) Recrystallisation of impure potassium chloride (4) Treatment of sel's mixts, recovery of epsom salt and Glauber's salt (5) Recovery of anhydrous sodium sulphate from Glauber's salt.

(1) Hot extraction of potassium chloride from mixed salt

Ground mixed salt of 20 to 30 mesh size containing 18 to 20 per cent potassium chloride is mixed in a definite ratio of 1 kg mixed salt with 1 gallon or 4.5 litres of 36° Be bittern in a dissolver. The slurry is stirred and heated to 110°C by steam when most of the potassium chloride goes into solution. The concentration of potassium chloride in the hot liquor raises up to 5 to 5.5 g per 100 ml. on complete extraction. Magnesium sulphate and sodium chloride remain insoluble in the liquor. The slurry is filtered hot in a pressure filter, to maintain the temperature of the liquor hot (not below 85°C), so that carnallite is not lost due to crystallisation during the filtration along with the sel's mixts cake. The hot filtrate is then fed to crystallisers where, on cooling to room temperature (30°C), carnallite crystals are separated out from the slurry in a centrifuge. The effluent is reused for extraction of potassium chloride from fresh mixed salt, as the composition of the mother liquor will be practically the same as that of 36° Be bittern. The sel's mixts cake obtained from pressure filter containing mainly kieserite and sodium chloride is passed on to sel's mixts dissolvers for further treatment.

(2) Decomposition of carnallite

Carnallite crystals are then decomposed with water added in the ratio of 2:1 (2 kg carnallite to one kg or litre of water). Most of the magnesium chloride goes into solution with small amounts of sodium and potassium chloride leaving behind a residue of impure potassium chloride. The decomposed slurry is centrifuged in order to separate impure potassium chloride from the mother liquor. The effluent (mother liquor) has density 32.5° Be. This is further concentrated to 36° Be by forced evaporation, when the composition compares reasonably with hot carnallite liquor. This is fed to the carnallite crystalliser for further recovery of carnallite. The impure potassium chloride containing mainly 60 to 65 per cent potassium chloride and 35 to 40 per cent sodium chloride is passed on to recrystallisers or purifiers where it is further purified.

3) Recrystallisation of impure potassium chloride

The impure potassium chloride is heated with a solution saturated with both the salts, namely, sodium chloride and potassium chloride at room temperature. The impure potassium chloride (containing 60 to 65 per cent KCl) and saturated NaCl-KCl solution is heated to 110°C by steam. At high temperature, potassium chloride goes into solution. The slurry is filtered hot in a pressure filter. The cake contains mostly sodium chloride with small amounts of potassium chloride. This cake is reused for preparing saturated NaCl-KCl solution. Hot clear filtrate is cooled in crystallisers to room temperature to obtain pure potassium chloride. The crystal slurry is then centrifuged. Potassium chloride obtained contains less than 3 per cent sodium chloride and 3 to 4 per cent moisture. The product is further dried in a drier to obtain a product containing not more than 1 per cent moisture with an assay of potassium chloride not less than 96 per cent. Sodium chloride in the final product is controlled by a slight wash during centrifuge. Mother liquor (saturated NaCl-KCl solution) is recycled for recrystallisation of another batch of impure potassium chloride. Mother liquor cannot be used indefinitely as magnesium chloride content in the mother liquor goes on increasing. When the magnesium chloride in mother liquor reaches 7 per cent (w/v) the solution is used for carnallite decomposition (instead of water as stated earlier). Fresh saturated NaCl-KCl solution is prepared from sodium chloride cake containing potassium chloride and impure potassium chloride.

(4) Treatment of sel's mixts and recovery of epsom salt and Glauber's salt

A) Sel's mixts cake obtained after hot extraction of mixed salt is dissolved in water at room temperature so as to dissolve most of magnesium sulphate. After dissolution the slurry is filtered. The filter cake contains mostly sodium chloride and insolubles and hence it can be sent to waste. The clear filtrate is cooled to 10°C by refrigerated brine, when epsom salt crystallises out. The epsom salt is then centrifuged and the mother liquor obtained is used for Glauber's salt recovery.

B) The mother liquor obtained from centrifuging epsom salt is saturated with sodium chloride (sodium chloride content in the liquor reaches to 21 g. per 100 ml). The saturated liquor is then cooled to -5°C by refrigerated brine when Glauber's salt ($Na_2SO_4.10H_2O$) crystallises out. The crystal slurry is centrifuged and the mother liquor which contains mainly sodium chloride is allowed to go to waste through a heat exchanger where it is used to cool the incoming filtered sel's mixts solution.

5) Recovery of anhydrous sodium sulphate

The process consists of melting Glauber's salt and precipitating anhydrous sodium sulphate at 60°C by addition of powdered sodium chloride. The addition of sodium chloride depresses the solubility of sodium sulphate which results in precipitation of anhydrous sodium sulphate. The method in detail is as follows. Glauber's salt is first melted at 60°C and the solution contains 37 g of sodium sulphate per 100 ml. Finely powdered sodium chloride is added to the solution and the mixture is stirred at 60°C for half an hour. During this time anhydrous sodium sulphate separates out and sodium chloride enters the solution. The slurry is centrifuged. The effluent is mixed with the mother liquor from epsom salt which is used for Glauber's salt separation. The centrifuged anhydrous sodium sulphate is further dried to get a product containing less than 1 per cent moisture with an assay of sodium sulphate not less than 97 per cent.

3A) EXTRACTION OF POTASSIUM CHLORIDE AS CARNALLITE, DECOMPOSITION OF CARNALLITE AND PURIFICATION OF IMPURE POTASSIUM CHLORIDE TO OBTAIN FERTILISER GRADE POTASSIUM CHLORIDE, AND COLLECTION OF SEL'S MIXTS CAKE

Laboratory experiments

1) 400 g of ground mixed salt (30 to 40 mesh size) analysing 37.72 per cent magnesium sulphate 13.87 per cent magnesium chloride 18.00 per cent sodium chloride and 21.14 per cent potassium chloride was mixed with 3.2 litres of 36° Be bittern. The heating was carried out in glass beaker with stirring arrangement when the bittern was heated to 117°C, it started boiling. The ring burner was closed and stirring was carried out at 110 to 115°C for half an hour. 100 ml of hot solution was filtered on small b~~eak~~uchner funnel and the solution and the separated solid was heated again to 110°C. 5 ml of the sample was diluted to 500 ml and the concentration of potassium chloride in hot solution was found out (4.9 per cent KCl in hot solution). The contents of the beaker were filtered on a buchner funnel with filter cloth. The hot solution was cooled to room temperature and the carnallite obtained was centrifuged. The details of the analysis are given in the Table 48. The recovery of potassium chloride from mixed salt was 85 per cent.

2) Studies were carried out to find out whether mixed salt can be separated in fractions rich in potassium chloride or major portion of sodium chloride could be eliminated by mechanical means such as seiving 316 lbs of ground mixed salt

Table 48 EXTRACTION OF MIXED SALT (Laboratory results)

	Mixed salt		36° Be bittern		Carnallite		Sel's mixts		36° Be bittern	
Quantity	400 g		1.6 L		400 g		350 g		1.55 L	
Composition	Per cent	Total salts (g)	Per cent (w/v)	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent (w/v)	Total salts (g)
KCl	21.14	84.6	1.50	24.0	19.50	78.0	2.50	8.8	1.40	21.8
NaCl	18.00	72.0	2.02	32.3	4.50	18.0	15.90	55.7	1.98	30.7
$MgCl_2$	13.87	55.5	35.42	566.5	24.71	98.8	8.87	31.0	31.90	495.4
$MgSO_4$	37.72	150.9	7.12	113.8	0.51	2.0	40.72	142.5	7.76	120.2

in roller crusher was seived by using vibrating screen; and four fractions were collected (1) Coarser fraction 124 lbs (2) Fraction below 10 mesh 51 lbs (3) Fraction below 18 mesh size 82 lbs (4) Fraction below 20 mesh 59 lbs. Fractions 1,2,3 and 4 were analysed for sodium and potassium content by using flame photometer. The results are given below:

Sample	KCl	NaCl
	Per cent	
1	15.80	28.50
2	15.07	25.12
3	15.96	30.42
4	15.88	28.57

The experiment showed that it was not possible to separate a fraction rich in potassium chloride by such mechanical means.

3) <u>Seive analysis of mixed salt</u>

Grinding of mixed salt on roller crusher gave following seive analysis, of mixed salt which was used for experiments.

Particle size (B.S.S)	lbs	Per cent
+ 10 mesh	6	16
- 10 + 14 mesh	6	16
- 14 + 17 mesh	10	26
- 17 mesh	16	42
	38 lbs	100

The seive analysis of mixed salt passing through first set of rollers showed that 42 per cent of mixed salt was crushed below 17 mesh size; while after passing through the second set of rollers gave 78 per cent mixed salt below 17 mesh size.

4) Measurement of bulk densities

The following bulk densities of various solid material available in the process were measured.

a) Mixed salt	59.98 lbs/cu.ft.	=	961 kg/cumm.
b) Sel's mixts	110.20 lbs/cu.ft.	=	1766 kg/cu.m.
c) Carnallite	57.8 lbs/cu.ft.	=	925.8/cu.m.
d) Potassium chloride (centrifuged)	57.8 lbs/cu.ft.	=	925.8 kg/cu.m.
e) Potassium chloride dried at 110°C	58.05 lbs/cu.ft.	=	1090 kg/cu.m.
f) Epsom salt	51.26 lbs/cu.ft.	=	821.2 kg/cu.m.

5) Studies on concentration of potassium chloride in hot extraction of mixed salt

Studies were carried out to study the concentration of potassium chloride reached by hot extraction of mixed salt with 36°Be bittern in the counter-current method revealed the following results. Hot bittern obtained after extraction from the first vessel was taken to the second vessel where it met with fresh mixed salt. The concentration of potassium chloride in hot bittern rose from 3.5 to 5.5 per cent (w/v) leaving 2.5 per cent potassium chloride in sel's mixts of the first vessel and 5.8 per cent potassium chloride in the sel's mixts of the second vessel. The two sel's mixts were mixed and when treated with fresh bittern at 110°C showed that potassium chloride concentration in hot bittern was only 3.25 and again 2.5 per cent potassium chloride was left out in the sel's mixts. Treatment of sel's mixts again with fresh bittern showed that 1.5, 2.1 and minimum 0.8 per cent potassium chloride was left out with sel's mixts.

The method did not work well because the hot bittern was already concentrated with potassium chloride in the first vessel itself. Addition of hot bittern in a second and third vessel was not met with any advantage. In fact the carnallite obtained by second heating of sel's mixts with fresh bittern contained more of sodium chloride and 1.5 to 2 per cent potassium chloride was always left out with the sel's mixts. The test samples drawn during heating of mixed salt with 36° Be bittern showed the following results. The experiment was performed in the following manner. 4 litres of 36° Be bittern was first heated to 110°C and 1 kg of ground mixed salt was added. The temperature of bittern fell down to 100°C as a result of addition of mixed salt. The temperature of the reaction mixture was then raised to 110°C. Readings of potassium chloride concentration in the hot test samples showed the following results.

15	minutes after addition	3 per cent KCl
30	" "	3.2 "
40	" "	4.01 "
45	" "	4.0 "

It was obvious that a minimum half an hour stirring at 110°C was essential.

