SECTION 2

CHAPTER 3

UTILISATION OF MIXED SALT AND BITTERNS FOR THE MANUFACTURE OF POTASH ALUM

1. Review of previous work
2. Description of the process
3. Basic Chemistry of the process
4. Laboratory studies
5. Pilot Plant Studies
6. Cost Estimate
7. Discussion

1. REVIEW OF PREVIOUS WORK

Alum

The English word alum is derived from Latin word alumen. Greek equivalent for alumen was stypteria, the feminine form of an adjective meaning astringent. From the Latin, the word found its way into modern European languages alum in English, alun in French, alaun in German and allume in Italian[33]. The ancients seem to have applied the term to number of substances of astringent taste, commonly to an iron sulphate with little of aluminium sulphate and were unacquainted with our present alum. The present crystallised alum has been known to the medieval chemist, but it appears to have been confused with other astringent substances. The term alum has been applied very loosely. Even at present the word common alum refers to potash alum which is a double sulphate of potassium and aluminium of the formula $KAl(SO_4)_2.12H_2O$ (also written $K_2SO_4.Al_2(SO_4)_3.24H_2O$) and to ammonium alum which is exactly the same except that ammonium ion replaces the potassium ion. Both these crystallise in ocetahedra of the regular or isometric system. Both are colourless or white crystalline salts with sweetish -sourish astringent taste and practically the same chemical action for all the purposes for which they are used. Both these items are in use from very early times and their history has been interwined down to the present day so that it is often difficult to distinguish them. Aluminium sulphate in trade is also called by several names such as alum, concentrated alum, patent alum, filter alum paper makers alum, pickle alum, sizing alum and also as alum cake and water alum. Further certain other minerals are also called alum such as feather alum, plume alum and manganese alum which do not belong to isomorphous series or alums but which do contain aluminium sulphate. As chemistry developed, other salts which were discovered of analogus composition and the same crystal form in which other elements replace the potassium and and ammonium and even the aluminium and sulphur are termed as alum. In short alum is applied as a generic term to the whole series.

Alums have a general formula $M' - M'' (SO_4) 12H_2O$ in which one of the sulphates is that of monovalent cation and the other sulphate that of trivalent cation. The monovalent cation is usually an alkali metal ion. Ammonium alum is prepared from alum shales by addition of decomposed urine while potash alum is obtained from ashes of plants. Potash alum is also made in large quantities directly from the minerals known as alum stone or alunite. Many countries such as Italy, Hungary having such deposits of mineral alum utilise a simple process of calcination and treatment with sulphuric acid to obtain true alums. Form 1700 A.D. onwards, potash alum continued to be cheaper than ammonium alum, until the cost of the latter was lowered by the production of ammonium sulphate as a product of gas works (1845 onwards). The use of ammonium alum was thus greatly increased. The discovery of Stassfurt potash deposits in 1861 gave a new impetus to the use of potassium alum. The great world war cut off the supply of potash and stimulated the use of ammonia alums. The two salts are used interchangeably depending on their relative market price. Sodium alum has been discovered by Gehlen, the discovery has been confirmed by Zeuner and others. The existence[34] has been however questioned by Ostwald and others. More recent investigations such as by Auge Smith[35], Wedman, Lettman Strock have conclusively proved the existence of sodium alum. As a result sodium alum has made its appearance in the industry much later, say by the end of 18th century. The alkali elements Cs, Rb,K, Na form alums with aluminium; out of which cesium forms the most stable alum. The stability of alums decreases with increase in atomic weight from cesium to sodium. Since lithium has lower atomic weight than sodium existence of lithium alum seems uncertain[36,37]. Sanders[38,39]and Dobbins have concluded that no lithium alum exists as stable solid phase between 0 and 50°C.

Just as capacity of the alkali metals increases to form alums with increase in the radius of monovalent ion similarly the solubilities of alums decrease with increase in the radius of monovalent ion. The solubilities of alums (Ref. 40 to 44) at various temperatures are available in literature. Alums are soluble in dilute acids and insoluble in alcohol[45]. The hydrate on drying or heating dehydrates to give burnt alum. Hydrated potash alum melts at 92°C and looses all water of crystallisation at 200°C. Ammonium alum melts at 95°C and looses ammonia and sulphuric acid leaving a residue of alumina at red heat.

Potash alum occurs naturally in such minerals as alunite and kalinite ($K_2Al_6(SO_4)_4OH_{12}$) sp. gr. 2.58; $KAl(SO_4)_2$ $12H_2O$ sp. gr. 1.75) such natural deposits are not occuring in India. Practically all alums and aluminium sulphate are now made from bauxite and sulphuric[46] acid when manufacture of true alums entails just one step additional to aluminium sulphate process. Commercially aluminium sulphate is produced by treating bauxite of 200 mesh with 60° Be sulphuric acid and in order to make various true alums, sulphate of monovalent metals such as K_2SO_4, $(NH_4)_2SO_4$ is added to dilute solutions of $Al_2(SO_4)_3$ in the proper amounts and concentration of mixed solutions followed by cooling gives alum crystals. As natural deposits of potassium sulphate are not available, potassium chloride deposits are used. The various steps involved are (1) potassium chloride is separated from other salts by well known process. (2) then converting the same to K_2SO_4 by reacting with $MgSO_4$ or Na_2SO_4 (3) The potassium sulphate is then reacted with aluminium sulphate to form potash alum.

Some attempt has been done by earlier workers to prepare potash alum directly from waste liquors containing potassium sulphate or potassium chloride. No processes are reported in literature for utilisation of natural mixed salts obtained by evaporation of bitterns, except two American patents.[49,50] T.H. Wright[47,48] utilises an aqueous solution containing potassium chloride which is treated with magnesium sulphate or sodium sulphate and a solution of aluminium sulphate to form potash alum which is allowed to crystallise. The solution is acidified with sulphuric acid. One of the U.S. patent uses an alkaline aqueous mineral potassium chloride or sulphate solution which is treated with sodium sulphate and rendered slightly acidic. $Al_2(SO_4)_3$ is added and potash alum is crystallised. References are available in literature for treatment of alumina with bisulphates of monovalent bases, sulphuric acid and alum by contact process, similarly production of iron free alum is made by reduction of ferric iron to ferrous state and then addition of potassium sulphate to obtain alum. Availability of aluminium sulphate and alums from bauxite by sulphuric acid or acid sulphate of sodium potassium and ammonium in autoclave under pressure is given by R.Jocobson.[51] Treatment of bauxite to obtain alumina by furnacing in presence of sulphur dioxide, air and steam, lixiviating the product and then decomposing the resultant ferruginous solution with sodium thiosulphate. Sodium sulphate is reduced by carbon and air to obtain sulphur dioxide and subsequent utilisation of sulphur dioxide for regeneration of sodium thiosulphate and for furnace operation, is given by J.Morel.[52] Recovery at Tonapat[53] which deals with separation of potash alum from mineral 20 per cent alum. Production of aluminium sulphate and alums is also discussed by J.B.Lal[54] and V.N.Nigam. Purification[55] of aluminium sulphate using ethanol and crystallisation of alums is discussed by Holding and Rechsel respectively.

2. DESCRIPTION OF THE PROCESS

The process consists of treating mixed salt with aluminium sulphate solution, whereby substantially the entire potash content in the mixed salt recovered in the form of a valuable chemical as potash alum, having the chemical composition $K_2SO_4 \, Al_2(SO_4)_3 24H_2O$. It is known that potash alum is manufactured by employing potassium sulphate and aluminium sulphate in proper proportions. If natural deposits of potassium sulphate is not available, potassium chloride deposits are used. It has hitherto been preferred to separate the potassium chloride from other salts by well-known process and then converting the same into potassium sulphate by reacting with magnesium sulphate or sodium sulphate. The potassium sulphate obtained is reacted with aluminium sulphate to form potash alum.

Solid potash alum can be obtained practically free from other salts directly by adding mixed salt containing potassium chloride, sodium chloride, magnesium sulphate and magnesium chloride to a saturated solution of aluminium sulphate. In the above treatment, potassium chloride is converted to potassium sulphate at the expense of magnesium sulphate present in the mixed salt. The potassium sulphate formed therein combines with aluminium sulphate to form potash alum. If the alum formed is in excess than its solubility, it precipitates out from the solution leaving behind the other salts in the solution. Thus solid potash alum is obtained practically free from soluble salts, arsenic and iron. Hence various individual steps of conversion and separation of potassium sulphate according to the conventional method as cited above are not required in this process. The present study sets forth the optimum conditions for treating the mixed salt for obtaining the potash alum.

The mixed salt is obtained by the conventional solar evaporation of sea bittern collected between 36 to 38° Be or alternatively by the recycling of 36° Be bittern with 30° Be bittern as (Chapter 2) already referred to in the earlier part of the thesis. The mixed salt is powdered and added to concentrated aluminium sulphate solution (30 to 35 g $Al_2(SO_4)_3$ per 100 ml.). The quantity of mixed salt added is in such a proportion that one gram of potassium chloride requires 2.3 g of $Al_2(SO_4)_3$ calculated on the basis of the equation $2KCl + MgSO_4 + Al_2(SO_4)_3 = K_2SO_4\ Al_2(SO_4)_3 + MgCl_2$. In general, there will be sufficient quantity of magnesium sulphate in the mixed salt to complete the above reaction. The reaction takes place during the agitation of the above mixture which is raised to 40 - 45°C due to the heat of the reaction. The slurry is heated to 100°C whereby all salts go into solution. Afterwards, stirring is discontinued and the solid suspension are allowed to settle for fifteen minutes. The hot supernatent liquid is pumped through filtration units to a crystalliser where alum crystallises out on cooling. The slurry is centrifuged and washed to obtain high grade potash alum assaying 99 to 99.5 per cent purity as $K_2SO_4(Al_2SO_4)_3\ 24H_2O$. The recoveries of potassium and aluminium sulphate are 85 per cent.

