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"SALT INVESTIGATIONS .. RECOVERY OF POTASSIUM FROM BITTERNS"

PART ONE

by

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APPENDIX

RECOVERY OF BROMINE FROM BITTERNS.

ABSTRACT

Imported potassium salts are obtained from materials which require only simple and cheap methods of treatment. Because of the complex nature of salt bitterns, more costly methods of extraction are required. It is unlikely that any of the methods of treatment which were investigated would produce potassium salts at sufficiently low costs to compete with overseas prices. By solar evaporation of the bittern a potassium-enriched salt was obtained, from which a saleable product could probably be produced. This method of recovering the potassium might be economic if a suitable market were found for large quantities of magnesium salts. There does not appear to be a ready market for magnesium salts at the present time.

1. INTRODUCTION.

Most of the world's supply of potash is obtained from deposits of potassium salts (1, 2, 3). However, increasing amounts of potash are being obtained from natural brines and in some cases from alunite and silicate materials, kelp, cement and flue dusts etc. (2, 4). As the market price for potash salts is relatively low, only sources which require simple methods of treatment can be used economically. Alunite and silicate materials, kelp, etc. are economic sources only in a few instances (2). Potash is recovered from the natural brines of several lakes in the U.S.A. and from the Dead Sea (5, 6, 7). In each case the brines are almost completely free from either magnesium or sulphate and the potassium bearing salts obtained on evaporation are suitable for the production of high grade potassium salts.

Recovery from sea water is more difficult owing to the presence of magnesium and sulphate in concentrations greater than that of the potassium. More costly methods of recovery are required because of the nature of the salts produced on evaporation. Only one method of recovering potassium from sea water was noted in the literature (8, 9). This was a patented process but there was no indication of its use in any large scale production of potassium salts.

Australia's potash requirements are all imported at present. No economic deposits of potassium salts have been found in South Australia and chemical analyses of brines from natural lakes show that most of them contain magnesium and sulphate and the concentration of potassium is very low. Sea water is therefore the most promising source of potash salts in South Australia.

Large quantities of salt bitterns, which are produced in the recovery of sodium chloride from sea water by solar evaporation, are normally discarded as a waste product. The potassium concentration of the bittern is about 15 times that of sea water and approximately one half of the total salts have been removed during the evaporation as sodium chloride. Salt bitterns are available in South Australia and should be preferred to sea water as a source of potassium.

Samples of bittern obtained from Solar Salt Ltd., Port Augusta were used in these investigations. The methods of recovery and chemicals which could be used were restricted by economic considerations and only four methods, namely, ion exchange, solvent extraction, direct precipitation and evaporation were attempted. Several procedures were used in the evaporation tests to produce potassium-enriched products. The recovery of fertilizer grade potassium from these products was investigated also.

Magnesium salts and bromides are concentrated in the bittern with the potassium. No attempt was made to recover the magnesium as there does not appear to be a ready market for the sale of magnesium salts. Preliminary tests on the recovery of bromine have been carried out and the results are reported in the appendix.

2. MATERIAL EXAMINED.

2.1 Sea Water

Three samples of sea water were obtained for chemical analysis. Sample S.W.1 was taken at the Grange beach and Samples S.W.2 and S.W.3 were obtained from Solar Salt Limited, near Port Augusta. Sample S.W.2 which was collected at the No. 1 pump was slightly lower in salt content than the average because of the influence of the tide at the time of sampling. Sample S.W.3 was taken at the No. 2 pump, 2 miles South of the No. 1 pump. Little evaporation takes place between the pumps and the samples are usually equivalent. The chemical analyses of the samples are given below :-

Chemical Analyses of Sea Water

Sample	S.W.1	S.W.2	S.W.3
Specific Gravity	1.027	1.033	1.047
Temperature, °C.	29	30	30
pH	8.1	8.1	8.3
Chemical Composition	g/l.	g/l.	g/l.
Na	11.48	14.2	15.5
K	0.43	0.54	0.77
Mg	1.40	1.71	2.48
Ca	0.54	0.52	0.74
Cl	20.38	25.5	29.3
SO_4	3.15	3.5	5.1
CO_3	0.07	0.1	0.1
Br	0.07	0.09	0.13
Total	37.52	47.16	54.12

2.2 Salt Bitterns

Bittern, B.1, which was taken from the No.2 crystallizer of Solar Salt Ltd. on 29th January, 1957, was used in most of the tests.