(6) Mixed salt varying composition

Studies were carried out on mixed salt samples of varying composition such as (1) obtained from Kharaghoda containing 24.75 per cent magnesium sulphate, 16.91 per cent sodium chloride, 3.7 per cent magnesium chloride and 19.52 per cent potassium chloride. The studies showed that due to much less concentration of magnesium chloride in mixed salt and retention of 10 to 13 per cent magnesium chloride in sel's mixts cake the 36° Be bittern was deprived of magnesium chloride content with the result that the efficiency of extraction was only 50 to 60 per cent. Utilisation of bittern with 30 per cent total chloride content or 37 to 38 per cent magnesium chloride content, showed 80 to 85 per cent recoveries of carnallite(see table 49-A).(2) In case of Kandla mixed salt which contained only 10 to 14 per cent potassium chloride 40 to 50 per cent sodium chloride, the efficiency of extraction was 80 to 85 per cent but yield of carnallite obtained was half that obtained by utilisation of mixed salt of normal composition. It was found ~~out~~ that addition of double the quantity of mixed salt was not suitable as the ratio of solid to liquid was doubled which created different problems such as choking in dissolvers and filter capacities were low. Moreover sel's mixts cake contained 50 per cent sodium chloride which also effected the recovery of epsom salt. The difficulties were solved by using 1) a little less mixed salt 1.40 kg equivalent to 20 per cent KCl instead of 2 kg and by satisfying with less recoveries of carnallite. (2) The hot extracted solution was allowed to settle for an hour to remove the excess of sodium chloride coming in the filter cake. (3) Due to long storage, magnesium chloride content of mixed salt was drained off and a part of potassium chloride was converted to schoenite.

Table 49 A EXTRACTION OF KHARAGHODA MIXED SALT

(Ratio 0.454 kg (1 lb) with 1 litre of 36° Be bitterns and two extractions). Composition of Kharaghoda mixed salt:- KCl 19.52, NaCl 16.91, $MgCl_2$ 3.7, and $MgSO_4$ 24.75 per cent.

	Mixed salt	Carnallite obtained		Carnallite obtained		KCl recovery Per cent	Analysis (hot liquor)		36° Be bittern used for extraction.
		Per cent KCl	Quantity (g)	Per cent KCl	Quantity (g)		I	II	Per cent (w/v)
							Per cent (w/v)		
1	0.454 kg (1 lb)	16.98	150	15.7	140	54.26	4.02	3.8	34.9 $MgCl_2$ (Total chloride 28)
2	0.454 kg (1 lb)	17.6	153	18.42	190	70.86	4.25	4.8	37.3 $MgCl_2$ (Total chloride 29)
3	0.454kg (1 lb)	18.02	188	18.4	192	78.84	4.25	4.0	38.6 $MgCl_2$ (Total chloride 30)

Table 49 B TREATMENT OF MIXED SALT CONVERTED TO SCHOENITE

0.9 kg (2 lbs) mixed salt was heated with 4 litres of 36° Be bittern and two extractions were carried out.

<u>Composition of mixed salt sample</u> $CaSO_4$ 1.18, K_2SO_4 17.86, $MgSO_4$ 12.84, $MgCl_2$ 7.32, and NaCl 51.50 per cent.

Composition Quantity	Carnallite 450 (g) Per cent	Carnallite 1800 (g) Per cent	Residue I 1200 (g) Per cent	Residue II 1210 (g) Per cent	Mother liquor Per cent 1	Mother liquor Per cent 2	Mother liquor weight/volume 3
KCl	19.20	12.69	2.02	0.92	0.84	1.4	0.87
NaCl	3.74	1~~2~~8.64	28.23	25.90	1.52	1.52	1.5
$MgSO_4$	0.56	0.81	22.47	29.95	5.50	4.48	4.46
$MgCl_2$	31.29	22.41	13.34	13.07	38.06	36.89	39.03

Per cent recovery of KCl	62.8 ~~96.4~~	as pure carnallite
	15.86 ~~18.3~~	as impure carnallite
	Total recovery ~~87.3~~ 78.74	

In the treatment of such mixed salt it was observed that it was also possible to extract carnallite with 36° Be bittern with higher concentration of magnesium chloride content such as 37 per cent. Recoveries of potassium as carnallite were 78.79 ~~80~~ per cent (table 49-B).

(7) Studies on separation of sodium chloride in carnallite

A saturated solution (36° Be bittern) with carnallite was allowed to cool to room temperature and various fractions were isolated between different temperature ranges (Table 50). (1) First fraction between 110°C to 90°C gave approximately 150 g. carnallite analysing sodium chloride 4.33 per cent magnesium chloride 22.13 per cent potassium chloride and 19.33 per cent. (2) Second fraction separated between 90°C to 80°C gave 90 g of carnallite NaCl 1.07, KCl 26.78, and $MgCl_2$ 30.78 per cent. (3) Third fraction separated between temperature range of 80 to 35°C contains sodium chloride 5.72, magnesium chloride 27.8 and potassium chloride 17.08 per cent. The result showed that sodium chloride had separated in the first fraction and in the last fraction and it was not possible to obtain carnallite free of sodium chloride.

Table 50 AMOUNT OF CARNALLITE CRYSTALLISATION AT VARIOUS TEMPERATURE RANGES FROM HOT EXTRACTED SOLUTION

No.	Temperature range	Per cent separation
1	100 to 80°C	4.4
2	80 to 60°C	36.2
3	60 to 40°C	36.8
4	40 to 30°C	19.6

8) Decomposition of carnallite

Carnallite as obtained by extraction of mixed salt analysed potassium chloride 18 to 20 per cent, sodium chloride 4 to 6 per cent, and magnesium chloride 28 to 30 per cent. Impurity of sulphate as magnesium sulphate was negligible but often due to leaks or improper fixing of filter cloth 0.5 per cent magnesium sulphate was obtained in carnallite. The decomposition of carnallite was studied to find out whether technical grade potassium chloride could be directly obtained. It was observed that when the carnallite was decomposed with 1:1 ratio 20 per cent potassium chloride was obtained as 94 to 95 per cent purity. The end liquor when treated with fresh carnallite gave impure potassium chloride assaying 50 per cent potassium and sodium chlorides. When carnallite was decomposed with water 1:0.5 ratio, 876 ~~80~~ per cent recovery of potassium chloride (from the original) was directly obtained as impure potassium chloride; the analysis of impure potassium chloride was 60 to 65 per cent potassium chloride. The results are reported in Tables 51 and 52.

9) Recrystallisation of impure potassium chloride

Impure potassium chloride containing 60 to 65 per cent potassium chloride was treated with NaCl-KCl solution (saturated with both these salts at 25°C) and heated to 110°C (112°C B.P). The purity and yield of potassium chloride obtained and the increase in concentration of magnesium chloride in solution in each cycle was studied (Tables 53 and 54).

Studies carried out on the amount of carnallite and KCl separation from hot solutions are reported (Tables 50 and 55).

Table 51 DECOMPOSITION OF CARNALLITE (1 kg carnallite + 500 ml. water) (At room temp.)

Contents	Carnallite 1 kg		Impure KCl 345 g		End liquor obtained 850 ml 32° Be	
	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)
KCl	22.36	223.6	56.2	196.00	3.25	27.63
NaCl	10.15	101.5	20.56	70.94	3.60	30.63
$MgCl_2$	26.45	264.5	2.50	8.60	30.10	255.85
$MgSO_4$	nil	-	-	-	-	-

Recovery of KCl as impure KCl was 87.6 per cent

10) Studies on separation of sodium chloride along with pure potassium chloride in recrystallisation of impure potassium chloride

A saturated solution of potassium and sodium chloride containing KCl 11.0, NaCl 20.5, $MgCl_2$ 4.15, $MgSO_4$ 0.0 per cent was used for the purification of impure potassium chloride obtained by decomposing of carnallite. The composition of impure potassium chloride was KCl 67.61, ~~and~~ NaCl 24.11 per cent and $MgCl_2$ 0.4 per cent. The details of the results are reported in Table 55.

Table 52 DECOMPOSITION OF CARNALLITE (in 1:1 ratio)

500 g carnallite was decomposed with 500 g water. The recovery of potassium chloride was 20 per cent and product was contain~~ing~~ed 95 per cent potassium chloride. The decomposed liquor was treated with 500 g fresh carnallite to recover the KCl in solution. The second fraction of impure potassium chloride thus obtained contained 50 to 58 per cent potassium chloride and the overall recovery was 80 per cent.

	Carnallite 500 g		1st Fraction 47 g		Solution A 920 ml		Carnallite 500 g		IInd Fraction. 230 kg		Solution B. 940 ml	Total salts (g)
	Per cent	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)	Per cent (w/v)	
KCl	22.36	111.8	95	44.65	7.3	67.15	22.36	111.8	58.34	134.11	3.05	28.67
NaCl	10.15	50.8	5	2.35	5.27	48.5	10.15	50.8	43.04	99.00	3.60	34.04
$MgCl_2$	28.45	142.2	-	-	14.28	132.2	28.45	142.2	2.06	4.74	29.50	278.3
Recovery of KCl per cent			20						60		(20 loss)	

Table 53 RECRYSTALLIZATION OF IMPURE POTASSIUM CHLORIDE - FIRST CYCLE (Laboratory Experiments)

	KCl - NaCl mixture		Extraction solution		Recrystallized KCl		Solid residue		End liquor		Deviation
	Wt.800 g		vol. 4000 ml		470 g		Wt. 219 g		vol.3840 ml		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	61.0	488.0	10.5	420.1	97.4	457.8	6.16	13.5	11.5	441.6	+ 0.4
NaCl	31.01	248.1	19.5	780.0	1.54	7.4	91.02	199.3	21.5	825.4	+ 4.05
$MgCl_2$	0.4	3.2	3.8	152.9	0.29	1.4	0.65	1.44	4.2	158.6	- 1.67

1) Recovery of KCl 92.9 per cent

2) Concentration of $MgCl_2$ in extraction solution has risen from 3.2 to 4.2 during the first cycle.

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Table 54 RECRYSTALLISATION OF IMPURE POTASSIUM CHLORIDE (SECOND CYCLE); - EXTRACTION SOLUTION OF THE FIRST CYCLE WAS RECYCLED (laboratory experiment)

	Impure potassium chloride		Extraction (NaCl-KCl) solution		Recrystallised KCl		Solid residue		End liquor		Deviation
	800 g		3840 ml		400 g		410 g		3750 ml		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	66.4	531.2	11.5	441.6	97.94	391.76	25.37	104.0	12.5	477.5	+ 0.46
NaCl	25.1	200.8	21.5	825.4	1.784	7.14	70.2	287.82	19.0	712.5	- 18.7
$MgCl_2$	0.4	3.2	4.15	158.6	0.28	1.12	0.67	2.75	4.34	162.8	+ 4.88

Concentration of $MgCl_2$ in extraction solution has risen from 4.2 to 4.34 per cent during the second cycle.

Table 55 FRACTIONS OBTAINED BY COOLING HOT NaCl-KCl SOLUTION TO VARIOUS TEMPERATURES

	Temp.	Vol. of liquid ml	Analysis of liquid at different temps. % KCl	%NaCl (w/v)	$\%MgCl_2$	Separation of solid between various temperature ranges (g)	Per cent separation of solid	Composition of solid %KCl	%NaCl
1)	110	800	23.5	20.5	3.85	31	29.83	96.78	3.22
2)	80	715	20.5	19.0	4.02	30	28.85	96.80	3.20
3)	60	700	18.0	19.0	4.00	38	36.55	97.05	2.95
4)	40	685	15.0	19.5	4.28	5	4.85	97.17	2.83
5)	30	685	11.5	19.5	4.36				
						104			

II A 2) Description of pilot plant experiments

The Grinding operation of mixed salt was carried out with an edge runner and the mixed salt was seived through a mechanical vibrator giving 20 to 30 mesh B.S.S size of which 70 per cent ~~was~~ pass~~ing~~ed through 30 mesh. 36° Be bittern containing about 35 g magnesium chloride per 100 ml was pumped to the dissolver up to a previously made mark showing 500 litres of bittern. 114 kg of mixed salt was added to the dissolver through a bucket elevator. While charging of the mixed salt stirring was going on and the contents of the dissolver were kept under agitation. The slurry was heated by steam at 10 to 20 psi. Mixed salt addition was completed in ten minutes and the steam was raised to 30 psi. After attaining the temperature (110°C) the slurry was stirred for half an hour at the same temperature. Arrangements were made in the meantime to filter 100 to 200 ml hot liquor on the buchner funnel. The hot filtrate was heated to 110°C in the laboratory; 10 ml of the hot solution was made to litre and the sample analysed on flame photometer for potassium chloride content. Testing two to three samples with 5 to 10 minutes interval gave an exact idea whether the bittern was saturated with carnallite or in other words potassium chloride was extracted in the hot bittern. In case of good extraction, the liquor showed 4.5 g KCl per 100 ml. The other indirect test which should show 20 to 22 g carnallite from the cooled hot sample per 100 ml of the solution. The hot slurry was then taken to a sparkler pressure filtration unit through a slurry pump. Mechanical stirring in the dissolver was continued till the whole solution was filtered in the sparkler unit. The time required for this operation was 10 to 12 minutes. Compressed air was passed after closing the inlet valve of the sparkler unit. The slurry pump was stopped and most of the solution was flushed out by compressed air. The outlet valve of the sparkler unit was then closed and scavanger valve was only kept open. Air at 50 psi. was slowly built up in the unit by increasing slowly the compressed air. After the scavanging operation was over, the compressor was stopped and the pressure in the vessel was released. The top of the sparkler unit was opened and the inside cartridge was removed out by a hand operated hydraulic crane. Removal of hot cake was done after allowing it to cool for two hours and sel's mixts was stored separately for further treatment. The results are given in the table 56-A. Recovery of potassium chloride as carnallite from mixed salt in this operation was 83 per cent. Results of crystallisation of carnallite in Swanson-Walker crystalliser are given in Table 57.