Above process may be also carried out by preparing a saturated solution of mixed salt and then mixing with concentrated solution of aluminium sulphate in the above proportion. The effluent after the removal of potash alum contains magnesium chloride, magnesium sulphate, sodium chloride and potash alum. Concentrations of magnesium chloride and sulphate are not high enough to crystallise out with alum. The only possibility of contaminating the product is by sodium chloride as the effluent is saturated with alum and sodium chloride. The precipitation of sodium chloride with alum is prevented by addition of calculated quantity of water to the reaction mixture. By knowing the amount of sodium chloride in the mixed salt, dilution is affected in such a way that all sodium chloride is retained in the solution at the temperature of cooling. If the product is still contaminated with sodium chloride over the prescribed limit, it is removed by simple washing or by recrystallisation.

3. BASIC CHEMISTRY OF THE PROCESS

The process consists of (1) recovery of mixed salt from sea bittern and (2) utilisation of mixed salt for the recovery of potassium chloride as potash alum using aluminium sulphate. Mixed salt consists of four salts namely (1) potassium chloride (18 - 20 per cent), (2) sodium chloride (15 - 20 per cent), (3) magnesium sulphate (25 - 35 per cent) and 4) magnesium chloride (6 - 8 per cent).

Manufacture of alum from mixed salt is achieved by treating mixed salt with a saturated solution of aluminium sulphate at 100°C whereby most of the salts are dissolved; potassium chloride from mixed salt is converted to potassium sulphate at the expense of magnesium sulphate which is also present in the mixed salt. Usually magnesium sulphate available in mixed salt is in excess than stoichiometric ratio for complete conversion of potassium chloride to potassium sulphate; each gram of potassium chloride requires only 0.81 g. of magnesium sulphate to produce 1.17 g of potassium sulphate (6.36 g of potash alum) and 0.64 g of magnesium chloride. The potassium sulphate thus formed combines with aluminium sulphate to form potassium alum. If the alum formed at hot is in excess than its solubility at room temperature it precipitates out from the hot solution when cooled to room temperature leaving behind other salts in mother liquor. As the entire process is based on solubility relationships of salts at higher and lower temperatures the purity of the product can be easily controlled. The main reactions involved are as follows:

1) $2\ KCl + MgSO_4 = K_2SO_4 + MgCl_2$

2) $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O = K_2SO_4Al_2(SO_4)_3.24H_2O$

3) $2KCl + MgSO_4 + Al_2(SO_4)_3 + 24H_2O = K_2SO_4\ Al_2(SO_4)_3$
$- 24H_2O + MgCl_2$

The reaction products obtained on treatment of mixed salt with aluminium sulphate solution are potash alum and magnesium chloride. The concentration of magnesium chloride in the solution is increased. The total magnesium chloride will be, magnesium chloride from mixed salt plus the magnesium chloride formed due to the potassium chloride and magnesium sulphate reaction. In order to control the operation for obtaining good grade alum in presence of sodium chloride, magnesium sulphate and magnesium chloride, mutual solubility relationships of these salts with alum at 30°C (crystallisation temperature) are studied. The data are given in Table 75, 76, 77; whereas solubility of potash alum is given in Fig. 29, 30, 31.

4 LABORATORY STUDIES

Solubility determination

Effect of sodium chloride on solubility of potash alum is studied. Following procedure is adopted for determining the solubility of salts. A saturated solution of potassium alum is taken and known quantities of finely powdered sodium chloride is added, stirred for four hours, and filtered. Solutions are analysed. Precautions are taken to maintain the temperature constant during filtration. The Table No. 75 indicates that the solubility of potash alum does not decrease appreciably with increase in sodium chloride concentration. The data also show that potash alum cannot be recovered from end liquor by saturating with sodium chloride.

The effect of magnesium chloride concentration on solubilities of other salts and alum is studied in similar way and is given in Table 76. Magnesium chloride solutions of different concentrations are taken and saturated with sodium chloride and potash alum. The mixture is stirred for four hours and filtered solutions are analysed. The table indicates that with increase in magnesium chloride concentration, solubility of potash alum does not decrease appreciably. The data also indicates that precipitation of sodium chloride with alum can be controlled if the concentration of magnesium chloride in the end liquor is controlled. The only constituent which is absent in Table 76 is magnesium sulphate. The Table 77 shows

Table 75 SYSTEM K_2SO_4 $Al_2(SO_4)_3$ - NaCl - H_2O at 30°C

Constituents	grams per 100 ml					grams per 100 grams of solution				
	1	2	3	4	5	1	2	3	4	5
K_2SO_4	2.75	2.75	2.75	2.40	2.40	2.57	2.45	2.36	1.95	1.99
$Al_2(SO_4)_3$	5.85	5.85	5.86	4.86	4.86	5.48	5.21	4.70	3.94	3.93
NaCl	0.08	9.00	17.00	29.00	30.00	0.075	8.01	14.55	23.51	24.28
Sp. gr.	1.068	1.123	1.168	1.234	1.236	-	-	-	-	-

Table 76/SYSTEM K_2SO_4 $Al_2(SO_4)_3$ - NaCl - $MgCl_2$-H_2O at 30°C

Per cent	grams per 100 ml				grams per 100 gram of solution			
Constituents	1	2	3	4	1	2	3	4
K_2SO_4	2.50	2.50	2.50	2.50	1.983	1.95	1.94	1.93
$Al_2(SO_4)_3$	4.91	4.91	4.91	4.91	3.894	3.83	3.81	3.79
NaCl	25.00	23.00	20.00	15.00	19.83	17.92	15.52	11.58
$MgCl_2$	11.68	16.18	19.78	28.76	9.05	12.61	15.35	22.21

Table 77 SYSTEM K_2SO_4 $Al_2(SO_4)_3$ - NaCl - $MgCl_2$ - $MgSO_4$ - H_2O at 30°C

Per cent	grams per 100 ml			grams per 100 grams of solution		
Constituents	1	2	3	1	2	3
K_2SO_4	2.50	2.50	2.55	1.99	2.0	2.02
$Al_2(SO_4)_3$	4.91	4.91	4.94	3.92	3.93	3.92
NaCl	17.00	15.00	13.50	13.54	12.00	10.70
$MgCl_2$	10.10	10.12	10.12	8.04	8.10	8.03
$MgSO_4$	Nil	5.88	13.01	--	4.70	10.31

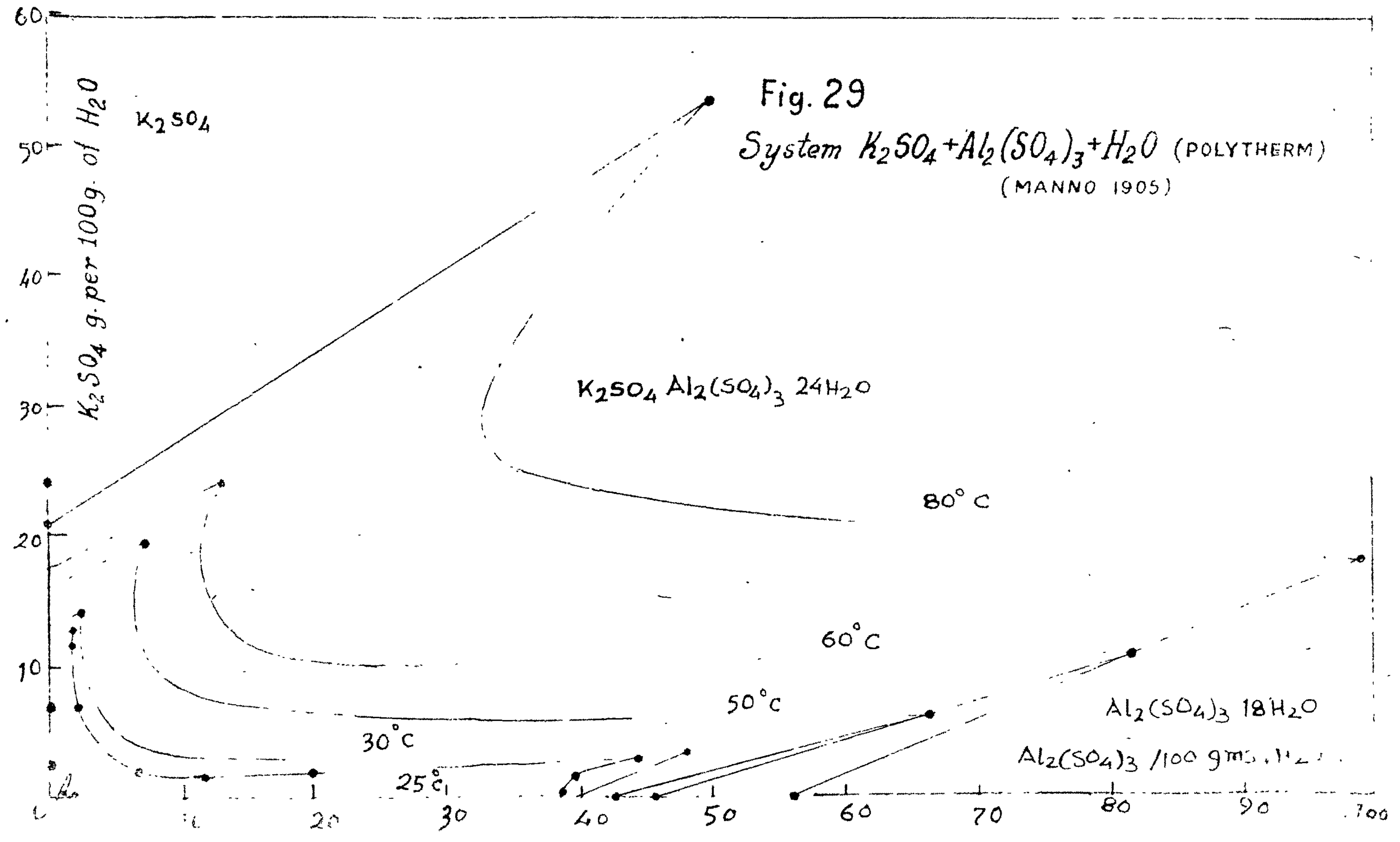


Fig. 29

System $K_2SO_4 + Al_2(SO_4)_3 + H_2O$ (POLYTHERM)

