

PRODUCTION OF MARINE CHEMICALS IN PAKISTAN Part II: Studies on Manufacture of Chemicals from Seawater Bittern

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Studies on the production of chemicals like magnesium sulphate, magnesium chloride and potassium chloride have been carried out and a simple process has been developed. The different steps of the process are all physical operations such as evaporation, chilling, crystallization, filtration, drying etc. excepting desulphatation. Based on the data collected from laboratory and small scale operations a plant of 1 ton/batch capacity has been designed, fabricated, and installed. Material balance related parameters have been established on the basis of the experiment on the said plant.

INTRODUCTION

Bittern is the waste product of the sea salt industry and is not being appropriately exploited in Pakistan. It can be a potential source of potassium and magnesium salts. Developed countries the usual suppliers of technology to Pakistan have not worked for the exploitation of bittern since it is an inferior source of potash compared with carnallite for which they have considerable deposits. It may be observed from the data listed in Table 2 that $MgSO_4$ is present in bittern to a considerable extent and is prohibitive in the separation of carnallite from the mother liquor. This is one of the main reasons, for marine bittern not being the source for potash elsewhere in the world, excepting some of the developing countries [1].

When marine bittern evaporates, crystallization proceeds via epsomite ($MgSO_4 \cdot 7H_2O$) and kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) to carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) and finally bischoffite ($MgCl_2 \cdot 6H_2O$) [1]. The process of crystallization is not well marked and admixtures are always noted. Any process for potash recovery therefore has to reduce the sulphate content so that the carnallite phase is dominant.

Several investigations in the past [2,3], have considered sea bittern containing about 1.9 % KCl, as a candidate for the recovery of potassium salts and a large number of processes have been proposed for the recovery of several valued salts. These are either chemical or physical processes, or a combination of chemical and physical processes [4,5,6,7]. The physical processes involve simple concentration techniques to isolate a particular phase of the salt, while chemical and physico-chemical processes involve

precipitation using chemicals and evaporation of liquors. Studies on the use of methanol for the recovery of potassium magnesium sulphate double salt, from the sea water bittern have also been reported [8].

The recovery of potash or any other single chemical from bittern is uneconomical and is not generally practised. This is not because the process is expensive, but because it is not desirable to ignore the high local prices of the other compounds present in the bittern. The exorbitant prices of analytical and laboratory grade magnesium and its compounds, are likely to pay for the economical operation of a pilot plant for processing bittern.

THE PROCESS

The process developed for the utilization of bittern for the recovery of salts takes into account, the natural sequence of separation of salt followed successively by magnesium sulphate, carnallite, potassium chloride and magnesium chloride. The flow sheet evolved on the basis of the laboratory studies is illustrated by Fig. 1.

The process comprises preconcentration of bittern by solar evaporation to a density of $35^\circ Be$; after filtering off sodium chloride still contained by bittern, the solution is cooled to $4-6^\circ$ and centrifuged to obtain magnesium sulphate. The filtrate is chemically desulphated by adding calcium chloride solution and the precipitated calcium sulphate is centrifuged off. The resulting filtrate is solar evaporated to remove the undesirable sodium chloride which would otherwise be problematic in subsequent operations.

The evaporated solution is again centrifuged and the

filtrate heated to 123-126° [5] and allowed to cool whence carnallite, a double salt of magnesium chloride and potassium chloride is separated in the form of crystals and magnesium chloride remains in the mother liquor. The residue after recovery is treated with water and the solution thus obtained is heated to 116° to yield potassium chloride. The aqueous solution of magnesium chloride is crystallized by solar evaporation or low temperature heating and the crystals of magnesium chloride are filtered off and dried.