The following experiments in which extraction of 114 kg (250 lbs) of mixed salt with 500 litres of 36° Be bittern was carried out showed that the efficiency of carnallite extraction from mixed salt was 85 per cent (Table 56 B) and on an average the carnallite obtained contained 19 to 20 per cent potassium chloride with 4 to 6 per cent sodium chloride as impurity. The steam consumption noted from the condensed steam from steam trap was found to be on an average 70 litres.

Table 56 A EXTRACTION OF MIXED SALT (Pilot plant data)

(Scale of operation: 114 kg of mixed salt and 500 litres of bittern (36° Be)

Description	Mixed salt		36°Be bittern		Anal-ysis (hot liquor)	Carnallite		M.L.after centrifuge 450 litres 36° Be		Residue (Sel's mixts) 100 kg		Dev-iat-ion
Quantity	114 kg (250 lbs)		500 litres			95.5 kg (210 lbs)						
Density			36°Be									
Composition	Per cent	Total salts (kg)	%	Total salts (kg)	% (w/v)	%	Total salts (kg)	% (w/v)	Total salts (kg)	%	Total salts (kg)	(kg)
KCl	20.0	22.8	1.5	7.5	5.6	19.8	18.91	1.8	8.10	2.1	2.1	1.2
NaCl	18.0	20.52	3.5	17.5	-	6.0	6.73	3.4	15.3	16.6	16.6	0.4
$MgCl_2$	13.8	15.73	34.4	172	36.0	28.6	27.3	34.0	153	8.0	8.0	0.6
$MgSO_4$	30.8	35.11	6.5	32.5	-	0.8	0.8	6.9	31	35.4	35.4	0.4
Insolubles	1.2	1.37	-	-	-	-	-	-	-	1.4	1.4	-
Combined moisture & free moisture	16.2	18.47	-	-	-	-	-	-	-	-	-	-
Total salts	83.8	95.53	45.9	229	-	58.2	52.7	46.1	207	62.1	62.1	1.4
Balance	16.2	18.47	-	-	-	44.8	42.8	-	-	37.9	37.9	-

Table 56 -B EXTRACTION OF MIXED SALT (Pilot plant experiments)

	KCl reading in extraction liquor at 110°C. %(w/v)	Carnallite obtained (kg)	Composition of carnallite KCl (Per cent)	NaCl	Recovery of KCl %	Steam condensed litres
1)	4.9	100	19.5	4.5	85 average	70
2)	5.0	95	19.47	6.0		70
3)	5.2	98	19.80	6.2		69.5
4)	4.95	97	19.00	4.8		70

20 g of carnallite was obtained per 100 ml of hot (extracted) solution.

Table 57 CRYSTALLISATION OF CARNALLITE IN S.W.CRYSTALLISER

Hot extracted bittern obtained by treatment of 114 kg mixed salt /500 litres of bittern was filtered and 250 litres of hot bittern was pumped to S.W. crystalliser and cooled to room temperature by circulation of tap water. Rate of feed of tap water was 300 gallons/hr.

Time	Water temp. Inlet (°C)	Outlet (°C)	Bath temp. (°C)	Time	Water temp. Inlet (°C)	Outlet (°C)	Bath temp. (°C)
3-00	30.5	38	85	4-20	30.5	32	39.8
3-10	30.5	37	74	4-30	30.5	32	38.1
3-20	30.5	35	64	4-40	30.5	32	37.0
3-30	30.5	34	56.5	4-50	30.5	31.5	36.1
3-40	30.5	33	51	5-00	30.5	31.5	35.5
3-50	30.5	32.5	46.5	5-10	30.5	31.5	35
4-00	30.5	32	43.5	5-20	30.5	31.5	34.6

Total time required 2 hours and 20 minutes.

Decomposition of carnallite

47.8 litres of water was exactly measured and added to a stainless steel open pan evaporator fitted with anchor type stirrer moving at 60 r.p.m. 95.5 kg of the carnallite was added to water (manually). While the charging of the carnallite was continued the stirring was going on and the contents of the dissolver were kept under constant agitation. The sequence of the operation was found necessary as the load on the motor was increased which often trips off if the sequence was reversed. The mass was stirred for 10 to 15 minutes and samples were taken to measure the density with 30 to 40° Be hydrometer preferably graduated at 28°C. Samples were also drawn to estimate potassium content in the solution by flame photometry. In absence of flame photometer, density and total chloride reading was relied upon. The slurry was then centrifuged. The results are given in Table 58. Recovery of potassium chloride as impure potassium chloride from carnallite was 85 per cent.

Decomposition of carnallite in one to one ratio as carried out in laboratory experiments to obtain directly potassium chloride from carnallite was repeated on pilot plant scale. 27.24 kg (60 lbs) of carnallite containing 20.2 per cent potassium chloride, 5.2 per cent sodium chloride, 28.3 per cent magnesium chloride was mixed with 27 litres of water and stirred. The solution was filtered to obtain 2.3 kg (5 lbs) of solid which analysed 94 per cent potassium chloride and 6 per cent sodium chloride. The solution obtained above was again treated with fresh 27.24 kg (60 lbs) of carnallite of the same composition. The impure potassium chloride obtained was 12 kg (26 lbs) containing 50 per cent potassium chloride and 50 per cent sodium chloride. The analysis of the end liquor solution was similar to carnallite decomposed liquor obtained by 1:0.5 ratio treatment. Composition of the first solution was KCl 7.3, $MgCl_2$ 15.6, NaCl 5.6 per cent, while of the second solution was KCl 3.5, NaCl 2.8 and $MgCl_2$ 28 per cent. Thus on an average only 20 per cent of the total potassium chloride was obtained as 94 per cent pure product, while the remaining 60 per cent potassium chloride was obtained as impure potassium chloride containing 50 per cent potassium chloride and 50 per cent sodium chloride.

Evaporation of carnallite decomposed liquor

91 litres of carnallite decomposed liquor obtained after centrifuging the impure potassium chloride was pumped to a stainless steel steam jacketted evaporator. The density of carnallite decomposed liquor was 32.5° Be before starting the evaporation. Heating was done by steam. Samples were taken when the density of the hot solution was approaching 37° Be (at 110°C). The hot sample was immediately cooled to room temperature, filtered on buchner funnel. The filtrate was tested for density, (37° Be hot showed 36° Be at room temperature) and potassium chloride content by flame photometer. As soon as the potassium chloride value was shown between 1.5 to 1 per cent, the heating was stopped and the hot slurry was allowed to cool in small trays to obtain additional

Table 58 DECOMPOSITION OF CARNALLITE

(Scale of operation:- 95.5 kg of carnallite and 47.8 litres of water).

Description	Carnallite		Water	Impure Potassium chloride		Decomposed liquor		Deviation
Quantity	95.5 kg		47.8 L	25 kg		91.3 L		(kg)
Density	-		-	-		32.5° Be		-
Composition	Per cent	Total salts (kg)		Per cent	Total salts (kg)	Per cent (w/v)	Total salts (kg)	
KCl	19.8	18.0	-	64.1	16.0	3.4	3.1	0.2
NaCl	6.0	5.7	-	12.0	3.0	3.0	2.7	-
$MgCl_2$	28.6	27.3	-	8.7	2.2	26.5	24.2	0.9
$MgSO_4$	0.8	0.8	-	trace	-	1.0	0.9	0.1
Insolubles	-	-	-	-	-	-	-	-
Combined & free moisture at 110°C	44.8	42.8	-	7.2 8.0	3.8	-	-	-
Total salts.	55.2	52.8	-	84.8	21.2	-	30.9	0.6
Balance	44.8	42.8	-	15.2	3.8	-	-	-

KCl yield = 84.6 per cent Decomposed liquor = 15.4 per cent crop of carnallite. The composition of the end liquor after separation of carnallite agreed practically with the 36° Be bittern used for extraction of mixed salt. The results of the experiments are given in Table 59. The recovery of potassium chloride as carnallite from carnallite decomposed liquor was 80 per cent.

Recrystallisation of impure potassium chloride

155 litres of saturated NaCl - KCl solution 29° Be containing 14 per cent potassium chloride 18 per cent sodium chloride, and 0.5 per cent magnesium chloride was measured and added to 100 litre (25 gallon) capacity stainless steel steam jacketted evaporator. Steaming and addition of 25 kg impure potassium chloride was simultaneously started. When the temperatures of 110°C was reached, a sample of hot solution was immediately filtered on buchner funnel and analysed by flame photometer only for its potassium chloride content. As soon as the analysis showed 24 g potassium chloride per 100 ml of solution, the heating was slowed down and the hot slurry was filtered in sparkler pressure filter. The operation was clean and smooth. The stirring of the slurry in the vessel was continued during filteration as the slurry would settle fast. The cake in the filtration unit was analysed for potassium chloride to find out the loss of potassium chloride with the cake. The analysis of the end liquor showed that the composition was similar to the earlier one with the difference that magnesium chloride was concentrating in the saturated NaCl-KCl-liquor. The recovery of potassium chloride from impure potassium chloride was

Table 59 EVAPORATION OF CARNALLITE DECOMPOSED LIQUOR

Scale of operation 91 litres of carnallite decomposed liquor was evaporated.

Description	Decomposed liquor		Salt separation at 37° Be hot (110°C)		End liquor		Deviation
	Per cent (w/v)	Total salts (kg)	Per cent	Total salts (kg)	Per cent (w/v)	Total salts (kg)	(kg)
Quantity	91 litres		15.9 kg		50 litres		-
Density	32. 32.5° Be		-		36.0°Be		-
KCl	3.4	3.1	19.0	3.0	1.5	0.75	0.65
NaCl	3.0	2.7	12.0	2.0	1.5	0.75	0.05
$MgCl_2$	26.5	24.2	32.0	5.1	36.2	18.1	1.0
$MgSO_4$	1.0	0.9	0.4	0.06	2.5	1.2	0.36

94 per cent (Table 60).

Regeneration of saturated NaCl-KCl liquor

It was found out that after 5 to 6 cycles the concentration of magnesium chloride in the saturated NaCl-KCl solution was raised to 7 to 8 per cent.

At this stage, the saturated NaCl - KCl solution was regenerated as follows. 50 litres of the solution analysing 11.5 per cent potassium chloride 19.0 per cent sodium chloride and 7.08 per cent magnesium chloride was mixed with 50 kg carnallite. The mixture was stirred for half an hour and samples were taken to find ~~out~~ the density which was 32.5° Be indicating all carnallite was decomposed. The slurry was centrifuged to obtain impure potassium chloride and carnallite decomposed liquor. The results are given in Table 61. The ratio of carnallite decomposition with water was 1 kg carnallite with 500 ml of water (or 1:0.5), while that when NaCl-KCl solution was used as above, the ratio was 1 kg carnallite with 1 litre of rejected KCl-NaCl solution (1:1). This simple modification of the process saved the costlier treatment of soda ash with saturated NaCl- KCl solution for eliminating the unwanted magnesium chloride concentrating in the crystallising liquor.