(MANNO 1905)

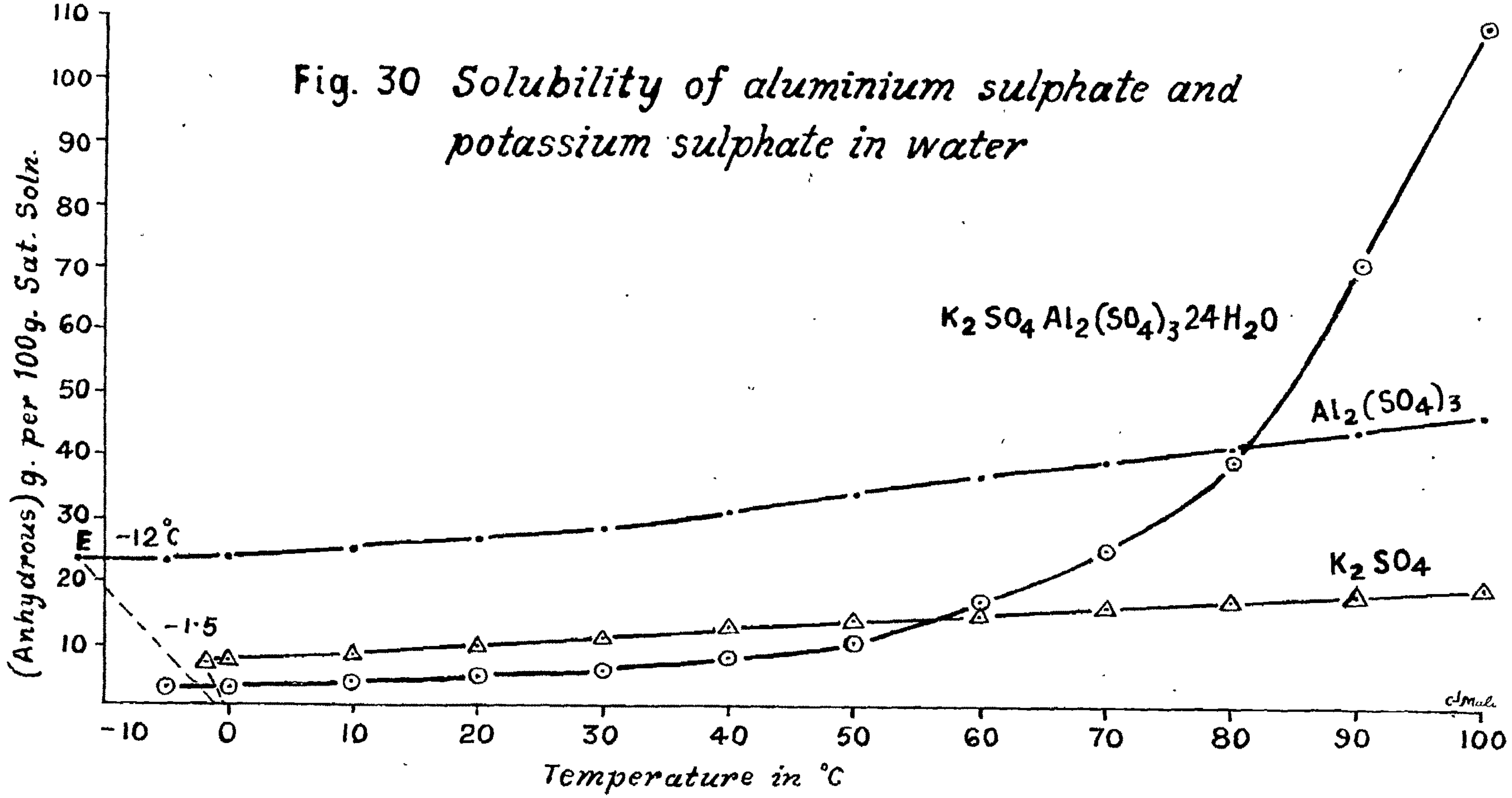
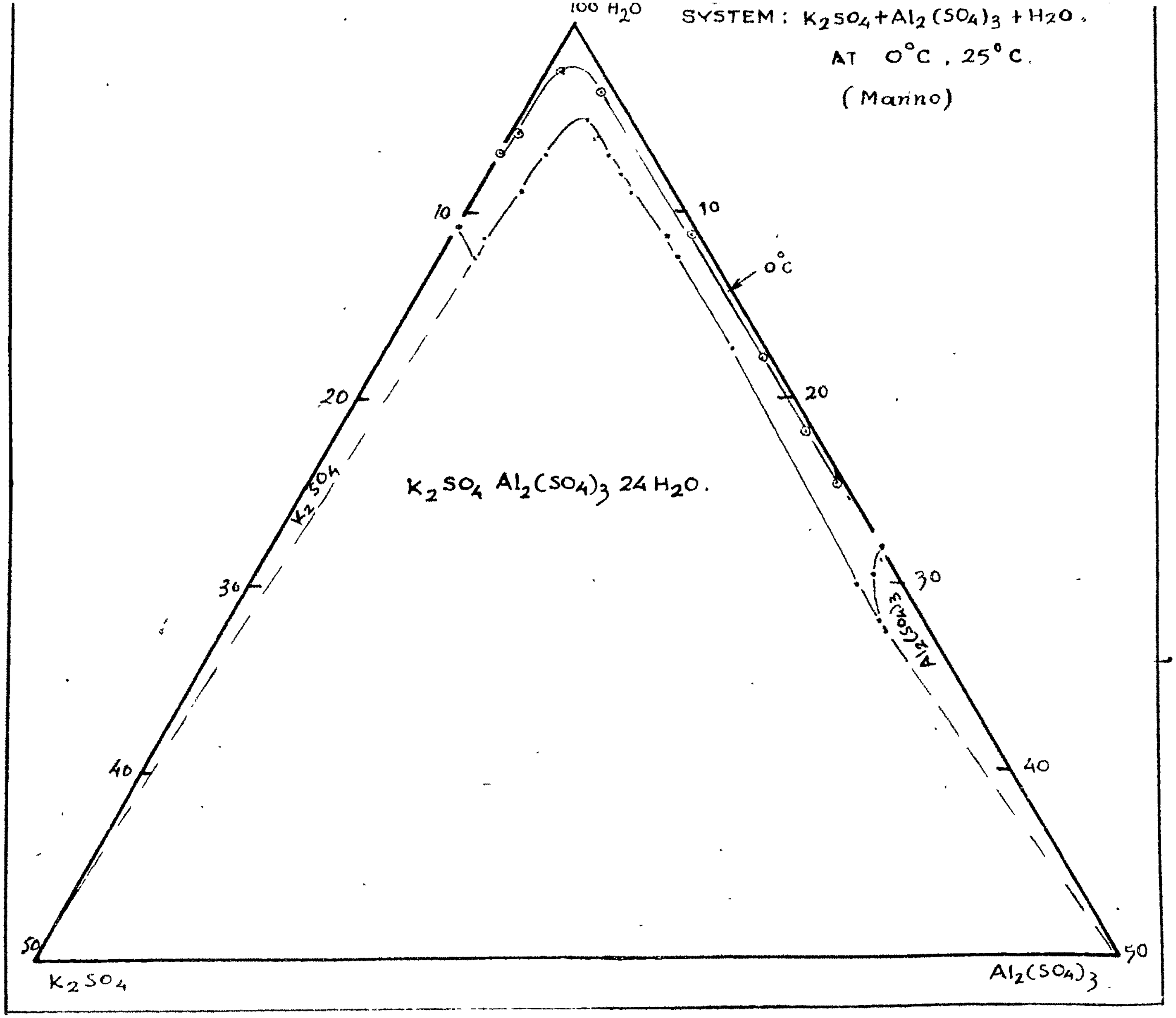


Fig. 30 *Solubility of aluminium sulphate and potassium sulphate in water*



SYSTEM : $K_2SO_4 + Al_2(SO_4)_3 + H_2O$.
AT 0°C , 25°C.
(Marino)

that if magnesium chloride concentration is kept at ten per cent and the system contains magnesium sulphate, sodium chloride and alum, the concentration of sodium chloride decreases further to 15 and 13.5 per cent, corresponding to 6 per cent and 13.1 per cent magnesium sulphate respectively. Analysis of the end liquor after crystallisation of alum shows following composition.

End liquor composition
(g/100 ml)

KCl	2.2 (2.57% K_2SO_4)
NaCl	16.0
$MgCl_2$	10.0
$Al_2(SO_4)_3$	6.1
$MgSO_4$	6.6

When concentration of magnesium chloride in solution is 10 per cent sodium chloride solubility is 16 per cent. The solubility of alum in water at 30°C is 15.43 or in other words 2.84 g of K_2SO_4 and 5.57 g $Al_2(SO_4)_3$ per 100 ml. Thus solubility is not much changed due to presence of other salts such as magnesium sulphate, magnesium chloride and sodium chloride.

Adjustments of the final volume of the end liquor

The foregoing account gives a key to adjust the final volume of the end liquor, that is, liquor left after crystallisation of alum at room temperature. This can be better illustrated by the example given below.

45 kg of mixed salt containing 20 per cent KCl, 20

per cent NaCl 30 per cent $MgSO_4$ and 5 per cent $MgCl_2$ is to be treated with aluminium sulphate solution to obtain potash alum.

a) Requirement of $Al_2(SO_4)_3$

Total KCl x factor = $Al_2(SO_4)_3$
9 kg x 2.3 = 20.7 kg

If 35 per cent solution is available 72.5 litres of solution will be required to complete the reaction.