PILOT PLANT STUDIES

Almost all the important units required for the process were identified during laboratory studies. The design of these units was simple excepting the chiller, which called for carrying out studies on a small scale to collect necessary data. A small chilling unit of 25 litres/batch capacity was therefore, designed and got fabricated, to study the crystallization behaviour of magnesium sulphate. Factors such as yield, purity, effect of concentration of magnesium sulphate in the original feed and kinetics of the process was initially studied on this unit. A chilling unit of 200 lit/batch capacity was then used to verify the data on crystallization pattern of magnesium sulphate. Based on these data, a larger unit of 500 kg/batch capacity was designed and fabricated alongwith other units as shown in flow-sheet Fig.1. A brief description and specifications of the various units/equipments used in the process are listed in Table 1.

Before describing the process in detail it would be pertinent to mention the peculiarities of the raw materials.

RAW MATERIALS

1. *Bittern*. The composition of bittern, made available from saltworks usually had a density between 28° and 30°Be and was found to be very sensitive to changes of temperature, humidity, wind velocity and its direction. The daily uneven changes in these parameters bring about irreproducible changes in the composition of bittern and it is difficult to get a product of identical composition for a given density. Average composition of various densities obtained from salt works of Karachi is listed in Table 2. Usually a 28°Be bittern having an average composition: NaCl 14.9%, KCl 1.4%, MgCl₂ 6.3% and MgSO₄ 4.1% was utilised in the process.

2. *Calcium chloride*. A 30% solution of technical or commercial grade calcium chloride (95 % CaCl₂.2H₂O) was used. However, calcium chloride could also be prepared reacting lime with magnesium chloride, the end product

and obtaining magnesium hydroxide as a by-product.

The following is a step-wise description of operations/processes.

i. *Solar evaporation*. Pre-concentration of bittern by solar evaporation is the first step of the process. It was undertaken to make the process economical and to suit to conditions identical to salt works. Crystallization proceeded almost under equilibrium conditions during solar evaporation.

Evaporation was carried out in six concrete plastered tanks divided into two rows, lined with water proof cement. Lining of thick plastic polythelene sheet was provided to check seepages and to conserve solar heat from dissipating into the ground [9]. The tanks were so constructed that in each row the concentrated solution could be transferred by gravity from 1st to 2nd then to the 3rd tank. Bittern of 28°-30°Be, transported in tankers was transferred to the solar evaporation tanks where it was allowed to evaporate to the desired concentration of 35°Be which reached within four to five days. The tanks were covered with polyethylene sheets during the nights to avoid possible dilution due to condensation of vapours. The concentrated bittern was centrifuged to remove sodium chloride which crystallized out during the concentration period.

ii. *Chilling*. The unit for chilling of bittern comprised a compressor with a built-in air cooler and a stainless steel coil, immersed in a stainless steel tank fitted with an agitator. The unit was also provided with a thermometer and temperature controller. The concentrated bittern (35°Be) was transferred to the chilling unit and the whole mass was cooled to 4°. A uniform temperature was maintained by stirring. The bittern became lean in sulphate ion concentration as the temperature decreased. This was because of the crystallization of magnesium sulphate which separated out from the liquor. The average quantity, purity and analysis of magnesium sulphate obtained from a series of experiments on chilling of bittern of various densities carried out at different scales of operation are listed in Table 3.

iii. *Chemical desulphation*. The filtrate resulting from centrifugation of chilled MgSO₄ was fed to either of the two tanks fitted with a stirrer and placed at some elevation. Requisite quantity of 30 % calcium chloride solution, to remove total SO₄ ions was added slowly. Agitation was continued for another half hour beyond the complete addition of calcium chloride solution. Removal of sulphate ions as calcium sulphate has been found essential, since other wise they interfere further processing [10]. Precipitated calcium sulphate was centrifuged and the filtrate