Table 60 RECRYSTALLISATION OF IMPURE POTASSIUM CHLORIDE

Scale of operation 25 kg of impure potassium chloride and 155 litres of NaCl - KCl solution

Description	Impure potassium chloride		NaCl-KCl solution		NaCl-KCl hot solution at 112°C	Potassium chloride pure		Mother liquor NaCl-KCl solution		Residue balance	
Quantity	25 kg		155 litres		-	16 kg		152 litres		4.6 kg	
Density	-		29°Be/28°C		31.0°Be/112°C	-		29.0°Be/28°C		-	
Composition	Per cent	Total salts (kg)	Per cent (w/v)	Total salts (kg)	Per cent (w/v)	Per cent	Total salts (kg)	Per cent (w/v)	Total salts (kg)	Per cent	Total salts (kg)
KCl	64.0	16.0	14.0	21.7	24.0	94.0	15.0	14.0	21.3	30.4	1.4
NaCl	12.0	3.0	18.0	27.9	18.6	3.0	0.5	18.0	27.4	65.2	3.0
$MgCl_2$	8.7	2.2	0.5	0.7	-	-	-	1.9	2.9	-	-
Combined moisture	7.3	3.8	-	-	-	3.0	0.5	-	-	4.4	0.2
Free moisture	8.0	-	-	-	-	-	-	-	-	-	-
Total salts		21.2		49.3	-	97.0	15.5 ~~97.0~~	3300	51.6	95.6	4.4
Balance		3.8				3.0	0.5			4.4	0.2

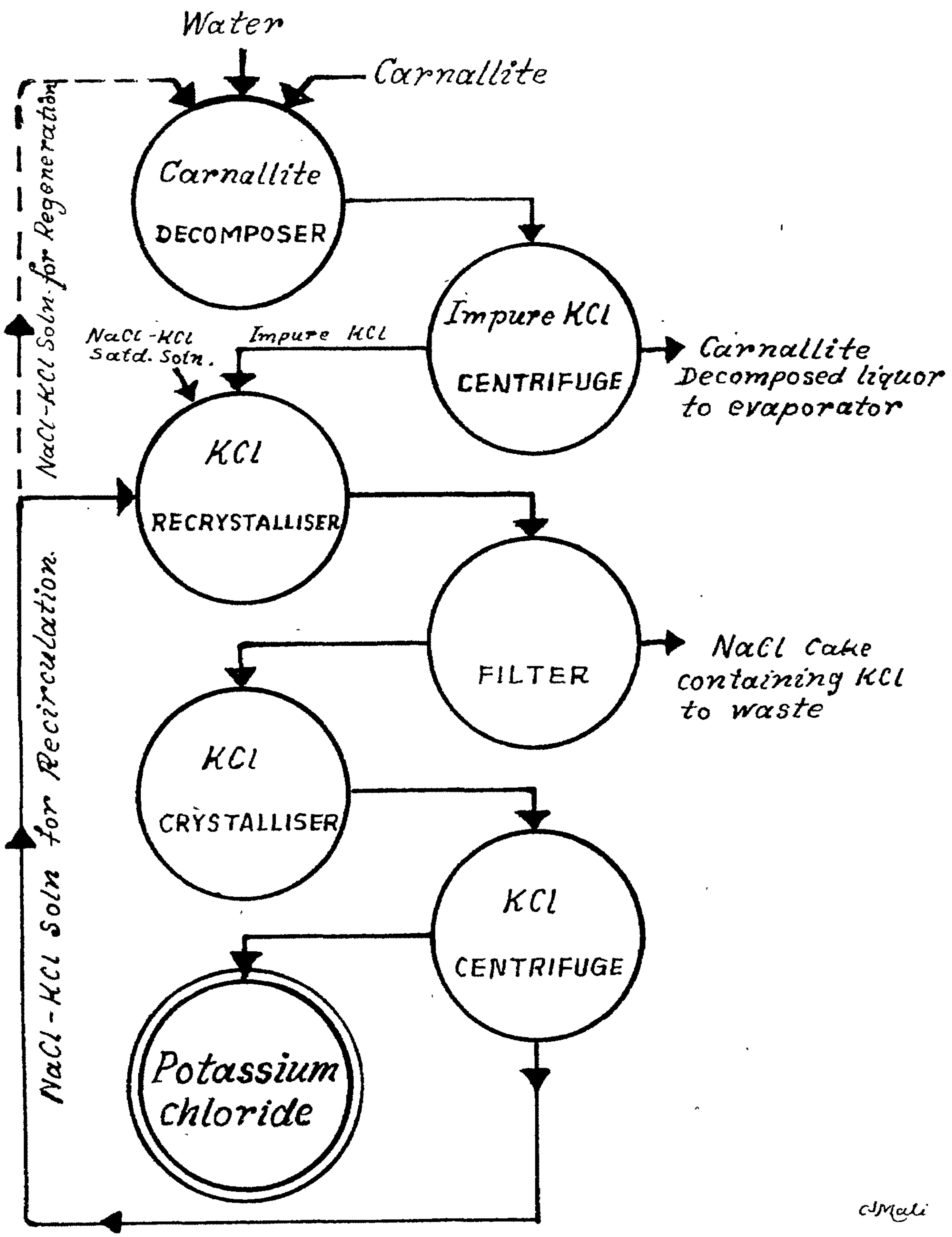
Table 61 REGENERATION OF NACl -KCl SOLUTION CONTAINING HIGH MAGNESIUM CHLORIDE CONTENT

Scale of operation 50 kg of carnallite and 50 litres of NaCl-KCl solution

	Extraction liquor (27.5° Be')		Carnallite		KCl-NaCl mixture		Decomposition liquor (30.5°Be')		Deviation
	50.00 litres		50.00 kg		23.00 kg		70.00 litres		
	Per cent (w/v)	Total salts (kg)	Per cent	Total salts (kg)	Per cent	Total salts (kg)	Per cent (w/v)	Total salts (kg)	(kg)
KCl	11.50	5.75	21.00	10.50	55.89	12.85	4.90	3.43	0.03
NaCl	19.00	9.50	4.97	2.48	39.20	9.02	4.25	2.98	0.02
$MgCl_2$	7.08	3.54	32.03	16.02	0.53	0.12	27.76	19.43	0.01

FIG. 25

FLOW SHEET FOR REGENERATION OF NaCl-KCl SATURATED SOLUTION.



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TREATMENT OF SEL'S MIXTS TO OBTAIN EPSOM SALT AND SODIUM SULPHATE AS BY-PRODUCTS

3-B-1 Laboratory experiments

Dissolution of sel's mixts

Experiments were carried out to find out how a saturated solution of magnesium sulphate could be obtained from sel's mixts cake. The composition of sel's mixts was not constant due to slight variations in mixed salt and the time required for filtration. The sel's mixts was dissolved in water by addition of sel's mixts to water in different proportions to find out which ratio would give a saturated solution of magnesium sulphate and at the same time the losses of magnesium sulphate in the residue was minimum. It was observed from Tables 62, 63 and 64 that 1:1 ratio was suitable to obtain maximum quantity of magnesium sulphate in solution. The tables showed how the solubility of sodium chloride and magnesium sulphate was almost similar and with the concentration of magnesium chloride in solution, the solubility of both the salts was reduced. The table 63 also pointed out that magnesium chloride could be washed off if sel's mixts contained magnesium chloride in excess by leaching sel's mixts with water in ratio of 5:1 where the losses of magnesium sulphate were minimum. The table 64 showed that it was not possible to obtain clear sel's mixts solution as fine kieserite particles remained in suspension. With the addition of extra water over the 1:1 ratio, the density of the solution was less, but even then, it was taking a long time to settle the solution and the maximum amount of such settled solution obtained was only 74 per cent. The

Table 62 TREATMENT OF SEL'S MIXTS TO STUDY EXTRACTION OF DIFFERENT SALTS

(Analysis of sel's mixts 25.3% $MgSO_4$ 25.3% NaCl 13.0% $MgCl_2$ 2.5% KCl)

Expt. No.	Ratio of treatment of sel's mixts with water	$MgSO_4$	$MgCl_2$	NaCl	KCl	R E M A R K S
		Per cent (w/v)				
1	1 : 1	20.57	9.00	13.00	0.60	Analysis of solution obtained.
		80	100	85	80	Per cent extraction efficiency
2	2 : 1	16.00	17.00	8.00	2.00	Analysis of the solution obtained
		29	80	23	60	Per cent extraction efficiency
3	3 : 1	15.00	16.00	6.00	1.26	Analysis of solution obtained
		16	58	11	22	Per cent extraction efficiency
4	4 : 1	10.00	23.00	3.00	1.20	Analysis of solution obtained
		6	52	3	14	Per cent extraction efficiency
5	5 : 1	9.00	26.00	2.00	1.00	Analysis of solution obtained
		5	42	2	13	Per cent extraction efficiency

Table 63 DISSOLUTION OF SEL'S MIXTS (Laboratory experiment 1)

No.	Ratio Sel's /Water mixts	Description	Quty.	$MgSO_4$	$MgCl_2$	NaCl	KCl	Recovery of $MgSO_4$ in solution	Loss of $MgSO_4$ in residue
1	3 : 1	Solid	420 g	36.34	5.10	38.37	1.70	20.2	79.8
	600 g/200 ml	Soln.	270 ml	14.30	18.90	6.20	2.70		
2	4 : 1	Solid	310 g	37.03	5.50	37.50	3.74	22.7	77.3
	400 g/100 ml	Soln.	155 ml	11.55	16.46	9.12	2.44		
3	5 : 1	Solid	390 g	37.80	7.70	29.75	2.06	6.9	93
	500 g/100 ml	Soln.	143 ml	9.81	23.50	3.64	2.80		
4	1 : 1	Solid	-	-	-	-	-	-	-
	500 g/500 ml	Soln.	710 ml	18.66	9.10	16.50	0.60	99.9	-

Table 64 DISSOLUTION OF SEL'S MIXTS (Laboratory experiment 2)

Analysis of sel's mixts $MgSO_4$ 29.75, $MgCl_2$ 11.68, NaCl 16.5 and KCl 2.6 per cent

	Ratio kg/litres	Settling period hours	Decanted solution		Total solution obtained		Residue	$MgSO_4$ in 100 g of residue (per cent)	Analysis of solution			
									$MgSO_4$	$MgCl_2$	NaCl	KCl
			ml	Per cent	ml	Density °Be'	(g)		per cent(w/v)			
1	1 : 1	88	485	37.31	1300	33°	230	15.92	18.77	8.94	10.00	1.5
2	1 : 1.3	71	1025	63.45	1615	29°	200	13.75	15.89	7.21	9.0	1.6
3	1 : 1.5	69	1365	73.94	1847	27°	200	7.80	14.85	6.35	8.0	1.6

results showed that filtration under pressure was essential.

Separation of epsom salt

(1) 2 litres of sel's mixts solution was chilled to + 10°C with constant agitation. The separated solid on analysis showed that it was containing 41.72 per cent magnesium sulphate (93.19 per cent epsom salt). The impurities of magnesium chloride and sodium chloride were minimised by washing the product with water in the centrifuging operation. The recovery of epsom salt was 50 per cent that of the original present in the sel's mixts solution (see Table 65). Separation of epsom salt was better in presence of higher concentration of magnesium chloride.

(2) Sel's mixts solution containing $MgSO_4$ 23.43 per cent, $MgCl_2$ 9.58 per cent, and NaCl 12.0 per cent was chilled to 10°C. The mother liquor showed $MgSO_4$ 12.0 per cent, $MgCl_2$ 10.62 per cent and NaCl 12.29 per cent. The yield of epsom salt was 340 g. assaying $MgSO_4$ 42.37 per cent, $MgCl_2$ 0.9 per cent, and NaCl 1.4 per cent. The recovery of magnesium sulphate was 61.38 per cent.

(3) Effect of $MgCl_2$ on separation of epsom salt.