6) Magnesium chloride to be handled

45 kg mixed salt containing 5 per cent $MgCl_2$ = 2.25 kg $MgCl_2$. Now magnesium chloride formed due to reaction will be

KCl x per cent recovery x factor = $MgCl_2$
9 kg x 90/100 x 0.6386 = 5.17 kg

Total $MgCl_2$ = $MgCl_2$ in mixed salt + $MgCl_2$ due to reaction
= 2.25 + 5.17 kg
= 7.42 kg

In order to adjust 10 per cent $MgCl_2$ in end liquor, the final volume of end liquor after crystallisation of alum should be 74 litres.

c) Water to be added Water removed by crystallisation of alum is calculated as follows:

KCl x per cent recovery x 6.359 x 0.4556
= 9 kg x 90/100 x 6.359 x 0.4556
= 23.46 kg of water (Say 23.5 litres).

Now if live steam is used for heating, it is observed that about 20 litres of water is condensed in reaction mixture while heating to 100°C. Hence only 3 litres of water is required to be added to reaction mixture.

Total sodium chloride in mixed salt is only 9 kg which gives 12 per cent (w/v) NaCl. As the saturation of NaCl is 16 per cent, all NaCl will be retained by the end liquor and good grade alum will be obtained.

Mixed salt containing over 25 per cent sodium chloride is to be employed for the process, end liquor volume will have to be increased by addition of extra quantities of water such that NaCl is retained in the solution which will result in decreasing the yields or otherwise impure alum will be obtained. If a small amount of sodium chloride separates out along with alum, it is easier to wash it out during centrifuging. Magnesium chloride which is one of the reaction product controls the solubility of sodium chloride in solution. Hence it is essential that mixed salt contains minimum amounts of magnesium chloride. This can be achieved simply by storing the mixed salt on platforms to drain off the adhering magnesium chloride before it is processed.

Mixed salt as such is a stable mixture of four salts; however on ageing when stored for more than a year magnesium chloride drains off slowly and potassium chloride reacts with magnesium sulphate to form potassium sulphate. It is observed that as long as potassium chloride is present and the magnesium chloride formed in the reaction is continuously drained off, the reaction proceeds further. Reaction with $MgSO_4$ starts first with potassium chloride and in absence of potassium chloride it proceeds with sodium chloride. As magnesium sulphate is in excess than stoichiometric ratio for complete conversion of potassium chloride to potassium sulphate, potassium sulphate combines with magnesium sulphate to form less soluble double sulphates. Various double salts are formed as intermediate compounds such as schoenite ($K_2SO_4MgSO_46H_2O$) and glaserite ($3K_2SO_4.Na_2SO_4$). For potash alum manufacture any of these salts can be used.

Preparation of potash alum (laboratory experiments)

Experiment 1 :- Mixed salt obtained from sea bittern contained $KCl/MgSO_4$ 20/35 while that from inland bitterns was usually 20/25 or even less. Potash alum was prepared using mixed salt containing 18.4 per cent, 22.1 per cent NaCl, 24.0 per cent $MgSO_4$ and 3.1 per cent $MgCl_2$ as generally obtained from inland bitterns (Kharaghoda). One kilogram of the mixed salt of above composition was added to 1150 ml of aluminium sulphate solution containing 423.2 g of aluminium sulphate. Aluminium sulphate was added in such a proportion that 1 g KCl reacted with 2.3 g $Al_2(SO_4)_3$ in presence of magnesium sulphate. The reaction mixture was diluted with water and heated to 100°C whereby all the salts went into solution. Analysis of the hot solution showed (g/100 ml), 11.42 per cent K_2SO_4, 22.82 per cent

$Al_2(SO_4)_3$, 9.78 per cent NaCl, 9.25 per cent $MgCl_2$, 5.00 per cent $MgSO_4$. The hot liquor was allowed to settle and the hot supernatent clear liquor was siphoned out from the top to another beaker and cooled to room temperature. Alum slurry was centrifuged and washed with water to free the adhering mother liquor and to obtain high grade potash alum. The only impurity was sodium chloride which was 2 to 2.5 per cent without washing the cake in the centrifuge, but was reduced to 0.2 per cent by little washing the product in the centrifuge. The yield was 1080 g. and the purity of alum was 99 per cent. The effluent or mother liquor measured 33°Be and was 1300 ml in volume, containing 2.6 per cent K_2SO_4, 10 per cent $MgCl_2$, 8.9 per cent $MgSO_4$, 16 per cent NaCl and 4.5 per cent $Al_2(SO_4)_3$ (g/100 ml.).

The recovery of potassium as potash alum was 84.2 per cent. Considering the solubility of alum in the liquor, the small loss was inevitable. 72 per cent of magnesium sulphate present in mixed salt was used up to convert potassium chloride to potassium sulphate. Ten per cent of the added aluminium sulphate remained in the end liquor. The results are given in Table 78.

Experiment 2

Molar ratio of KCl to $MgSO_4$ is 1:0.92 while from inland bitterns it is usually 1:0.77. Mixed salt having normal composition as generally obtained from sea bittern was used for preparing potash alum. 3 kilograms of mixed salt containing 19.2 per cent KCl, 12.5 per cent NaCl, 35.2 per cent

Table 78 PREPARATION OF POTASH ALUM FROM MIXED SALT AND ALUMINIUM SULPHATE

(Laboratory experiments data sheet 1)

	Mixed salt		Aluminium sulphate solution		Water added	Potash alum		End liquor		Deviation
Quantity	1 kg		1150 ml		800 ml	1080 g		1300 ml		
Density								33° Be		
Composition	Per cent	Amount in g	Per cent (w/v)	Amount in g		Per cent	Amount in g	Per cent	Amount in g	Amount in g
K_2SO_4	-	-	-	-	-	16.78	185.2	2.6	33.8	.1
KCl	18.4	184	-	-	-	-	-(155)*	-	(28.9)*	nil
NaCl	22.1	221	-	-	-	1.25	13.5	16.0	208.0	+ .5
$MgSO_4$	24.0	240	-	-	-	-	-	8.9	116.0	-
$MgCl_2$	3.1	31	-	-	-	-	-	10.0	130.0	-
$Al_2(SO_4)_3$	-	-	36.8	423.2	-	33.7	364.7	4.5	58.5	nil

Recovery of KCl as $K_2SO_4\ Al_2(SO_4)_3\ 24H_2O$ is 84.2 per cent

*KCl equivalent to K_2SO_4

$MgSO_4$ and 3.2 per cent $MgCl_2$ was treated with 3.5 litres of aluminium sulphate solution; heated to 110°C and filtered hot. The clear filtrate was cooled to room temperature to crystallise alum. The results are given in Table 79.

Experiment 3

Experiment 3 was performed similar to experiment No.1 except that mixed salt used in experiment No. 1 was from inland bitterns, while that used in this experiment was stored for a long time and which analysed 24.2 per cent K2 ~~Mg~~SO_4, 14.2 per cent $MgSO_4$, 34.7 per cent NaCl and 15.3 per cent KCl, accounting for 36 per cent potassium schoenite in the above salt. One kilogram of mixed salt was added to 2500 ml of aluminium sulphate solution containing 820 g. $Al_2(SO_4)_3$. 730 ml of water was added and the slurry was stirred and raised to 100°C. The potash alum was crystallised out as in experiment No.1 Yield of potash alum was 2 kg analysing 18 per cent K_2SO_4, 35.40 per cent $Al_2(SO_4)_3$ and 1.9 per cent NaCl. Sodium chloride was reduced to 0.2 per cent by washing in centrifuge. The final product analysed 99.0 per cent potassium alum free from iron. The results are given in Table 80.

Laboratory experiments 4

Preparation of potash alum using mixed salt having excess of sodium chloride (31.7 per cent sodium chloride). Experiments carried out using mixed salt containing 20.4 per cent KCl, 35.7 per cent $MgSO_4$, 31.7 per cent NaCl, 4.8 per cent $MgCl_2$ with aluminium sulphate solution (31.54 per cent

Table 79 PREPARATION OF POTASH ALUM FROM MIXED SALT AND ALUMINIUM SULPHATE

(Laboratory experiments data sheet 2)

	Mixed salt		Aluminium sulphate solution		Water added	Potash alum		End liquor		Deviation
Quantity	3 kg		3.5 L		nil	3.4 kg		2.2 L		
Composition	Per cent	Amount (g)	Per cent (w/v)	Amount (g)		Per cent	Amount (g)	Per cent (w/v)	Amount (g)	Amount (g)
K_2SO_4	-	-	-	-	-	18.21	619.1	-	-	-
KCl	19.2	576	-	-	-	-	(530)*	2.1	46.2	0.2
NaCl	12.5	375	-	-	-	2.23	75.82	13.5	299.2	-
$MgSO_4$	35.2	1056	-	-	-	-	-	2.9	632.0	-
$MgCl_2$	3.2	96	-	-	-	-	-	15.43	316.5	-
$Al_2(SO_4)_3$	-		38	1330		35.85	121.9	5.05	111.1	0.1

Recovery of KCl as potash alum (K_2SO_4 $Al_2(SO_4)_3 24H_2O$ = 92 per cent

The product was washed in centrifuge to remove NaCl.

The wash product contained below 0.1 per cent NaCl

* KCl equivalent of potassium sulphate

Table 80 PREPARATION OF POTASH ALUM FROM MIXED SALT AND ALUMINIUM SULPHATE (Laboratory experiments data sheet 3)

	Mixed salt*		Aluminium sulphate solution		Water added	Potash alum		End liquor		Deviation
Quantity	1 kg		2500 ml		730 ml	2 kg		2530 ml		
Density								30° Be		
Composition	Per cent	Amount (g)	Per cent	Amount (g)	-	Per cent	Amount (g)	Per cent (w/v)	Amount (g)	Amount (g)
K_2SO_4	24.2	242	-	-	-	18.0	360	-	-	-
KCl	15.3	153	-	-	-	-	-	2.4	60.7	-
NaCl	34.7	347	-	-	-	-	-	13.76	348	+ 1
$MgSO_4$	14.3	145	-	-	-	-	-	1.58	40	-
$MgCl_2$	-	-	-	-	-	-	-	2.33	58.95	.07
$Al_2(SO_4)_3$	-	-	32.8	820	-	35.4	708	4.43	112	-

Recovery of KCl as $K_2SO_4.Al_2(SO_4)_3\ 24H_2O$ = 85.57 per cent

* Mixed salt contains 36 per cent schoenite

$Al_2(SO_4)_3$) in the required ratio gave following results (Table 81). Yield and purity of alum are controlled by final volume of the end liquor.