Table 1. Units/equipments used in the process

Sr. No.	Equipment/unit	Capacity	Specification
* 1.	Chilling unit (small) (1)	25 lit/batch	Flanged top, fitted with gauge glass, stirrer, and cooling coils, complete with compressor, all contact parts, of 304 S.S.
+ 2.	Chilling unit (1)	200 lit/batch	Complete with stirrer, compressor, and air cooler. All contact parts 8118 stainless steel.
0 3.	Chilling unit (large)	400 lit/batch	Fitted with stirrer, provision to change rpm, complete with compressor. All contact parts of 304 S.S.
* 4.	Centrifuge " (small) (1) (basket type)	20 kg/batch basket dia. 17" height 8"	Complete with driving arrangements, provision to change rpm from 500-750.
+ 5.	Centrifuge (medium) (1) (basket type)	50 kg/batch basket dia. 21" height 9"	Complete with driving arrangement with electrical automatic brake.
0 6.	Centrifuge (large) (1) (basket type)	125 kg/batch basket dia. 36" height 16"	Fixed rpm 700.
* 7.	Desulphatation tanks (2)	3' x 2½' 300 lit/batch	Flanged top, complete with stirrer, gauge glass, outlet and inlet.
* 8.	Air dryer (cabinet type)	Cabinet 2½ x 4 x 5' 400 kg/batch	Complete with electrical heater, blower and provision for recirculation.
* 9.	Crystallizers (6)	125 lit/batch	Fitted with coil to circulate water for cooling
* 10.	Evaporators (3)	2" x 5' 300 lit/each	Direct fired evaporation tanks, fitted with co-axial chimney of 6" dia.
* 11.	Tanks (2)	2½' x 2' each	Fitted on trolleys with centrifugal pumps.
* 12.	Pumps (centrifugal type) (5)	max. capacity 40 rpm at 25 height	All contact point of stainless steel.

* Fabricated in PCSIR workshop ;

+ Imported ;

0 Fabricated in local market.

obtained thereafter was pumped to solar evaporation tank (s). The average analysis of CaSO_4 obtained on dry weight basis was NaClO . 1 %, KCl 2.2 %, MgCl_2 18.5 %, CaCl_2 0.7 % and CaSO_4 78.6 %. The product could be further purified by washing with water.

iv. *Solar evaporation of desulphated filtrate.* The filtrate of desulphated bittern got diluted (1.22 g/cc) during the earlier process of addition of calcium chloride solution. It was observed during laboratory investigations that when the desulphated bittern was directly heated for

Table 2. Composition of marine bittern of various densities in Pakistan (Average)

S.No.	Density of bittern		Analysis (percent W/W)			
	gm/cc	°Be	NaCl	KCl	MgCl ₂	MgSO ₄
1.	1.2221	26.4	16.62	1.86	5.36	5.69
2.	1.2408	28.1	14.93	1.37	6.26	4.09
3.	1.2512	29.2	8.37	2.42	10.46	6.52
4.	1.2602	29.9	8.31	2.41	11.04	6.85
5.	1.2700	30.8	6.49	2.86	13.55	7.18
6.	1.2811	31.8	7.37	2.56	11.86	7.30
7.	1.2954	33.0	4.94	3.46	14.73	7.78
8.	1.3020	33.6	2.79	3.87	18.03	5.90
9.	1.3151	34.7	2.55	4.16	19.28	6.38
10.	1.3209	35.2	0.91	1.42	25.50	4.54

Table 3. Magnesium sulphate obtained from various experiments

Density of bittern (g m/cc)	Percent W/W				Recovery (%)	Purity (%)	Experiment
	Sodium chloride	Potassium chloride	Magnesium chloride	Magnesium sulphate			
1.297	1.97	0.83	12.42	85.09	43.30	85.09	1 lit. batch
1.297	2.31	0.97	10.38	86.34	46.64	86.34	2 " "
1.297	2.67	1.03	14.46	81.84	47.00	81.84	2 " "
1.290	Traces	Traces	7.02	92.98	46.95	92.98	25 " "
1.290	4.06	Traces	7.65	88.29	50.28	88.29	25 " "
1.320	5.39	0.80	4.98	88.80	67.78	88.80	200 " "
1.317	12.18	1.62	0.18	86.01	68.39	86.01	200 " "

carnallite production sodium chloride started crystallizing out in the 113°-117° range, hence if not removed, it increased the NaCl purity in carnallite. Furthermore, the removal of salt during later operations was not easy and hence could add to the cost. Solar evaporation was introduced to make the process cost effective and also to bring about evaporation as well as crystallization under natural conditions. The solution and the solid obtained were analysed every morning which indicated that almost pure NaCl crystallized till such time that the density of the resulting solution reached 1.285, beyond which other constituents viz. KCl and MgCl₂ also started crystallizing. When the solution attained that desired density of 1.285₃

it was centrifuged to recover sodium chloride, and the filtrate was passed on for further processing. The analysis, purity and recovery of NaCl obtained from various experiments of solar evaporation of desulphated bittern are present in Table 4.