Sel's mixts solution obtained by treatment of sel's mixts with water in 1:1 ratio was mixed with 100 ml. of 40 per cent solution of magnesium chloride and chilled to + 10°C. The solid obtained was 150 g. and was of the composition $MgSO_4$ 35.5 per cent, $MgCl_2$ 10.5 per cent NaCl 19.10 per cent. The mother liquor analysed $MgSO_4$ 5.2 per cent, $MgCl_2$ 20.2 per cent and NaCl 7.8 per cent. The recovery of $MgSO_4$ as epsom salt was over 67 per cent which was mainly due to increase in

Table 65 CHILLING OF SEL'S MIXTS SOLUTION TO + 10°C

	Sel's mixts solution. 2 litres		Separated epsom salt 370 g		Mother liquor 1.66 litres		Recovery
Composition	Per cent (w/v)	Total salts (g)	Per cent (w/w)	Total salts (g)	Per cent (w/v)	Total salts (g)	
$MgSO_4$	15.35	3070.0	41.7	154.40	9.20	152.70	Recovery of $MgSO_4$ as epsom salt is 50.3 per cent
$MgCl_2$	9.65	193.0	2.1	7.77	11.16	185.20	
NaCl	13.21	264.2	3.3	12.21	15.16	251.90	
KCl	1.74	34.8	-	-	2.10	34.85	

concentration of $MgCl_2$ in solution. However the product was impure as sodium chloride also precipitated along with epsom salt. As seen in earlier Tables 62, 63 and 64 if the concentration of $MgCl_2$ in sel's mixts solution was higher the concentration of $MgSO_4$ was low with the result that only 50 per cent recoveries were possible.

(4) Chilling of sel's mixts solution to + 10°C gave 50 per cent recovery of epsom salt and a mother liquor containing $MgSO_4$ 9 per cent, $MgCl_2$ 4.5 per cent, NaCl 7.0 per cent and KCl 0.3 per cent. Chilling the above solution to + 5 or 0°C gave no additional recoveries of epsom salt. However when the sel's mixts solution of the above composition was mixed with solid magnesium chloride ($MgCl_2.6H_2O$) to obtain 26 per cent concentration of $MgCl_2$ in the solution and chilled to + 10 and + 5°C, the recoveries of 30 and 40 per cent $MgSO_4$ as epsom salt was again obtained. The purity of the product was low containing 10 to 15 per cent sodium chloride. Thus the higher recovery of epsom salt was always accompanied with separation of sodium chloride as impurity, which was difficult to wash in centrifuging alone.

The Sel's mixts solution of the composition containing 9 to 10 per cent $MgSO_4$ was saturated with sodium chloride. The concentration of sodium chloride increased from 7 to 21 per cent. The saturated solution with sodium chloride was then chilled to -5°C. The solid obtained was 215 g analysing pure sodium sulphate. The recovery was 85 per cent (Table66). It was observed that 85 per cent of magnesium sulphate was

Table 66 CHILLING OF SEL'S MIXTS SOLUTION AT -5°C

	Sel's mixts solution.		Sel's mixts solution after saturation with NaCl		Centrifuged solid		Mother liquer solution	
Quantity	1 litre				215 g		780 ml	
Density	28.6° Be'		32° Be		-		29° Be	
Composition	Per cent (w/v)	Total salts (g)	Per cent (w/v)	Total salts (g)	Per cent	Total salts (g)	Per cent (w/v)	Total salts (g)
$MgSO_4$	9.00	90	9.00	90	-	-	1.73	13.50
$MgCl_2$	4.50	45	4.50	45	0.85	1.83	13.62	106.30
NaCl	7.00	70	21.20	212	3.26	7.00	16.71	130.4
KCl	0.30	3	0.30	3	-	-	0.37	2.88
Na_2SO_4	-	-	-	-	42.23	90.30	-	-

Recovery of magnesium sulphate as Glauber's salt was 85 per cent.

converted to sodium sulphate with a purity of 91 to 92 per cent. It was also observed that as the magnesium chloride was formed due to conversion of magnesium sulphate to sodium sulphate by interaction of $MgSO_4$ and NaCl. The influence of initial concentration of magnesium chloride on sodium sulphate conversion was significant.

The concentrations of magnesium chloride in the initial solution beyond 6 per cent seriously affected the conversion and the adjustment of magnesium chloride concentration by suitable dilution was very necessary.

Effect of magnesium chloride on conversion of magnesium sulphate to sodium sulphate was clearly indicated by the following experiments.

Composition of sel's mixts solutions containing 9.4 per cent magnesium sulphate, 20.7 per cent sodium chloride with varying concentrations of magnesium chloride on chilling to -5°C gave following results.

1.Exp. No.	1	2	3	4	5
2.$MgCl_2$ g/100 ml	12.9	8.7	5.9	5.0	3.0
3.Efficiency of conversion	14.3	38.2	66.4	82.0	85.05

Solubility relations of magnesium sulphate with magnesium chloride and sodium chloride are such that it was found difficult to obtain a saturated solution of magnesium sulphate containing more than 18 to 20 per cent magnesium sulphate. The solution which on chilling to 10°C gave 50 per cent recoveries of magnesium sulphate as epsom salt (Table 65). The mother liquor obtained was saturated with sodium chloride to obtain sodium sulphate.

The conversion of magnesium sulphate to sodium sulphate was 85 per cent. Chilling below -5°C did not give substantial increase in the yields. Thus 92.5 per cent of magnesium sulphate was recovered. The total sulphate recovered as epsom salt was 50 per cent and sodium sulphate (42.5 per cent) from the original sel's mixts solution.

In recrystallisation of epsom salt and sodium sulphate it was observed that epsom salt separated completely between the range of 15°C to 10°C in the above experiments. Temperature range of separation was only 5°C. In crystallisation of Glauber's salt, it was observed that separation of Glauber's salt started between + 3°C to -5°C and temperature range of separation was only 8°C. The density and compositions of sel's mixts solution at various stages is given in Table 67.

Table 67 DENSITY AND ANALYSIS OF SEL'S MIXTS SOLUTIONS

No.	Density ° Be	Composition of solutions (per cent w/v) MgSO$_4$	MgCl$_2$	NaCl	KCl	Condition
1	31°	16.36	7.66	11.5	1.15	Sel's mixts solution before chilling
2	28.6°	9.50	8.00	12.00	1.25	Solution after separation of epsom salt at + 10 °C
3	32°	9.50	8.00	21.50	1.25	Solution after saturation with sodium chloride
4	28.5°	2.50	15.00	21.00	2.5	Solution after separation of Glauber's salt at -5°C

B-2 PILOT PLANT EXPERIMENTS (Sel's mixts treatment)

i) Dissolution of sel's mixts

100 kg of sel's mixts analysing 35.1 per cent magnesium sulphate, 16.8 per cent sodium chloride, 8.0 per cent magnesium chloride and 2.1 per cent potassium chloride was mixed with 100 litres of water (1:1 ratio) and stirred for one to two hours. Density of the solution was taken at every half an hour interval. When the density was almost constant, the stirring was stopped and the slurry was allowed to settle for some time. It was observed that due to dissolution of kieserite in water, the temperature of the solution was raised to 45°C and the colour of the solution which was white was changed to brownish. The slurry was filtered in sparkler unit. The recovery of the magnesium sulphate in solution from the sel's mixts was 88.6 per cent (Table 68).

ii) Separation of epsom salt

150 litres of the clear sel's mixts solution containing 31 kg of magnesium sulphate was pumped to the swenson walker crystalliser. Refrigerated brine of - 10°C was circulated in the outer jacket of the crystalliser. The slurry was stirred at 10°C for 15 minutes and then centrifuged. The yield of epsom salt was 50 per cent (Table 69).

iii) Separation of Glauber's salt

The mother liquor obtained after centrifuging epsom salt was saturated with sodium chloride. Samples were taken to see the concentration of sodium chloride in the solution. When the saturation was reached the 130 litres was pumped back

Table 68 DISSOLUTION OF SEL'S MIXTS (Pilot Plant Experiment)

Scale of operation 100 kg sel's mixts and 100 litres water

Description	Sel's mixts (Leached salt)		Water	Solution from sel's mixts		Residue (Balance)	
Quantity	100 kg		100 litres	150 litres		7 kg	
Density	-			33.0° Be			
Composition	Per cent	Total salts (kg)		Per cent	Total salts (kg)	Per cent	Total salts (kg)
$MgSO_4$	35.0	35.0		20.6	31.0	57.1	4.0
NaCl	16.8	16.8		11.2	16.2	7.1	0.5 ~~$MgSO_4$~~
$MgCl_2$	8.0	8.0		5.4	8.0	--	
KCl	2.1	2.1		1.4	2.1	-	
Insolubles	2.0	2.0		-	-	28.5	2.0
Water, combined and free	36.1	36.1		-		7.3	0.5
Total salt	63.9	63.9		38.6			

Recovery of magnesium sulphate from sel's mixts is 88.5 per cent.

Table 69 RECOVERY OF EPSOM SALT AND GLAUBER'S SALT BY CHILLING

Scale of operation: 150 litres of sels mixts solution

Description	Sel's mixts solution		Solid sep.at + 10°C		M.L.at + 10°C		NaCl added	M.L.after salt		Solid sep. at-5°C		M.L.at - 5°C	
Quantity	150 litres		33 kg		130 litres		14 kg	130 litres		35 kg		110 litres	
Density	33° Be'												
Composition	Per cent	Total salts (kg)	Per cent	Total salts (kg)	Per cent	Total salts (kg)		Per cent	Total salts (kg)	Per cent	Total salts (kg)	g/100 ml	Total salts (kg)
$MgSO_4$	20.6	31.0	46.7	15.4	11.5	14.9		10.8	14.0	0.5	0.17	2.5	2.8
NaCl	11.2	16.8	0.5	0.1	12.5	16.3		23.0	29.9	5.0	1.75	17.0	18.7
$MgCl_2$	5.4	8.0	-		6.1	7.9		6.0	7.8	-	-	13.6	14.9
KCl	1.4	2.1	-		1.6	2.1		1.6	2.1	-	-	1.9	2.1
Na_2SO_4	-	-			-	-				39.9			
Water combined			48.8	16.2	-	-				50.6			
Water Free			4.0	1.3	-	-				4.0			

Sep.$MgSO_4$ = 15.4 kg

Efficiency = 50 per cent

Converted $MgSO_4$ to Sodium sulphate 11.2 kg

Conversion effieiency 80 per cent

(Recovery of sulphate from sel's mixts as epsom salt and sodium sulphate is 90.3 per cent) to the swenson walker crystalliser and the refrigerated brine at -15°C was circulated in the outer jacket. The crystallisation of Glauber's salt started at -1°C and lot of crystals separated by the time the solution reached -5°C. The solution was stirred at -5°C for 15 to 20 minutes and centrifuged. The conversion efficiency was 80 per cent while the total recovery ~~as~~ magnesium sulphate as sodium sulphate from the original solution was 35.8 per cent. The residual end liquor containing 2.5 per cent magnesium sulphate, 17 per cent sodium chloride 13.6 per cent magnesium chloride and 1.9 per cent KCl was discharged as waste liquor (Table 69). Settling rate of sodium sulphate (Glauber's salt) and magnesium sulphate (epsom salt) was determined and is reported in Table 70.

Viscosities of various solutions obtained in the process at various temperatures were not actually determined. Data reported in the international critical tables, Hand book of physics and chemistry, corresponding to individual concentration of salts was utilised for the process. As it was difficult to determine the exact viscosity of 36° Be bittern and slurry at 110°C a comparative data of the rate of flow with 8.6 sparkler filter (laboratory model with attached pump) was collected and supplied to M/s. Kamitter and Co. to obtain bigger sparkler units for the pilot plant work. The supplied data is given in Tables 71 and 72.