Table 81 POTASH ALUM FROM MIXED SALT WITH HIGH AMOUNTS OF SODIUM CHLORIDE (Laboratory experiments)

Condition	Recovery of alum Per cent	Remarks
i) Mixture stirred boiled and kept overnight	98.8	With 3.4 per cent NaCl
ii) Mixture stirred with addition of 100 ml, water boiled and kept overnight	65	Pure alum crystallised with no NaCl
iii) Mixture + calculated quantity of water required for crystallisation of alum boiled and kept overnight	88	With 0.2 per cent NaCl

Laboratory experiments 5

Experiments using saturated solution of mixed salt instead of pulvarised mixed salt gave following results. Mixed salt solution 33° Be in density containing 10.0 per cent KCl, 13.0 per cent NaCl, 13.46 per cent $MgSO_4$ and 5.05 per cent $MgCl_2$ when treated with aluminium sulphate solution containing 28.7 per cent $Al_2(SO_4)_3$ gave following results which are tabulated in Table 82.

Table 82 PREPARATION OF POTASH ALUM FROM MIXED SALT SOLUTION (Laboratory experiments)

Condition	Recovery of alum Per cent	Loss of $Al_2(SO_4)_3$ Per cent
1) Mixture stirred at room temperature	71.2	28.8
2) Mixture boiled and kept overnight	72.0	28.0
3) Mixture stirred at 10°C for 15 minutes and centrifuged	85.4	15.0
4) Mixture stirred at -5° C for 15 to 20 minutes and centrifuged	86.8	13.4

Potash alum from bitterns

Bitterns of 29/30° Be density contains 2 to 2.5 per cent potassium chloride which is equivalent to 2.3 to 2.9 per cent of potassium sulphate or 12.30 to 15.78 per cent potash alum. As the solubility of alum is not much effected with the presence of other salts, it is not possible to obtain alum directly from 28° or 29°Be bittern. However during further concentration of bittern by solar evaporation a stage is reached where potassium chloride concentration is as high as 4 to 5 per cent. When concentrated bitterns of such compositions are treated with saturated solution of aluminium sulphate solution, alum separates out. The recoveries of potassium alum are low and loss of aluminium sulphate in the end liquor is high (Table 83). In Table 84 recoveries of alum from bitterns are given; bittern samples 1 and 2 show better recoveries; however in normal evaporation, such concentrations of potassium are not obtained, and recoveries of alum are only up to 50 to 55 per cent.

Table 83 PREPARATION OF POTASH ALUM FROM BITTERNS (Laboratory experiment 1)

Bittern samples	1		2		3	
Composition g per 100 ml						
KCl	5.60		6.00		4.50	
NaCl	4.10		7.00		4.60	
$MgSO_4$	6.63		6.29		6.62	
$MgCl_2$	25.40		23.20		24.50	
Condition of the exp.	Alum obtained (g)	Percent recovery	Alum obtained (g)	Percent recovery	Alum obtained (g)	Percent recovery
1) Bittern mixed with aluminium sulphate solution stirred at R.T. and centrifuged	20.50	57.60	22.50	58.96	11.45	40.00
2) Mixture boiled and kept overnight	21.50	60.37	24.60	64.46	12.00	42.00
3) Mixture cooled to 10°C and centrifuged	27.86	78.20	29.20	76.52	15.75	55.60

Table 84 PREPARATION OF POTASH ALUM FROM BITTERNS (Laboratory experiments 2).

Exp.	Bittern 500 ml 33° Be		$Al_2(SO_4)_3$ 131 ml(35°Be)		K-alum 47 kg		End liquor 608 ml		
Composition (w/v) I	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Per cent	Total salts (g)	Recovery and remarks.
KCl	4.10	20.50	-	-	15.31	7.20	2.25	13.68	35 per cent recovery of K as K-alum
NaCl	4.50	22.50	-	-	0.35	0.16	3.50	21.28	
K_2SO_4	-	-	-	-	17.87	8.40	-	-	65% $Al_2(SO_4)_4$ is lost in the end liquor
$MgSO_4$	6.72	33.60	-	-	-	-	4.08	28.50	
$MgCl_2$	24.63	123.15	-	-	3.11	1.45	21.00	125.7	
$Al_2(SO_4)_3$	-	-	36	47.16	35.06	16.48	5.05	30.68	
II	Bittern 500 ml 35.6°Be		122 ml 35° Be		39 g		600 ml		
KCl	3.8	19.0	-	-	15.27	5.96	2.25	13.50	31.26% recovery of K as K-alum
NaCl	2.25	11.25	-	-	0.36	0.16	1.85	11.10	
K_2SO_4	-	-	-	-	17.83	6.96	-	-	
$MgSO_4$	8.54	42.70	-	-	-	-	6.32	37.92	
$MgCl_2$	30.34	151.70	-	-	3.21	1.2	25.91	155.51	
$Al_2(SO_4)_3$	-	-	36	43.92	35.04	13.67	5.04	30.25	69% loss of $Al_2(SO_4)_3$
III	38.32°Be		60 ml		nil		560 ml		
KCl	1.85	-							
NaCl	15.50	-							
$MgSO_4$	7.05	-	-						
$MgCl_2$	10.82	-							
$Al_2(SO_4)_3$	-	-	36	21.6			Not analysed		No recovery

5 - PILOT PLANT STUDIES

Pilot plant experiments

Preparation of potash alum using mixed salt and aluminium sulphate (alumina ferric grade B) was carried out in laboratory with glass apparatus and the purity of the products was very high. On large scale production it was likely that potash alum might be contaminated during various processes as heating, pumping, filtration and crystallisation with undesirable salts. It was thus necessary to ascertain whether the product obtained in pilot plant would meet I.S. technical grade and B.S. pharmaceutical grade specifications. It was also necessary to study corrosion of materials of construction and how best contamination of metals could be avoided. In this connection it was essential to study the heating with live steam, the effect of dilution by condensation of steam and to ascertain the economic feasibility of the process.

Raw materials

A) Mixed salt: The usual composition of mixed salt obtained by evaporation of sea bittern was used for pilot plant experiments.

Mixed salt analysis
Per cent composition (on wet basis)

Potassium chloride	18 - 20
Sodium chloride	15 - 20
Magnesium sulphate	30 - 35
Magnesium chloride	6 - 8
Insolubles	0 - 1.5
Free and combined moisture (by difference)	25 - 30

Mixed salt 18 to 20 mesh size was preferable and grinding was carried out to above mesh size. Seive analysis of mixed salt taken after grinding mixed salt in edge runner for 15 to 20 minutes was as follows:

Mesh size (B.S.S.)	g	per cent
- 18 + 25	400	40
- 25 + 40	600	60
	1000	100

Mixed salt after grinding to desired mesh size (without drying) showed following bulk density, 57.72 lbs per cubic feet or 924.7 kg per cubic meter.

Aluminium sulphate

Aluminium sulphate comes to the market in two commercial grades (1) Iron free variety which is white and contains below 0.005 per cent of iron (as Fe) (2) Alumina ferric grade A and B are available in the market. 'A' grade contains 0.3 per cent iron while 'B' grade contains 0.5 per cent iron. The commercial variety of alumina ferric grade 'B' was purchased for pilot plant experiments and was of the following composition.

Analysis of alumina ferric grade B	
Al_2O_3	17.5 per cent
Insolubles in water	0.08 "
Fe_2O_3	0.45 "
Water of crystallisation	42.66 "

'Alumina ferric grade B' is cheaper than the other grades of aluminium sulphate available in the market. It is available in big lumps 4" to 6" size and needs crushing in jaw crusher to 1/4" to 1/2" size before it can be dissolved to obtain a concentrated solution. Aluminium sulphate is very soluble in water to the extent of 107.35 g per 100 g of water.

Preparation of aluminium sulphate solution

100 kg of crushed alumina ferric grade B was dissolved in 94 litres of water (hot condensed steam water), stirred for 2 hours and allowed to settle in wooden drum. It was observed that filtration of hot solution was difficult even with pressure filtration unit employing filter aid. The solution after settling, measured 35 to 36° Be'. If live steam was used for heating the solution, only 70 litres of water was required for every 100 kg. of crushed raw material. The rate of settling was very slow and to obtain a clear solution, 48 hours of settling period was found necessary.

Even though the volume of the turbid zone was 425 ml, out of one litre of the slurry solution, the insoluble matter was much less. As the solution was thick (1.33 sp. gr.) the fine particles remained in suspension. In pilot plant experiments, the turbid solution was diluted with water and the clear dilute solution was reused for preparing fresh solution.