Some of the sodium chloride was removed from bittern B.1 by evaporating 17.25 l. to 12.52 l. The salt which crystallized was removed by filtration and the filtrate was designated B.2. This liquor was used in the ion exchange tests. Chemical analyses of the bitterns, B.1 and B.2, were as follows :-

Chemical Composition of Bitterns

Sample	B.1	B.2
Specific Gravity	1.248	1.268
Temperature, °C.	29	27
pH	7.0	6.7
Chemical Composition	g/l.	g/l.
Na	71.0	56.8
K	10.25	13.6
Mg	36.5	49.6
Ca	nil	nil
Cl	186.2	186.4
SO_4	50.4	68.8
CO_3	0.5	0.6
Br	1.76	2.42
Total	346.6	375.2

3. ANCILLARY MATERIALS.

3.1 Synthetic Solutions

Synthetic solutions were prepared by dissolving "Analar" or "C.P." grade Magnesium Chloride hexahydrate, potassium chloride, potassium sulphate, sodium chloride and sodium sulphate in distilled water. The amounts of the various salts, which were required to give the correct proportions of cations and anions, were calculated from chemical analyses of the potassium-enriched products obtained by evaporation of bitterns.

3.2 Organic Solvents

Most of the organic solvents were of "C.P." grade. The xylene was obtained by distilling commercial xylene and collecting the fraction having a boiling point of 138 to 144°C. Lighting kerosene was dried over anhydrous sodium sulphate before use.

3.3 Dipicrylamine

"B.D.H." grade dipicrylamine was used in solvent extraction and direct precipitation tests. The reagent was impure and approximately five percent did not form a soluble calcium salt.

3.4 Calcium Oxide

The calcium oxide used in the precipitations was prepared by heating "Analar" grade calcium carbonate in a muffle furnace at 950°C.

4. RECOVERY OF POTASSIUM BY ION EXCHANGE.

Several references to ion exchange recovery of magnesium from sea water were noted (10, 11). If the magnesium could be removed from the bittern in this way, the recovery of potassium would be simplified. Salt bittern was passed through a bed of cation exchange resin to saturation. The potassium loading was greater than was anticipated and magnesium ions occupied only one half of the resin sites. It was thought that on elution, where less concentrated solutions were involved, the magnesium would be more strongly held and a fractionation of the magnesium and potassium would be obtained. The loaded column was eluted with a solution of sodium chloride to obtain elution data for magnesium and potassium.

4.1 Experimental Procedure and Results

4.1.1 - Absorption :

Zeocarb 225 resin was converted to the sodium form with a five percent solution of sodium chloride and 100 ml. of wet settled resin were transferred to a 11/16" I.D. glass column. After the resin bed had been washed with water, bittern B.2 was passed through the column at a flow rate of two ml. per minute. Samples were collected every half column volume and were analysed for sodium, potassium and magnesium. The osmotic effect of the strong solution on the resin beads caused the resin bed to decrease by approximately seven percent of its original volume. The resin loadings for potassium and magnesium were calculated from the effluent analyses. The sodium loading was obtained by difference, assuming a total resin capacity of 4.5 m.eq. per gram of dry sodium form resin. Effluent analyses and resin loadings are reported in Table 1.

TABLE 1.

RECOVERY OF POTASSIUM BY ION EXCHANGE

Absorption Test - 100 ml. W.S. Resin

Constituent		Na	K	Mg
Head Liquor,	g/l.	64.0	13.6	49.6
	g.eq./l.	2.78	0.34	4.14
Effluent Samples		g/l.	g/l.	g/l.
Displacement Volume		12.2	nil	2.0
0.5 Column Volumes		57.4	1.46	24.8
1.0 " "		59.6	7.12	42.8
1.5 " "		56.4	12.36	48.6
2.0 " "		54.8	13.88	49.6
3.0 " "		53.6	14.04	50.0
Resin Loading,	g.	-	0.93	1.48
	m.eq./g.(a)	1.7(b)	0.46	2.37

(a) m.eq./g. dry sodium form resin
(b) approximate only - obtained by difference.