v. *Carnallite production.* The filtrate obtained from step iv was heated to 123°, 126° and left overnight for the crystallization of the double salt, carnallite, KCl.MgCl₂.6H₂O. The resulting solution was centrifuged to separate carnallite from the mother liquor. The filtrate, a thick solution of magnesium chloride was heated to 135° left overnight. The magnesium chloride obtained after filtration was 90% pure. The resulting filtrate, a

dilute solution of $MgCl_2$ (about 28%) was recycled.

vi. *Potassium chloride production.* Carnallite obtained was dissolved in the minimum quantity of water in a dissolution tank, concentrated in an evaporator at 116° , transferred to crystallizer and left overnight. The solution containing potassium chloride was centrifuged to obtain potassium chloride. The analysis, purity and recovery of KCl obtained from various experiments are listed in Table 5. The filtrate, a dilute solution of $MgCl_2$ was mixed with the one obtained after complete desulphatation. The stepwise composition of salts and liquors obtained from a typical run in the process are listed in Table 6. The average recovery and purity of the products obtained from 200 lit/batch experiments are listed in Table 7.

MATERIAL OF CONSTRUCTION

The material of construction were selected in accordance with mini-pilot plant scale studies. Although 304 stainless steel was used to overcome corrosion, yet the latter problem was encountered during the pilot plant studies. Foccosion was observed after a few operations in the areas of welding, mostly PVC pipelines were used for the pilot plant experiments.

EVALUATION OF THE PROCESS

The process is illustrated by the flow sheet in Fig. 1 while the material balance flow diagram for processing

Table 4. Sodium chloride obtained from various experiments
(From desulphated bittern)

Density of bittern (g m/cc)	Percent W/W					Recovery (%)	Purity (%)	Experiments
	Sodium chloride	Potassium chloride	Magnesium chloride	Calcium sulphate	Calcium chloride			
1.297	86.33	0.80	6.07	1.92	48.80	38.33	86.33	2 lit. batch
1.297	85.57	0.60	8.23	3.43	3.17	33.33	85.77	2 " "
1.297	91.90	0.74	4.17	2.25	0.94	37.31	91.90	2 " "
1.290	88.71	9.95	Traces	Traces	1.34	34.92	88.71	25 " "
1.290	84.29	3.42	8.21	1.36	2.72	36.64	84.29	25 " "
1.320	81.20	11.30	4.90	Traces	2.60	31.74	81.20	200 " "
1.317	74.32	2.04	18.75	Traces	4.89	33.80	74.32	200 " "

Table 5. Potassium chloride obtained from various experiments

Density of bittern (g m/cc)	Percent W/W					Recovery (%)	Purity (%)	Experiments
	Sodium chloride	Potassium chloride	Magnesium chloride	Calcium sulphate	Calcium chloride			
1.297	35.84	56.93	2.45	2.55	2.23	50.63	56.93	2 lit. batch
1.297	34.95	52.75	6.95	1.40	3.75	45.17	52.75	2 " "
1.297	27.91	60.32	6.68	3.02	2.07	40.88	60.32	2 " "
1.290	26.09	66.04	5.02	Traces	2.84	53.33	66.04	25 " "
1.290	29.32	65.14	3.02	Traces	2.52	56.27	65.14	25 " "
1.320	28.21	62.11	5.67	Traces	4.01	60.99	62.11	200 " "
1.317	20.70	75.13	2.42	Traces	1.74	66.20	75.13	200 " "

Table 6. Stepwise composition of salts and liquors of a typical run in the process