Table 70 SETTLING RATE OF SODIUM AND MAGNESIUM SULPHATE

Sodium sulphate 14.71 g per 100 ml			Magnesium sulphate 9.30 g per 100 ml		
Time (min.)	Clear zone (cms)	Compact zone (cms)	Time (min.)	Clear zone (cms)	Compact zone (cms)
0	-	-	0	-	-
5	15.75	20	3	0.52	-
10	21.70	14.05	4	0.69	-
15	24.15	11.60	9	-	6.9
20	24.85	10.90	14	-	6.21
25	25.90	9.85	17	-	5.86
30	26.25	9.50	24	-	5.52
35	26.60	9.15	29	-	5.17
40	26.95	8.80	34	-	5.17

Precipitation of Anhydrous sodium sulphate from Glauber's salt

45 kg of Glauber's salt containing 42.6 per cent sodium sulphate 0.85 per cent magnesium sulphate and 5.3 per cent sodium chloride was added to steam jacketted stainless steel evaporator. The Glauber's salt was melted by heating with steam. When the temperature of the melted mass was 60°C the heating was slowed down and powdered sodium chloride (3 kg) was added slowly. The stirring was continued for 15 minutes during which sodium chloride was dissolved and the sodium sulphate precipitated out. A test sample was taken, filtered and analysed for sodium chloride content on flame photometer. When the sodium chloride content showed 20.8 g per 100 ml, the

Table 71 VISCOSITIES OF DIFFERENT SOLUTIONS AVAILABLE IN THE PROCESS

No.	Description of solution	Temp. °C	Viscosity centipoise
1	36° Be bittern	25°	3.36
	"	110°	Not available
2	Saturated solution of NaCl-KCl (liquor to KCl crystalliser)	25° 110°C	1.22 Not available
3	Sel's mixts solution (Liquor to $MgSO_4$ crystalliser	18° 25°	3.95 3.80
4	Liquor to sodium sulphate crystalliser (after saturation with sodium chloride)	25°	1.93

Table 72 COMPARATIVE RATE OF FLOW WITH 8 - 6 SPARKLER FILTER (LABORATORY MODEL) WITH THE ATTACHED PUMP

(Filter papers (filter media M) was used. Filter aid was not used in the experiment).

No.	Description of the solution	rate of filtrate Imp.gal.per hr.
1	Water (temp.,30.5°C)	130
2	Bitterns 36° Be, 40°C	127.5
3	Bitterns 36° Be, 110°C	125.0
4	Slurry consisting of bittern 36° Be + Mixed salt ratio 1 kg per gallon of 36° Be bittern	123.0

the slurry was centrifuged. Sodium sulphate was washed in centrifuge with one litre of distilled water to remove the adhering sodium chloride with the solid. The mother liquor containing 13.6 per cent sodium sulphate was mixed with the next batch in the Swenson-Walker crystalliser for Glauber's salt separation. Yield of anhydrous sodium sulphate was 82 per cent. Results of the experiment are given in Table 73 and 74.

Experiment 2

In this experiment 38.63 kg of Glauber's salt was melted at 60°C in stainless steel evaporator (100 litres cap.) with ancher type stirrer. The melted mass was stirred for a while and 4.3 kg of 30 to 40 mesh size powdered sodium chloride was added. The stirring of the slurry was continued at constant temperature 60°C for half an hour. The whole mass was immediately centrifuged (at 60°C). The anhydrous sodium sulphate contained 2.4 per cent sodium chloride and 0.6 per cent magnesium sulphate as impurities. Yield of anhydrous sodium sulphate was 86.66 per cent. The end liquor from centrifuge was recycled with next batch to obtain additional Glauber's salt at -5°C. The data ~~is~~ are reported in Table 73 and 74.

Table 73 PRECIPITATION OF ANHYDROUS SODIUM SULPHATE FROM GLAUBER'S SALT

(Pilot Plant experiment 1)

Scale of operation 45 kg of Glauber's salt

Contents	Glauber's salt		Common salt	Sodium sulphate	Sodium sulphate after washing		End liquor		Deviation
Quantity	45 kg		3 kg	-	16.5 kg		25 L		-
Composition	Per cent	Total salts (kg)	-	Per cent	Per cent	Total salts (kg)	% (w/v)	Total salts (kg)	(kg)
Na_2SO_4	42.6	19.16	-	94.12	95.45	15.75	13.6	3.4	0.01
$MgSO_4$	0.85	0.38	-	0.2	0.2	0.03	1.8	0.45	-
NaCl	5.3	2.38	-	2.1	1.05	0.22	20.8	5.2	0.06
Moisture	51.25	-	-	-	3.3	-	-	-	-

Sodium sulphate was washed with one litre of water during centrifuging.

Recovery of sodium sulphate from Glauber's salt was 82 per cent.

Table 74 PRECIPITATION OF (ANHYDROUS) SODIUM SULPHATE FROM GLAUBER'S SALT AT 60°C (Pilot plant experiment 2)

Description	Glauber's salt		Common salt added	Solid centrifuged		End liquor		Deviation
Quantity	38.63 kg		4.3 kg	15.63 kg		20 L		
Composition	Per cent	Total salts (kg)		Per cent	Total salts (kg)	Per cent (w/v)	Total salts (kg)	(kg)
Na_2SO_4	43.42	16.77	-	93.03	14.53	11.17	2.23	0.01
$MgSO_4$	0.99	0.38	-	0.62	0.10	1.84	0.37	0.08
NaCl	2.12	0.82	4.3	2.41	0.38	23.31	4.66	0.08

Recovery of anhydrous sodium sulphate was 86.66 per cent.

YIELD AND QUALITY CONTROL OF OPERATIONS IN EXTRACTION OF POTASSIUM CHLORIDE PROCESS

1) Extraction of potassium chloride

In pilot plant section, processing of 114 kg of mixed salt has been described. The following test controls are necessary to ensure good process efficiency. Mixed salt is ground to 20 to 30 mesh size before feeding.

Composition of mixed salt and 36° Be' bittern

	Per cent by weight	Per cent by volume
KCl	18 - 20	1 - 1.5
NaCl	15 - 20	2 - 2.5
$MgSO_4$	30 - 35	7 - 8
$MgCl_2$	6 - 8	34 to 36
Insolubles	0 - 2	-

The composition and density of feed bittern of 36° Be has to be checked, potassium chloride by flame photometer or at least total chloride has to be checked which is 29.5 to 30 g per 100 ml. It is observed that if the extraction is properly controlled, potassium chloride in the hot bittern rises to 5 to 5.5 g per 100 ml (flame photometer test) or in other words 20 to 22 g. of carnallite separate out per 100 ml of solution. The carrying out of this test, ~~it~~ is essential to ensure good extraction efficiency. The recovery of potassium chloride as carnallite in this operation is usually 80 to 85 per cent. Sel's mixts which is obtained as cake contains usually 2 - 2.2 per cent potassium chloride, 16 - 20 per cent sodium chloride, 35-37 per cent magnesium sulphate, 6 - 8 per cent magnesium chloride and 1 - 2 per cent insolubles. It is essential to test sample of sel's mixts for potassium chloride as the concentration of potassium chloride and magnesium chloride above the limits (shown above), cause difficulties in treatment of sel's mixts for the recovery of epsom salt and Glauber's salt.

2) Decomposition of carnallite

Composition of carnallite obtained by this process is usually 20-21 per cent potassium chloride, 4 to 6 per cent sodium chloride and 27-28 per cent magnesium chloride. Decomposition of carnallite is a very simple operation carried out at room temperature and except addition of water which has to be properly controlled, the operation as such requires little attention. At the end of the operation it is necessary to check density of the clear bittern by filtering a small portion of bittern or by allowing it to settle for 15 to 20 minutes. Density reading at 30°C (room temperature) shows 32.5° Be. If the density is low it is necessary to add a little extra carnallite or it may due to improper stirring. If the addition of carnallite is correct it may be necessary to find out whether carnallite is decomposed or not. This can be easily tested by analysing a small sample of the residue. Particularly during very cold nights in winter season, it is often necessary to add lukewarm water for carnallite decomposition. Recovery of potassium chloride as impure potassium chloride from carnallite is usually 80 to 85 per cent. The composition of impure potassium chloride is usually 60 to 65 per cent potassium chloride. Even though impure potassium chloride is the intermediate product, it is essential to centrifuge it, and preferably with a little wash with water to avoid contamination of the recrystallising liquor with magnesium chloride.

3) Evaporation of carnallite decomposed liquor

The operation is carried out by open pan evaporator or vacuum evaporator. The final volume is reduced by 25 per cent of the original volume. It is necessary to control the operation properly so as not to allow it to carry forward to separate magnesium chloride with carnallite or to obtain a low density bittern. The operation is controlled by taking samples when the density reading in the hot solution are nearly 37° Be. The sample is cooled immediately and filtered on a buchner funnel and the mother liquor is tested for potassium chloride which is nearly 1 to 1.5 g per 100 ml of the sample. To examine total chloride of the solution is another indirect test. The total chloride has to be nearly 29.5 g per 100 ml. If the operation is properly carried out, the recovery of potassium chloride as carnallite from the carnallite decomposed liquor is 80 per cent. That is to say, out of 20 per cent of potassium chloride lost into solution, while decomposing carnallite; only 16 per cent is recovered back as carnallite and 4 per cent is lost in the liquor which is recycled as 36° Be bittern for extraction.

4) Recrystallisation of impure potassium chloride

It is essential to analyse impure potassium chloride content before it is processed for purification. Separation of potassium chloride per cycle is 10 g per 100 ml of the recrystallising liquor. The quantity of the liquor required for recrystallisation is thus calculated. It is equally important to test the saturated NaCl-KCl solution before and after crystallisation to know the concentration of magnesium chloride in the liquor. If the concentration exceeds 7 per cent, the liquor is sent for regeneration and fresh liquor is prepared from impure potassium chloride. Limits of recycling the saturated NaCl-KCl liquor are fixed at 7 per cent concentration of magnesium chloride in the solution after which a fresh solution is used. Carrying out the operations in the above preferred manner maintains the efficiency of the operation giving high purity product. It is necessary to check the concentration of potassium chloride at 110°C by flame photometer (which has to be 24 g KCl per 100 ml). The yields of potassium chloride obtained in this operation is usually 94 to 95 per cent; 5 to 6 per cent is lost with the sodium chloride cake. However the cake can be reused for preparing a fresh NaCl-KCl solution as and when required. On large scale experiments it is suitable to wash the sodium chloride cake with water to reduce the losses of potassium. The washed liquor is used for preparing a fresh solution of NaCl - KCl.

5) <u>Regeneration of saturated NaCl-KCl solution</u>

It is found out on pilot plant experiments that usually after 5 to 6 cycles the concentration of magnesium chloride in the NaCl-KCl solution is raised to 7 per cent. Studies have revealed that utilising the above solution for decomposing the carnallite is the best solution. The ratio employed for this purpose is 1:1 and not 2:1 as in case of water. The mixture is stirred for half an hour and density of the clear liquor is tested, which measures 32.5° Be as in the case of carnallite decomposition.

6) <u>Sel's mixts treatment</u>

The operations are simple provided the potassium chloride extraction is efficiently carried out. The excess of potassium chloride or magnesium chloride in the sel's mixts cake gives difficulties for purity and yield of products. For this very reason it is essential to pass compressed air through the pressure filtration unit to remove the adhering mother liquor which contains both magnesium chloride and potassium chloride. A Little washing of sel's mixts in the pressure filtration unit is often required if the operation is not smooth. A sample of sel's mixts is taken, dissolved in water and tested for potassium on flame photometer. The sel's mixts cake is dissolved in water in 1:1 ratio (1 kg/1 litre). The dissolution requires one hour and at the end of the operation temperature of the solution rises to 45°C. The density of the solution is checked (33° Be) and slurry is filtered in pressure filtration unit. The clear liquor is analysed for magnesium, chloride, sodium and potassium ~~chloride~~ by titration and flamephotometry. The chloride required for potassium and sodium is substracted from total chloride and magnesium chloride is estimated from the remaining chloride value. Remaining magnesium is calculated as magnesium sulphate. Analysis by this method is carried out quickly and estimation of sulphate may not be required.

The yield of epsom salt at 10°C is usually 50 per cent. The yield can be increased by 10 per cent by dissolving the sel's mixts cake at 60°C instead of room temperature. A little wash in centrifuge is often necessary to get a product of good grade.