Table 85 SETTLING OF ALUMINIUM SULPHATE SOLUTION

Period of settling (hours)	Aluminium sulphate solution(35°Be') Turbid zone (cms)	Clear zone (cms)
0.00	35.00	0.00
1.00	34.65	0.35
1.30	31.15	3.85
2.00	27.30	7.70
2.30	24.85	10.15
3.30	21.00	14.00
5.30	19.25	15.75
7.30	17.50	17.50
12.00	16.45	18.55
24.00	15.00	20.00
30.00	14.50	20.50
48.00	14.80	20.20
72.00	14.80	20.20

Description of pilot plant experiments

45 kg of mixed salt of 18 to 25 mesh size containing 18 to 20 per cent potassium chloride was mixed with 20 litres of water and 60 litres of 35 per cent aluminium sulphate solution. The reaction mixture was stirred in wooden vats with wooden stirring arrangement and heated with live steam at (20 to 30 lbs) 1.4 to 2.1kg per sq.cm pressure to 100°C, thereby most of the salts were dissolved. The reaction

Table 86 MATERIAL BALANCE DATA FOR POTASH ALUM FROM MIXED SALT (Pilot plant experiment)

Basis 45 kg mixed salt per batch

Description	Mixed salt		Aluminium sulphate solution		Potash alum		End liquor		Deviation
Quantity	45 kg		60 litres		45 kg		70 L(29.5°Be)		-
Composition	Per cent	Amount (kg)	Per cent (w/v)	Amount (kg)	Per cent	Amount (kg)	Per cent (w/v)	Amount (kg)	(kg)
K_2SO_4	-	-	-	-	18.28	-	-	-	-
KCl	20.12	9.05	-	-	-	7.2*	2.56	1.8	.05
NaCl	20.23	9.1	-	-	-	-	13.00	9.1	-
$MgSO_4$	23.20	10.44	-	-	-	-	6.65	4.66	-
$MgCl_2$	9.98	4.49	-	-	-	-	13.00	9.1	-
$Al_2(SO_4)_3$	-	-	35	20.82	36.00	16.56	6.10	4.27	.01

1) Water added to reaction mixture was 20 litres.

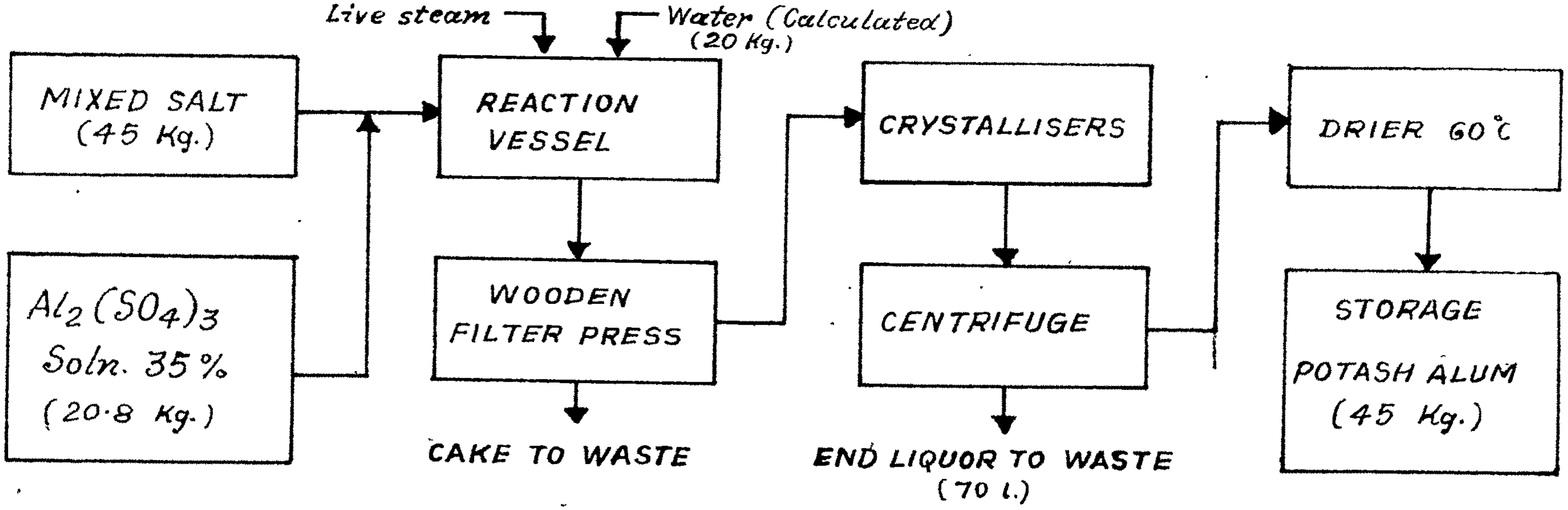
2) Water condensed from steam (live steam) during heating was 20 litres.

Purity of the product potash alum was 99.5 per cent (B.P.grade).

Recovery of KCl as potash alum was 80 per cent.

* KCl equivalent of K_2SO_4 was 7.2

Fig. 32 PROCESS FLOWSHEET FOR THE RECOVERY OF POTASH ALUM FROM MIXED SALT



MIXED SALT
Percent

KCl	18·20
NaCl	15·20
$MgSO_4$	30·35
$MgCl_2$	6·8
Insolubles	0·1·5

ALUMINAFERRIC
Grade B

Al_2O_3	17·15
Fe_2O_3	0·45
Insolubles	0·08

POTASH ALUM

K_2SO_4	18·36
$Al_2(SO_4)_3$	35·94
(K-alum	99·63)
Insolubles	0·05
Fe below	0·007
Cu, As	Nil

END LIQUOR
(70 L.) 29·5°Be

KCl	2·2
NaCl	16·0
$MgCl_2$	10·0
$Al_2(SO_4)_3$	6·1
$MgSO_4$	6·6

Mali

mixture was then stirred at the same temperature for 10 to 15 minutes and filtered using filter press or laboratory model mild steel sparkler (model 8.3) pressure filter. 0.7 kg per sq. cm (10 lbs) of pressure was developed at the end of the operation. Compressed air at 1.4 to 3.5 kg per sq. cm (20/50 lbs) pressure was then passed through the unit to flush out the last drop of the liquid. The hot filtered solution was cooled rapidly to obtain pure uniform grade alum crystals. The cold slurry was then centrifuged and the product was tested for chloride (qualitative test). It was found helpful to wash with one litre of distilled water in centrifuge to remove adhering mother liquor and any other soluble impurity such as sodium chloride. The product was then dried below 60°C with occasional stirring with wooden scoops. 45 kg of mixed salt would give 46 kg of pure potash alum. Results of yield and purity are reported in material balance Table 86 and Fig. 32.

Major equipments used for pilot plant studies

a) Dissolver

Wooden vat was used with wooden stirrers rotating at 60 r.p.m. It was observed that wooden vat having a volume of(4 cu.ft.) 0.12 cu.m. could be used for treatment of 45 kg of mixed salt containing 18 to 20 per cent KCl with 60 litres of aluminium sulphate solution (35 per cent) to produce potash alum. Dimensions of the wooden vat were as follows.

Diameter 47 cms. at the top, 52 cms. at the bottom with 59.7 cm. height. 0.25 H.P. was the power required for the stirring assembly.

b) Pressure filter

M.S.sparkler filter (Model No.8 - 3) painted with epilux No.4, anticorrosive paint was used. Usually most of the solid would dissolve at higher temperature and cake space was not significant. It was observed that filtration should be carried above 75°C as crystallisation of potash alum would start at 70°C(178°F). Cotton filter cloth (double thick) was used; rayon media filter papers also worked well. Rate of filtration was 6 litres per minute per 765 sq. cms. of filtering area and temperature of the filtrate remained usually between 85 to 90°C. Acid proof terylene cloth was also tried but no special advantage was observed. Ordinary filter papers (Whatman No. 1) cut to the size and put two on each plate also worked well. Density of the hot filtrate varied between 30 to 32° Be'. Addition of settling agents such as "separan A.P.30", 1 to 10 p.p.m was tried and found helpful for settling. Normally settling would not take place within an hour but by use of "separan A.P.30" it was accomplished in 12 to 15 minutes. However, filtration was found essential since in the process of decantation, the light flocculent precipitate was sucked up and crystallised alum contained more insoluble matter.

c) Crystallisers

Glazed tile (porcelain tile) tank was constructed. The tiles used were 15 x 15 x 0.6 cms. Acid proof cement was used for fixing these tiles on ordinary cement concrete structure. Tank was constructed actually on 5 cms. concrete slab with

15 cms. supporting walls so as to make it leak proof. Porcelain pipe was provided to remove the end liquor or slurry. Dimensions of the tank were as follows. Size of the tank 97 cms. length x 47 cms. breadth x 41 cms. height (38" x 18.5" x 16"), Capacity 0.18 cu.m. (6.51 cu.ft.) holding 181 litres of solution.

Wooden circular vats were also tried as crystallisers, 91.4 cms. (3') diameter, 30 cms. (1') height; having a capacity (7.07 cu.ft) to hold 198 litres of liquor. Wooden vats were found cheaper.

d) <u>Drier</u>

Chemida tray drier was used containing 12 trays (six aluminium and six m.s. trays) painted with all purpose anticorrosive alkali and 10 per cent acid resistant paint. Alum drying was carried out at 50/60°C. A full batch of 45 to 55 kg of centrifuged alum required 2 hours for complete drying at 50°C. It was found necessary to stir by hand or wooden scoops occasionally during drying operation as caking was observed in absence of such a treatment.

Other details of the dryer were as follows:-

Cost Rs. 3000, 0.5 H.P. 3 phase 440 volts motor for air circulation with 12 trays. Tray size 80 cm. x 40 cm. x 3 cms (L.B.H). Capacity of each tray was roughly 5 to 6 kg.

e) <u>Jaw crusher</u>

Commercial alum (alumina ferric grade B) is available in big lumps and it is required to crush to a suitable size; available jaw crusher in the laboratory was used for the purpose; capacity was 12 to 15 kg/ hour for 1 to 1.25 cms. size material.

f) Aluminium sulphate solution tank

Wooden vats were used as they were found suitable and cheap. Size 82.5 cm. height with 53 cms. and 55.5 cms. top and bottom diameters. Volume was 6.723 cu.ft. with a capacity to hold (190 litres) of 35 per cent solution. ~~No~~ Stirring was carried out by wooden laddles or by passing live steam.