Description	Density °Be	Weight	Percent W/W					
			NaCl	KCl	MgCl ₂	MgSO ₄	CaCl ₂	CaSO ₄
Step-I								
Bittern (raw)	28	1000 kg	14.92	1.37	6.26	4.09	—	—
Bittern (conc.)	35	400 kg	3.31	2.47	13.52	8.23	—	—
NaCl	—	150 kg	82.9	2.14	11.60	3.36	—	—
Step-II								
Bittern (conc.)	35	400 kg	3.31	2.47	13.52	8.23	—	—
Filtrate-I	30.8	300 kg	3.04	2.66	17.38	3.64	—	—
MgSO ₄	—	50.84 kg	8.24	1.62	2.14	88.00	—	—
Step-III								
Filtrate-I	30.8	300 kg	3.04	2.66	17.38	3.64	—	—
Filtrate-II	26.1	290 kg	3.14	2.61	19.75	—	0.18	0.20
CaSO ₄	—	19 kg	0.11	2.16	18.47	—	0.68	78.58
Step-IV								
Filtrate-II	26.1	290 kg	3.14	2.61	19.75	—	0.18	0.20
NaCl	—	4 kg	90.65	4.13	3.43	—	1.79	—
Filtrate-III	32	200 kg	2.45	3.65	27.8	—	0.24	0.29
Step-V								
Filtrate-III	32	200 kg	2.45	3.65	27.8	—	0.24	0.29
Carnallite	—	27 kg	18.52	31.63	46.92	—	0.55	2.68
Filtrate-IV	—	110 kg	0.54	0.29	37.85	—	0.33	—
Step-VI								
Carnallite	—	27 kg	18.52	31.63	46.92	—	0.55	2.68
KCl	—	8 kg	25.7	69.5	2.51	—	1.39	—
Filtrate-V	—	27 kg	6.28	4.66	24.97	—	0.06	—

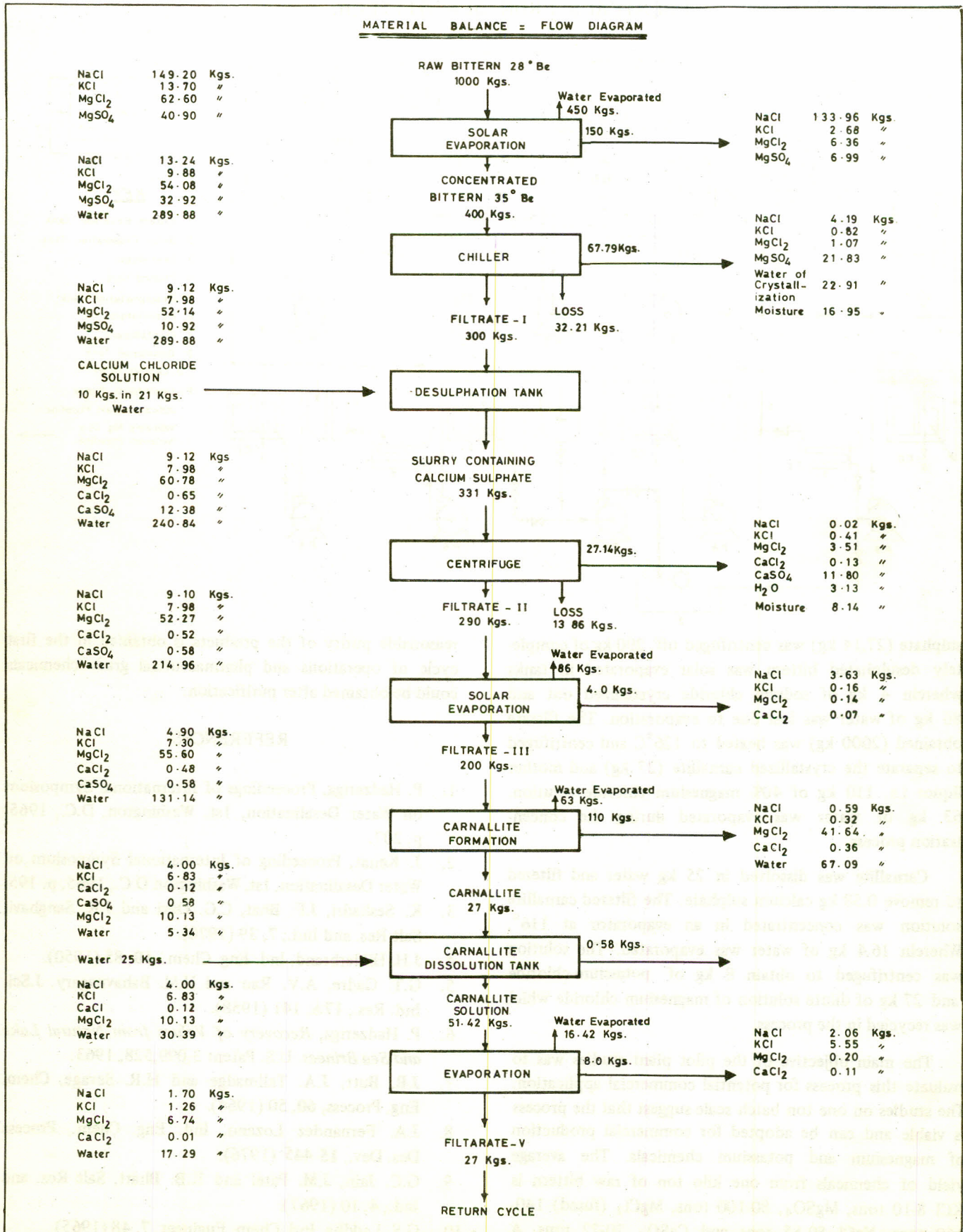
Table 7. Average recovery and purity of the products obtained (from 200 litres/batch)