Separation of Glauber's salt

The mother liquor obtained by centrifuging epsom salt is analysed for magnesium, chloride ~~and~~ sodium and potassium content. The analysis at this stage reveals the concentration of magnesium chloride in solution. It is ascertained by various experiments that the concentration of magnesium chloride which is one of the products of the reaction between magnesium sulphate and sodium chloride has to be maintained at or below six per cent. The concentration of magnesium chloride above six per cent effects the conversion efficiency appreciably. The mother liquor is diluted to adjust magnesium chloride concentration and saturated with sodium chloride. It is also necessary to find out whether the solution is saturated with sodium chloride, which is increased to 21 to 23 g per 100 ml. The solution is then cooled to -5°C and stirred at -5°C for 15 to 20 minutes. It is often required to add little sodium sulphate as seeding. A finely powdered sodium sulphate (handfull) is added at -1°C which helps immediate throw out of Glauber's salt, the recovery of which is usually 80 to 85 per cent.

Project estimate (summary) and process flow diagram are given on page 194 and 195.

PRODUCT ANALYSIS AND OTHER SPECIFICATIONS

(1) Potassium chloride (KCl)

Analysis of potassium chloride produced in pilot plant experiments was as follows:

	Per cent by wt.(dry basis)
Potassium chloride (as KCl)	97.0
Sodium chloride	3.0
Total magnesium as magnesium chloride or sulphate	Nil
Combined and free moisture	1.0
	100

A) Specifications for fertilizer grade potassium chloride or or sulphate:

Characteristic (Per cent by wt.)	Requirements KCl IS.2779-1964	K_2SO_4 IS.2764-1964
Potash as K_2O (Min)	58.0	48.0
Total chlorides as Cl' on dry basis (Max.)	-	2.5
Total sodium as (NaCl) on dry basis	3.0	2.0

B) Specifications for potassium chloride for chemical Industries

Colourless white crystals assaying not less than 99.5 per cent potassium as potassium chloride.

Water insolubles	(max.)	0.01 per cent by wt.
Sodium	(max.)	0.2 - 0.15 "
Calcium + Magnesium	(max.)	0.01 + 0.004 "
Iron (as Fe)	(max.)	0.004 to 0.005 "
Sulphate (as SO_4)		traces
Moisture		0.05 to 0.04 "

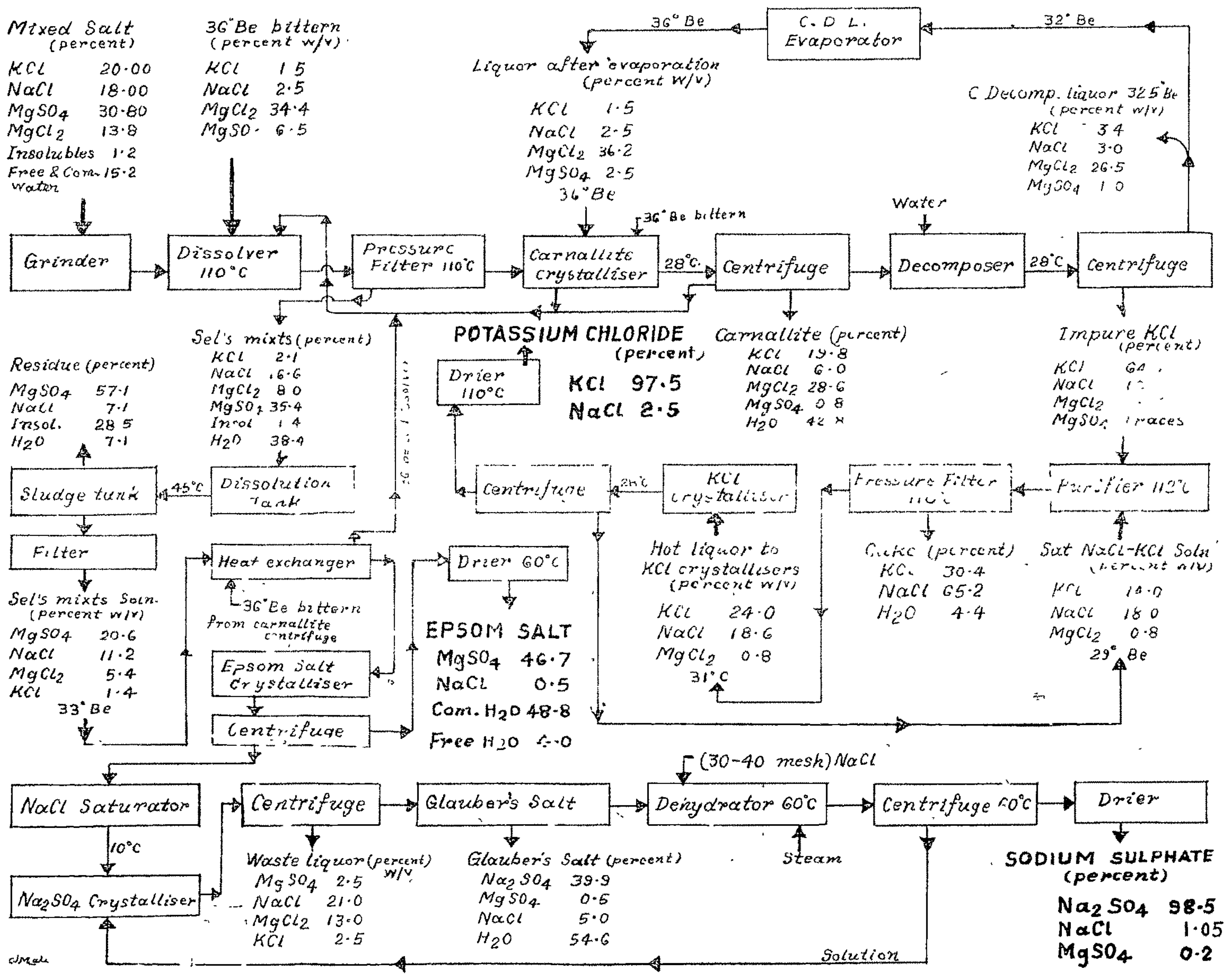
Indian standard specifications for epsom salt and the product produced in the pilot plant experiments.

Characteristic	REQUIREMENTS		
	Tech.gr.	Pharmaceutical grade	As produced in the plant.
Per cent by wt.	I.S.257/1950	I.S.377/1954	(Centrifuged-product)
$MgSO_4.7H_2O$	98 - 105	99.5 to 102	98.7
$MgCl_2$ (max.)	1.0	-	-
Chlorides of Na) Max K as NaCl)	0.5	<u>Total chloride</u> 0.12 Max.	0.5
Soluble iron (as Fe) Max.	0.007	To satisfy the test	below 5 ppm
Insolubles	0.20	-	0.10
Lead (Max.)	-	5 (ppm)	-
Arsenic (as As_2O_3)	-	2 (ppm)	-
Zinc	-	To satisfy test	
			48.8 combined water 4.0 free moisture

Glauber's salt ($Na_2SO_4.10H_2O$)

(Technical grade)	I.S.256-1950	As produced in the plant
Characteristics (per cent by wt)	REQUIREMENTS	(Centrifuged product)
$Na_2SO_4.10H_2O$ (min)	99.102	99.5
Insolubles in water (Max.)	0.10	0.10
Soluble iron (as Fe) (Max.)	0.007	below 5 ppm
pH .	7.5 to 8.0	7.0

FIG. 26 FLOW DIAGRAM AND THE COMPOSITIONS OF SOLIDS AND SOLUTIONS IN THE POTASSIUM CHLORIDE PROCESS



Requirements of sodium sulphate (Anhydrous)
Technical grade (I.S.Specifications 255-1950)
and the product produced in pilot experiments

Characteristic	Requirement		As produced in pilot plant (dried)
(Per cent by wt)	Grade A	Grade B	
Na_2SO_4 (min.)	99.2	96.0	98.7
Insolubles in water (max.)	0.25	2.0	0.13
Sodium chloride as (NaCl) max.	0.50	1.5	1.1
Soluble iron & aluminium as (Fe_2O_3)	0.05	0.10	-
pH	7 - 7.5	7 - 7.75	7.0

PROJECT ESTIMATES (Summary)

Project estimates for a commercially feasible smallest unit for the manufacture of 1000 tonnes of potassium chloride, 2160 tonnes of epsom salt and 900 tonnes of anhydrous sodium sulphate from 7200 tonnes of mixed salt per annum are summarised. The production capacity of the plant per day of 24 hours is 3.5 tonnes of potassium chloride 7.2 tonnes of epsom salt and 3 tonnes of sodium sulphate.

Capital investment for setting up the plant is estimated at Rs. 17,76,243/-. The capital investment is inclusive of costs of equipment, building and working capital but exclusive of cost of land. Return on capital investment (exclusive of working capital) is 22 per cent.

Project estimated for the manufacture of potassium chloride, epsom salt and sodium sulphate

I. Mode of operation: 3 shifts per day of 24 hours, 300 days per year.

II. Raw materials per year

1. Mixed salt	7,200 tonnes
2. Common salt	1,350 tonnes
3. Recycling materials	
a) 36° Be' bittern	33,000 kilolitres
b) Saturated NaCl-KCl solution ..	12,000 kilolitres

III. Products per year

1.	Potassium chloride	1,000 tonnes
2.	Epsom salt	2,160 tonnes
3.	Sodium sulphate	900 tonnes

IV. Capital investment

1)	Total erected equipment cost	Rs.13,48,613
2)	Buildings and other civil works	Rs. 2,11,530
3)	Fixed capital cost	Rs.16,10,143
4)	Working capital	Rs. 1,66,100
5)	Capital investment	Rs.17,76,243

V. Manufacturing cost per year

1)	Direct manufacturing cost.	Rs. 6,66,400
2)	Indirect manufacturing cost ..	Rs. 2,44,268
3)	Total manufacturing cost...	Rs. 9,10,668

VI. Revenue per year

1)	Potassium chloride @ Rs. 350/- tonne ..	Rs. 3,50,000
2)	Epsom salt @ Rs.300/- tonne..	Rs. 6,48,000
3)	Sodium sulphate @ Rs.300/- tonne ..	Rs. 2,70,000
4)	Total revenue ..	Rs.12,68,000

VII. Return on Capital investment

1)	Profits per year	Rs. 3,57,300
2)	Return on Fixed Capital Investment (excluding working capital). Say	22%

PHOTOGRAPHS (Fig. 27)

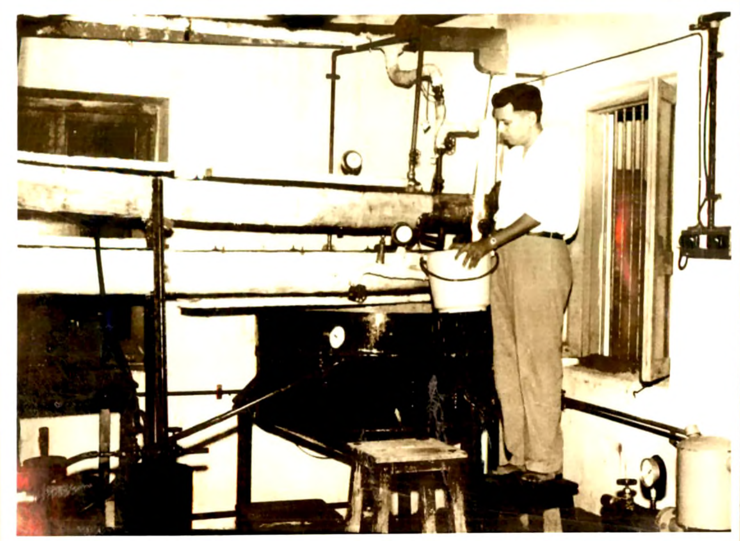
POTASSIUM CHLORIDE PILOT PLANT STUDIES

A) Hot extraction of mixed salt in screw conveyors(1)

B) Cooling of hot filtrate by tap water in tubular heat exchanger to obtain carnallite (2)