Quality control

As alums are used mostly for water purification, pharmaceutical purposes and as mordants for very sensitive colours, require quality control and no contamination of any unhygenic materials. Heavy metals such as lead, arsenic, copper, zinc must be minimum. Iron salts give off colours in dyeing and also in glazing of papers. Hence alum produced must be free from any iron contamination and contains minimum insoluble matter. It is tested on pilot plant experiments using wooden vats and wooden stirrers. It is possible to produce high grade potash alum free from impurities by using cheap raw materials such as mixed salt and alumina ferric grade B. Typical analysis of products produced in pilot plant experiments and B.P. and technical grade samples from market are tabulated in Table 87. The products obtained on pilot plant satisfy the specification tests for both technical as well as pharmaceutical grades.

Table 87 ANALYSIS OF ALUM SAMPLES FROM PILOT PLANT EXPERIMENTS

Samples	1	2	3	4	5	6	Requirements for	
Composition			PER CENT				Tech. grade	B.P. grade
K_2SO_4	18.22	18.26	18.25	18.26	18.29	18.40	18.20	18.29
$Al_2(SO_4)_3$	35.85	35.94	35.79	35.85	35.66	35.40	35.72	35.89
Insolubles in water	0.06	0.07	0.05	0.04	0.05	0.05	0.25	0.05
K-alum	98.26	99.63	99.20	99.54	99.32	99.06	99.0	99.5
Soluble iron as (Fe)	below 0.007 in all the samples						0.007	0.04
Soluble copper as (Cu)	All samples satisfy the test with NH_4OH (that is below 5 PPM)						-*	5 PPM max.
Soluble arsenic as (As)	All samples compare with blank test (with reagents alone)						-*	5 PPM max.

Additional data to check purity of the product was taken.

1.Total chloride	0.19	0.07	0.07	0.07	0.10	0.07
2.Total sulphate	40.4	40.34	40.18	40.3	40.26	40.12

NaCl can be calculated from the total chloride value. Total sulphate was converted to potash alum. Potassium was estimated by flame photometer as K_2SO_4 and remaining sulphate was converted to aluminium sulphate.

* = Not specific, Blank test = colour obtained with the addition of reagents alone.

Crystallisation conditions with results are tabulated in table No. 88 which show how the purity of the product has been achieved. The table shows two facts (1) filtration of hot solution is essential to avoid insoluble matter precipitating in alum; (2) rapid cooling of the hot solution gives fine crystals which are free from iron.

Table 88 CRYSTALLISATION OF ALUM

Sample	1	2	3	4
Condition	Hot solution filtered through pressure(sparkler) filter; cooled slowly.	Settled and decanted; cooled slowly	Filtered on vacuum filter cooled slowly	Filtered
	Per cent	Per cent	Per cent	Per cent
Insolubles in water	0.03*	0.06	0.06	0.016
Soluble iron(as Fe)	0.005	0.005	0.003	Traces, practically nil
K.alum. Assay not less than	99.80	99.80	99.80	99.80
Cu	satisfies the test with NH_4OH			
Zn	satisfies test with H_2S			
AS	* Matches with blank and satisfies the limit.			

* Matches with blank means matches with colour produced by only mixing the reagents without addition of iron.

Table 89 STANDARD SPECIFICATION OF POTASH ALUM

	I.S.258/1950 Tech.grade Percent (by wt)	I.S.378/1952 B.P.grade Per cent (by wt)
i) Potassium alum(not less than)	99.00	99.5
ii) Soluble iron (as Fe) max.	0.0007	0.04
iii) Insoluble in water max.	0.25	0.05
iv) Ammonia (NH_3) max.	0.20	0.10
v) Arsenic ~~Free acid~~ (as As_2O_3)	-	5 ppm
vi) Copper (no colour with NH_4OH)	-	To satisfy the test
vii) Zinc (no ppt.with H_2S)	-	-do-

Bulk density of potash alum

Potash alum after centrifuging showed bulk density 58.89 lbs per cubic feet or 943.4 kg per cubic metre. The sample on drying at 60°C in tray drier showed 54.53 lbs per cubic feet or 873 kg per cubic metre.

Seive analysis of potash alum

Seive analysis of dried potash alum showed following results:

Mesh size (B.S.S.)	g	per cent
- 10 + 18	490	32.67
- 18 + 25	140	9.33
- 25 + 44	195	13.00
- 44	675	45.00
		100.00

Nearly 45 per cent of alum was below 44 B.S.S. mesh size; further analysis of the dust showed that

Mesh size	per cent
- 44 + 85	67.5
- 85	32.5
	100

<u>Analysis of alum</u>

Following procedures described in the Indian Standard Specification tests were adopted for analysis of alum samples produced in various pilot plant experiments.

<u>Sampling</u>: Proper precautions were taken to draw representative samples of the product from each batch of pilot plant experiment. The samples were finely ground using pestal and mortar and then analysed (except for samples used for magnesium analysis).

Insoluble matter: Weighed accurately about 25 g of alum and dissolved in 250 ml of hot distilled water and then filtered through weighed sintered glass crucible (G.No.4). The residue was washed with hot water till free from soluble compounds and dried to constant weight at 110°C.

Determination of soluble iron (as Fe):

Weighed 1 g of material accurately and dissolved in water to make up 100 ml of final volume. 10 ml of this solution, 1 ml of hydrochloric acid (1.16 sp. gr) (free of iron)and 30 g of ammonium per sulphate, 15 ml of butanolic potassium thiocyanate were mixed in Nessler tubes (25 mm dia. 150 mm. in length) and shaken for 30 seconds vigorously. A control test and blank test were simultaneously carried out. The samples and blank tests were compared with standard control tests using standard iron solutions.

Determination of potash alum :-

Weighed accurately about 2 g of the material dissolved in 300 ml of water and filtered if any insoluble matter was there. To the filtrate and washings about 5 g of ammonium chloride and 10 ml. of dilute sulphuric acid were added. Boiled the solution and added 2 drops of methyl red. Added ammonium hydroxide solution drop by drop till the colour changed to distinct yellow. Boiled for 2 minutes and filtered through Whatman filter paper (No.41), washed the precipitate of mixed oxides of iron and aluminium with hot ammonium nitrate solution till free from chlorides. Ignited the precipitate to a temperature of 1100 to 1200°C in tared silica crucible to constant weight.

Potash alum per cent
by weight = $9.307(A-1.4297 B)$
where A = percentage of $Al_2O_3 + Fe_2O_3$
B = percentage of Fe determined by the above test. Results of aluminium estimation were higher as it was difficult to reach 1200°C on ordinary burners. Hence total sulphate was estimated and converted to alum.

Determination of ammonium salts Weighed accurately 1 g of alum and dissolved in ammonia free water and made to litre. 10 ml. of this solution 20 ml. of water were mixed with 1 ml. of Nesslar's solution, 5 ml. of sodium hydroxide (10 per cent (w/v) and volume was made upto 50 ml with ammonia free water in Nesslar's tubes. Control test was simultanesouly carried out using 1 ml. of standard ammonia solution (.01 mg NH_3/ml). Intensity of colour produced was compared.

Test for Arsenic

Gutzeit test Gutzeit apparatus was used for determination of arsenic. Dry acetate paper strips were prepared and placed in lower portion of the lower tube and glass wool moistened with lead acetate solutions was placed in little upper portion of the tube. Strips of sensitized mercuric chloride paper were kept in upper tube. One gram of alum was weighed, dissolved in 15 ml of water and then transferred into the bottle; washed the dish with a minimum quantity of water. 2 ml of ferric ammonium sulphate solution and 5 ml of stannous chloride were added and volume was made to 50 ml. 10 g of zinc shots were quickly added to the bottle which was immediately fitted with rubber stopper carrying glasst tubes with sensitized paper. The whole apparatus was then placed in warm water at 40°C for about 45 minutes. The stains produced were compared with standard stains similarly produced using standard, .005 mg of arsenic trioxide.

Test for copper and zinc

1 g of potash alum was accurately weighed and dissolved in 100 ml; the solution was made alkaline with ammonium hydroxide, boiled and then filtered. Clear filtrate would indicate absence of copper. As copper was absent in all tested samples, same filtrate was acidified with acetic acid and tested with H_2S (hydrogen sulphide). No precipitate would indicate absence of zinc.

Determination of free acid

3 g of alum was accurately weighed, dissolved in boiled 100 ml of distilled water and transferred to 250 ml beaker with watch glass cover. 10 ml standard sulphuric acid was added by a burette and contents were allowed to cool to room temperature. 20 ml of potassium fluoride solution was added with measuring cylinder and .5 ml of phenolphthalein was added with dropping pipette. The contents of the beaker were stirred and titrated with potassium hydroxide solution until pink colour persisted

for a minute. The excess of potassium hydroxide used over the dilute sulphuric acid in blank test would give the free acid in sample.

Determination of chloride

5 g of potash alum was accurately weighed and dissolved in 100 ml of hot distilled water. The solution was cooled and about 1 g of calcium carbonate (free of chloride) was added; the contents were shaken for two minutes and titrated directly with standard silver nitrate solution by Mohr's method[57].

Determination of total sulphate

Sulphate was estimated using the classical method[58] for sulphate estimation and total sulphate was converted to potash alum.

Determination of sodium and potassium

Sodium and potassium ions were estimated by flame photometer in concentration range of 0.1 per cent to 0.01 per cent range.

Testing for magnesium ion

1 g of alum was accurately weighed dissolved in 100 ml and aluminium was removed using ammonium chloride and ammonium hydroxide. The clear filtrate was estimated for magnesium with E.D.T.A. Actually testing or determinations of chloride, magnesium, sodium, potassium are not given in I.S. specification[59]. As alum was prepared from mixed salt which contained magnesium sulphate, magnesium chloride, sodium chloride and potassium chloride, all the tests were carried out. The chloride value was exactly balancing with sodium value obtained from flame photometer readings and hence it was presumed that sodium was present as sodium chloride and not as sodium sulphate.