	Recovery* (%)	Purity (%)
Magnesium sulphate	67.49	87.40
Calcium sulphate	95.34	79.73
Sodium chloride	29.10	85.36
Potassium chloride	58.46	68.91
Magnesium chloride	75.00	92.65

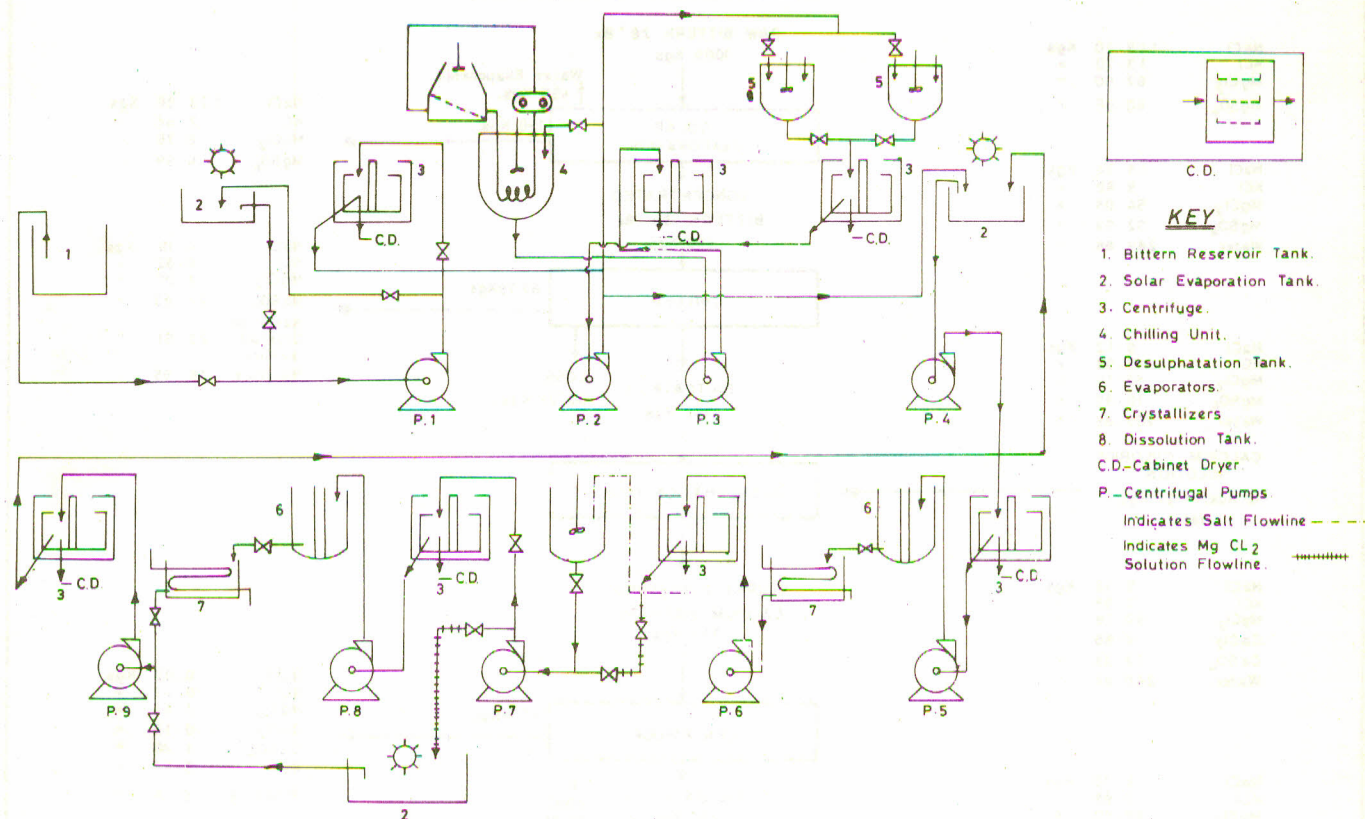
*On the basis of concentrated bittern

1 ton raw bittern for the recovery of chemicals viz. MgSO₄, CaSO₄, KCL, NaCl, and MgCl₂ is illustrated in Fig.2. A 28°Be bittern of average composition was chosen for the material flow description. A number of trial runs performed suggest that the quantities of materials produced from different intermediate streams, are in accordance with material balance flow diagram. A brief description of the material balance shown in Fig. 2 is as follows:

1000 kg of 28°Be bittern when solar evaporated, produced 150 kg of impure sodium chloride and 400 kg of 35°Be bittern, whereas 450 kg of water was evaporated during the process. 68 kg of magnesium sulphate was obtained by chilling 400 kg of concentrated bittern (35°Be). The resulting partially desulphated bittern was reacted with 31 kg of 33% CaCl₂ solution, the precipitated calcium



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sulphate (27.14 kg) was centrifuged off. 290 kg of completely desulphated bittern was solar evaporated in tanks wherein 4 kg of sodium chloride crystallized out and 86 kg of water was lost due to evaporation. The filtrate obtained (2000 kg) was heated to 126°C and centrifuged to separate the crystallized carnallite (27 kg) and mother liquor i.e. 110 kg of 40% magnesium chloride solution. 63 kg of water was evaporated during the concentration process.

Carnallite was dissolved in 25 kg water and filtered to remove 0.58 kg calcium sulphate. The filtered carnallite solution was concentrated in an evaporator at 116°, wherein 16.4 kg of water was evaporated. The solution was centrifuged to obtain 8 kg of potassium chloride and 27 kg of dilute solution of magnesium chloride which was recycled in the process.

The main objective of the pilot plant studies was to evaluate this process for potential commercial application. The studies on one ton batch scale suggest that the process is viable and can be adopted for commercial production of magnesium and potassium chemicals. The average yield of chemicals from one kilo ton of raw bittern is KCl 8-10 tons, MgSO₄, 80-100 tons, MgCl₂ (fused) 140-160 tons, NaCl 50-55 tons and CaSO₄ 20-22 tons. A

reasonable purity of the products is obtained in the first cycle of operations and pharmaceutical grade chemicals could be obtained after purification.

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