C) Hot extraction of mixed salt in specially prepared molybdenum steel dissolver (with copper coils) The photograph also shows grinder manually operated hydraulic crane bucket elevator sparkler filtration units and other units used for pilot plant experiments (3)

Fig. 27



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PHOTOGRAPHS (Fig. 28)

POTASSIUM CHLORIDE COMMERCIAL UNIT

KANDLA

A plant producing 1000 tonnes KCl and 2000 tonnes epsom salt per year by the hot extraction process

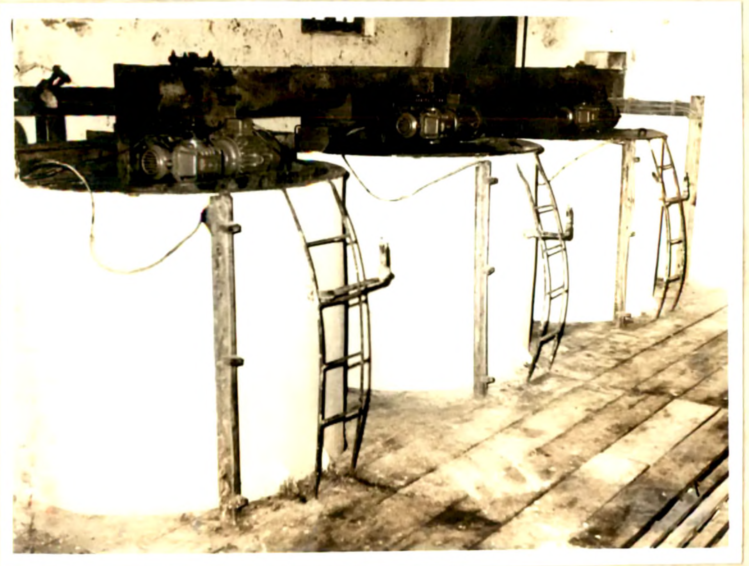
A) Dissolver section: Showing dissolvers screw conveyor for feeding mixed salt and 36° Be bittern feeding pipes (1)

B) Hot filtration section : Showing settlers wooden filter presses and part of carnallite crystallisers (2)

C) Carnallite crystalliser section: Showing carnallite crystallisers, stirring assemblies and hot filtrate feeding pipes (3)

D) Epsom salt crystallisers section: Showing swansonwalker crystalliser units (4)

Fig. 28



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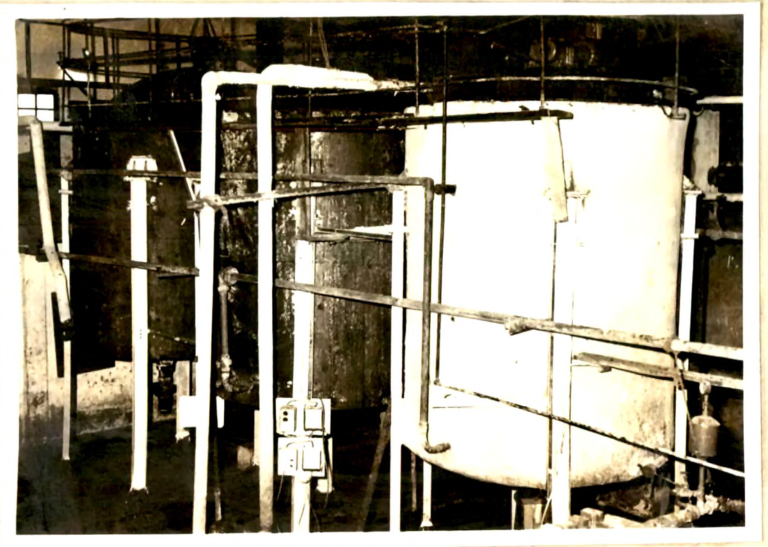

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DISCUSSION

It is known that the liquor left after desalting the sea water (brine) known as bittern forms a very cheap source for the manufacture of potassium chloride. Potassium chloride as such cannot be isolated by solar evaporation of bittern. The process generally used for the manufacture of potassium chloride from bitterns consist of two stages, the separation of carnallite by forced evaporation of bittern and treatment of carnallite with water for isolation of impure potassium chloride. As steam or coal is used for this purpose the process is uneconomical. Magnesium sulphate which separates with potassium chloride interferes in the separation of carnallite. The removal of sulphate partially either by refrigeration as epsom salt or completely by addition of lime or calcium chloride has been often tried. This has not either minimised the difficulties nor improved economy with the result that the processes have not attracted much attention in India.

The developed process utilises solar heat to concentrate the bittern of salt works to obtain (1) mixed salt containing potassium chloride, magnesium sulphate, sodium chloride, magnesium chloride and (2) concentrated 36° Be' bittern. Potassium chloride from the mixed salt is then extracted at hot by the concentrated bittern. Potassium chloride is separated as carnallite by cooling the hot bittern. Based on the van't Hoffs solubility relationships of the oceanic salts, the process sets forth the optimum conditions for obtaining the mixed salt and extraction of potassium chloride as carnallite in the presence of magnesium sulphate from the mixed salt. In addition to the recovery of potassium chloride, the process facilitates the recovery of other constituents from the bittern namely magnesium sulphate, sodium chloride or sodium sulphate by meta thesis of the above two salts by known methods.

The process in short consists of treatment of 28/29° Be bittern with 36° Be bittern in 1:1 ratio. The density by the addition of high density bittern is raised 1° Be. The treated bittern is concentrated by solar evaporation to 34.5° Be when impure sodium chloride assaying 84 to 87 per cent separates out. The solar evaporation is further continued until the density is reached to 36° Be. The 36° Be bittern contains 7.1 magnesium sulphate, 34.5 per cent magnesium chloride, 1.5 per cent potassium chloride and 2.5 per cent sodium chloride by volume. The volume reduction is approximately half of the original bittern (67 to 68 per cent). The 36° Be bittern is removed by gravity and salt crystallised are collected. The normal composition of mixed salt is 18 - 20 per cent potassium chloride, 15 - 20 per cent sodium chloride, 30 - 35 per cent magnesium sulphate and 6 to 8 per cent magnesium chloride. Evaporation is discontinued as soon as bittern contains only 1 to 1.5 per cent potassium chloride. This is easily done by using flame photometer, as gravimetric methods of potassium estimation are cumbersome, time consuming and require costly chemicals. At the beginning of the season when 36° Be bittern is not available direct evaporation of bittern from 30 to 38° Be is carried out; this is also done in two steps 30 to 36 °Be and 36 to 38° Be. The main advantage of mixing 30 and 36°Be bittern is that the mixed salt separates at lower density of 36° Be instead of 38° Be as in direct evaporation of bittern.

It is further found out that it helps absorption of solar radiation and evaporation is completed in comparatively less period than that for direct evaporation of bittern. Addition of dyes reduce the period of evaporation further; this helps in producing mixed salt in a still shorter period.

In the second stage the mixed salt and its own mother liquor (bittern of 36° Be) are heated to 110°C. The hot solution is filtered using pressure unit. The hot clear liquor when cooled to room temperature throws out potassium chloride as carnallite. The carnallite is centrifuged and the effluent is returned to the evaporator for second extraction. 70 per cent of potassium chloride present in the sea bittern is recovered as mixed salt of which 85 per cent is recovered as carnallite.

Laboratory experiments have shown that it is not possible to separate mixed salt in various fractions to isolate fractions rich in potassium chloride by simple means as mechanical seiving. Studies on concentration of potassium chloride reached in hot extraction show that, heating of mixed salt containing 18 to 20 per cent potassium chloride with 36° Be bittern in 1 kg : 4 litres ratio is essential. For pilot plant scale experiments 1 kg : 1 gallon (4.5 litres) of 36° Be bittern is considered more convenient. The saturation of potassium chloride in hot extract is 4 to 4.5 grams per 100 ml of solution and every time 20 grams of carnallite separates per 100 ml. Circulation of hot liquor (treated with mixed salt) to other vessels in sieves containing fresh mixed salt is not helpful as it involves more operations with very little or no positive advantage. The testing of samples of hot bittern is found essential to find out whether all the potassium is extracted in the hot solution. It is found out that half an hour stirring after reaching 110°C is necessary. Studies on treatment of mixed salt of varying composition and mixed salt already partly converted to schoenite show that the developed process is suitable for any type of mixed salt, a little adjustment is however found essential. Studies on decomposition of carnallite show that it is preferable to decompose carnallite 1:1 ratio and obtain one fifth of potassium chloride as 95 per cent pure product which is suitable as fertilizer potassium chloride while the rest (60 per cent) potassium chloride is obtained as impure potassium chloride containing potassium chloride and sodium chloride in almost 1:1 ratio. However it is considered more suitable to treat carnallite with 1:0.5 ratio of water and obtain a 80 per cent potassium chloride from carnallite as 60 to 65 per cent impure potassium chloride product. Studies on recrystallisation of impure potassium chloride lead to a conclusion that all potassium chloride from impure potassium chloride is not extracted, some potassium chloride is left with the sodium chloride fraction. The recoveries are only 92 to 94 per cent. However the sodium chloride fraction is used to prepare fresh NaCl-KCl solution and losses are minimised. Similarly it is seen that it is not possible to obtain potassium chloride more than 97 to 98 per cent purity by single recrystallisation of impure potassium chloride as some sodium chloride separates along with potassium chloride. The studies also reveal that the concentration of magnesium chloride in the recrystallising NaCl-KCl solution is increased slowly in every cycle. The problem is successfully solved by utilising the recrystallising liquor whenever it attained more than 5 to 6 per cent magnesium chloride for the decomposition of carnallite. This treatment minimises the losses of potassium chloride and maintains the efficiency of recrystallisation. The studies on crystallisation of carnallite at various temperature ranges show that maximum amount of carnallite is crystallised between 80 to 40°C. While studies on crystallisation of potassium chloride from hot NaCl-KCl solution show that most of the potassium chloride separates between 110 to 40°C while very little is separated out between 40 to 30°C.

From studies in dissolution of sel's mixts it is observed that 1:1 ratio (1 kg sel's mixts/1 litre water) is suitable to obtain maximum amount of magnesium sulphate in solution and at the same time getting a concentrated solution of magnesium sulphate.

It is observed that the concentration of magnesium chloride in the sel's mixts plays an important roll in separation of epsom salt and sodium sulphate. The concentration of magnesium chloride is helpful for the separation of epsom salt but at the same time it is disadvantageous to have more than 6 per cent magnesium chloride in the liquor for sodium sulphate crystallisation. As magnesium chloride is one of the product of the reaction excess of concentration of magnesium chloride prevents the forward reaction. Experiments in crystallisation of epsom salt and sodium sulphate show that epsom salt is separated between 15 to 10°C and temperature range is only 5°C. while in Glauber's salt temperature of separation is from + 3°C to -5°C.

The entire process is based on the phase relations of oceanic salts. At every stage the process is controlled by solubility temperature relationship of various systems. Recovery of mixed salt and extraction of carnallite from mixed salt using byproduct 36° Be bittern is developed on the basis of van't Hoffs solubility relationships of oceanic salt systems: $NaCl-KCl-MgCl_2-MgSO_4-Na_2SO_4-H_2O$ at 25° and 83°C. The decomposition of carnallite is based on $KCl - NaCl - MgCl_2 + H_2O$ at 25°C; where as crystallisation of ~~impure~~ pure potassium chloride from impure potassium chloride is based on $NaCl-KCl-H_2O$ at 30 and 110°C (polytherm). The recovery of byproducts namely epsom salt and sodium sulphate is based on reciprocal salt pair system $2NaCl + MgSO_4 = Na_2SO_4 + MgCl_2$. The application of the above system is discussed in the chemistry of the process, Chapter 2.

The process is suitable for salt works producing nearly 1 lakh tonnes of salt per year, where small commercially viable units producing 1000 tonnes of potassium chloride, 2000 tonnes of epsom salt and 900 tonnes of sodium sulphate can be established.

It is essential to combine recovery of potassium salt with byproduct recoveries to make the units commercially feasible.