6) COST ESTIMATES (Summary)

Manufacture of potash alum: Project costs

(Basis 1 tonne of mixed salt per batch and ten batches per day; 300 days per year).

A) List of equipment:	Qty.	Approximate cost in Rs.
Wooden reaction vessels 2.55 cu.m. area	2	4,200
Bucket elevator	2	12,000
Salt grinder and two jaw crushers capacity 10 tonnes per 8 hours	1) 2)	13,000
Acid proof brick lined cement tanks to hold 14000 litres of solution	3	18,000
Filter press 24" x 24" x 12 plates	3	21,000
Crystallising wooden vats	5	10,000
Compressor	1	10,000
Drier electrically heated capacity 500 kg per hour	2	15,000
Slurry pumps	3	6,000
Boiler, capacity steam 10 tonnes per day	1	50,000
Weighing machine	1	2,000
Centrifuges (capacity kg/hr.)	2	30,000
Overhead tank (cap. 200 gal.)	1	3,000
Total process equipment cost		1,94,200

		approx. cost in Rs.
B) Overheads 33 per cent of process equipment cost ..		64,086
1) Installation and erection charges (10 per cent) on process equipment.	19,420	
2) Piping and fittings (5 per cent on process equipment) ..	9,710	
3) Electrical equipments installation etc. (5 per cent on process equipment) ...	9,710	
4) Transport charges (3 per cent on process equipments) ..	5,826	
5) Insurance and taxes (4 per cent on process equipments)	7,768	
6) Instrumentation (3 per cent on process equipments).	5,826	
7) Contingency (3 per cent on process equipments)	5,826	
	64,086	
Plant and Machinery, erected cost ..		2,58,286
Say..		2,58,300
C) Capital outlay		
Plant and machinery erected cost		2,58,300
Building and Civil Works		1,14,690
Laboratory equipment ..		3,500
Fixed Capital Total. ...		3,76,490
Working capital based on 3 months' working cost ..		1,60,915
Total ..		5,37,405
Say ..		5,37,500

(D) Manufacturing cost(per annum)
Direct costs

a) Raw materials

	approx.cost in Rs.
1) Mixed salt 10 tons/day at Rs. 10/- ton at factory site ..	30,000
2) Alumina ferric grade B 9 m.tons/day at Rs. 120/- m.ton + Rs.30/m.ton for transportation ...	4,05,000
Total ...	4,35,000

b) Utilities:

1) Electricity 541200 kWh/yr	81,180
2) Steam 1332 tons at Rs. 15/ton	19,980
3) Water 11250 kilolitres at Rs. 0.67 per kilolitre	7,500

c) Labour and Supervision:

	Per day 3 shifts	Wages/annum Rs.
Chief chemist at Rs. 600 p.m.	1	7,200
Shift chemist at Rs. 300 p.m	3	10,800
Operators at Rs. 150 p.m.	17	30,600
Helpers at Rs. 100 p.m.	45	54,000
Mechanic/Electric fitter at Rs. 200 p.m.	1	2,400
		1,05,000

	Rs
d) Maintenance:	
Capital service (replacement and spares at 5 per cent on erected plant and machinery)	12,915
e) Maintenance on civil works at 3 per cent on Rs.1,14,690 ..	3,440
Total ...	16,355
f) Indirect costs:	
Depreciation, 10 per cent on erected plant and equipment ..	25,830
Depreciation, 5 per cent on Civil Works ..	5,734
Interest (9 per cent) on Working Capital ..	14,482
Total..	46,046
Total cost of production of 3363 m.tons of potash alum ..	7,11,061
Cost per tonne of alum ..	211.40
Selling price assumed per tonne of potash alum ..	250
Profit per annum ..	1,29,750
Return on capital investment on Rs. 3,76,490 excluding working capital(per cent) ..	34.4

7) DISCUSSION

Mixed salt separated by controlled evaporation of 29° Be bittern formed a cheap raw material for producing technical and pharmaceutical grade potash alum. Studies on precipitation of potash alum from mixed salt using aluminium sulphate solution showed that as long as potassium was present, the reaction took place between potassium sulphate (formed due to reaction of magnesium sulphate and potassium chloride) with aluminium sulphate to form a less soluble double salt alum. Studies on solubility of potash alum in presence of oceanic salts such as sodium chloride, potassium chloride, magnesium sulphate and magnesium chloride showed that the solubility of potash alum was not much affected by the presence of these ions in solution. As a matter of fact, the presence of sufficient quantity of magnesium sulphate is helpful for the reaction to proceed between potassium chloride and magnesium sulphate to form potassium sulphate and magnesium chloride. Otherwise extra addition of $Al_2(SO_4)_3$ or $MgSO_4$ or Na_2SO_4 would be necessary. Each gram of potassium chloride present in mixed salt required 0.8 gram of magnesium sulphate thus nearly 53 to 54 per cent of magnesium sulphate present in the mixed salt was utilised for conversion of potassium chloride to potassium sulphate.

The presence of magnesium chloride in the end liquor formed by the above reaction and that present in the mixed salt would have a direct effect on the concentration of sodium chloride that could be retained in solution at crystallising temperature. The solubility studies had helped to control the precipitation of sodium chloride with alum or indirectly control the purity of the alum. At 10 per cent concentration of magnesium chloride, 16 per cent sodium chloride was retained in solution. Thus lesser the concentration of sodium chloride in mixed salt, better were the recoveries. It was also observed that the high concentration of magnesium chloride in the solution was unfavourable for the first reaction and on lowering the concentration by dilution with water effected the yield. Thus it was found out that maintaining ten per cent concentration of magnesium chloride in the crystallising liquor was the optimum condition to obtain a pure alum and high yield. In laboratory experiments, it was observed that addition of aluminium sulphate solution in stoichiometric ratio over the total potassium chloride present in the mixed salt was sufficient. Magnesium sulphate present in the mixed salt or bittern helped in the conversion of potassium chloride to potassium sulphate and requirement of aluminium sulphate was in the ratio of 1:2.3 ($KCl/Al_2(SO_4)_3$.

1) $2KCl + MgSO_4 = K_2SO_4 + MgCl_2$

2) $K_2SO_4 + Al_2(SO_4)_3 + 24\ H_2O = K_2SO_4Al_2(SO_4)_3 24H_2O$

Excess of aluminium sulphate added over the 1:2.3 stoichiometric quantity by weight did not improve the recovery but was lost in the end liquor. Laboratory experiments showed that it was preferable to add clear saturated solution of aluminium sulphate to mixed salt rather than addition of crushed aluminium sulphate to mixed salt or mixed salt solution. Difficulties of filtering the hot crystallising liquor enhanced when the powdered aluminium sulphate was used. While carrying out pilot plant experiments where live steam was preferred for heating the reaction mixture, condensed steam in the reaction mixture increased the final volume of the end liquor. Water requirement for crystallisation of alum was calculated in advance and only calculated quantities of water taking into consideration the volume of the condensed steam was added to control the yield and purity of the crystalling alum. The laboratory data showed that recoveries were slightly improved if alum was separated at 10°C instead of room temperature, where the solubility was further reduced. However, the extra recoveries obtained over the room temperature were much less to warrant the chilling to + 10 or + 5°C for pilot plant experiments.

The major portion of potassium chloride in the mixed salt was present as kainite $KCl\ MgSO_4 3H_2O$ with sodium chloride and magnesium chloride. This mixed salt on ageing or on long storage would give rise to potassium schoenite ($K_2SO_4 MgSO_4 6H_2O$) or glaserite ($Na_2SO_4\ 3K_2SO_4$) by a complicated reaction in situ between KCl, $MgSO_4$ and NaCl. By washing or exposure to rain, $MgCl_2$ and NaCl were removed, leaving behind mixed salt rich potassium schoenites. This type of mixed salt or any salt mixture containing potassium chloride, potassium sulphate, magnesium sulphate, sodium sulphate and sodium chloride could be used for this process. Inland salt works using subsoil brine which contained less than 18-20 per cent concentration of magnesium sulphate in the mixed salt, need addition of extra magnesium sulphate or sodium sulphate to obtain alum by this process. This was necessary only when the magnesium sulphate fell short below the stoichiometric quantities.

The reactions are based on solubility relationships at 100° and 30°C and it was found helpful to recover highest yield with minimum impurity in the final product. The solubility of sodium chloride in water in presence of alum was very high compared to solubility of alum. A wash in centrifuge was found very helpful to remove the adhering mother liquor and sodium chloride in centrifuge alone.

Recoveries of potassium ion as potash alum were good. The product was of industrial importance and price available per K_2O is high compared to the price available for potassium chloride, potassium sulphate or schoenite.

Chemical	Total K_2O Per cent	Selling price per tonne Rs.	Price per K_2O
KCl	60	300	5
K_2SO_4	52	400	7.7
$K_2SO_4Al_2(SO_4)_3$ $24H_2O$	10 * (10 per cent Al_2O_3)	250	15
$K_2SO_4.MgSO_4.6H_2O$	22	150	6.8

* Aluminium sulphate 18 per cent Al_2O_3 costs Rs. 170 per tonne. Approximate cost per unit of Al_2O_3 is taken as Rs. 10. This has been deducted from alum and cost per unit of K_2O has been worked out.

Potash alum is still employed in preference to other alums in many industries particularly sizing of papers and as mordant in dyeing for development of certain lakes. Potash alum occurs naturally in other countries as mineral alunite or kalinite. The process has been worked out with an object to utilise indigenous raw materials and conditions are set forth to obtain a technical as well as pharmaceutical grade potash alum from mixed salt and alumina ferric grade B which is also the cheapest source of aluminium sulphate. The process confers three positive advantages such as (1) it is better and cheaper than the conventional process of manufacture;(2) it is suitable for cottage scale industries and a small unit can be set up for utilisation of mixed salt available nearby; (3) at the same time assuring the producer better price per K_2O. Lastly it fulfils the natural deficiency, as potash alum does not occur as a mineral form in India as it does in many other countries.