4.1.2 - Elution :

The loaded resin bed from the absorption test was loosened by back washing and then given a forward wash to remove the bittern. This procedure was adopted after one column had been cracked by the swelling of the resin beads during forward washing of the resin. The column was eluted with five percent sodium chloride solution at a flow-rate of two ml. per minute and eluate samples were taken every half column volume. Sodium, magnesium and potassium were determined in all samples.

The magnesium and potassium resin loadings were not accurate because the column had not been completely eluted. Eluate analyses and column loadings are shown in Table 2.

TABLE 2.

RECOVERY OF POTASSIUM BY ION EXCHANGE.

Elution Test.

Constituent	Na	K	Mg
Eluent, g/l.	19.4	nil	nil
Eluate Samples	g/l.	g/l.	g/l.
Displacement Volume	10.2	2.22	5.90
0.5 Column Volumes	9.9	1.94	3.29
1.0 " "	11.0	2.19	3.84
1.5 " "	11.2	2.22	3.72
2.0 " "	12.0	2.22	3.34
2.5 " "	13.0	2.23	2.83
3.0 " "	14.4	2.09	2.20
4.0 " "	15.6	1.56	1.51
5.0 " "	17.1	0.70	0.92
Approximate Resin Loading,			
g.	-	1.05	1.63
m.eq./g. (a)	-	0.50	2.61

(a) m.eq. per g. dry Na form resin.

4.2 Discussion

Although some upgrading of the potassium occurred on absorption, only one tenth of the resin sites were occupied by potassium and about one half with magnesium. Both the magnesium and the potassium had broken through in one half a column volume and had saturated the resin in two column volumes.

The concentration of potassium in the effluent rose above the head value after two column volumes indicating that some of the absorbed potassium was being displaced from the resin. The concentrations of the cations on the resin were similar to those in the bittern; hence, neither potassium nor magnesium was separated.

The magnesium and potassium were eluted together and no fractionation occurred. More than five column volumes of eluent were required to elute the column; hence the concentration of the potassium in the eluate was much lower than that of the original solution. The magnesium and potassium loadings calculated from the elution data were in reasonable agreement with the results obtained from the absorption test. The higher values were due to inefficient washing of the resin before elution as shown by the concentration of salts in the displacement volume. Further investigations were not carried out because it was apparent that treatment by conventional ion exchange methods would result in a very inefficient recovery of the potassium. Also, it would be difficult to use this treatment on a plant scale without preliminary dilution of the bittern.

5. RECOVERY OF POTASSIUM BY SOLVENT EXTRACTION.

No reference could be found to the recovery of potassium by a solvent extraction process. The solubilities of the alkali chlorides and sulphates in organic solvents decrease in the order Li, Na, K (12) and the solubilities of metal ions increase with ionic charge (13). Therefore, sodium and probably magnesium would be extracted preferentially from a salt bittern. An indirect recovery of the potassium might be obtained in this way; however, the cost of removing large amounts of sodium and magnesium would probably exceed the value of the recovered potassium. A direct extraction of the potassium might be obtained if a suitable organic complexing agent were dissolved in the solvent. The investigations were confined to the latter method of recovery.

The organic complexing agents reported as being specific for potassium were of two distinct types (14). The first type consisted of aromatic amines and phenols which were made reactive by the presence of one or more nitro groups. Included in this group were picric acid, o- and p- nitrophenols, 2.4 dinitrophenol and dipicrylamine. The second type were aromatic compounds containing sulphonic acid groups. 6 Chloro 5 nitrotoluene 3 sulphonic acid is a member of this group. Many other compounds of these types are known (15) but most of them were unsuitable because of solubility characteristics or their "exotic" nature. Several of the remaining compounds were not available from the chemical suppliers. Four reagents, namely, dipicrylamine, o- and p- nitrophenols and 2.4 dinitrophenol were examined. Dipicrylamine, which was the most specific reagent for potassium and which produced the strongest complex (14), was used in the extraction tests.

5.1 Experimental Procedure and Results

5.1.1 - Solubility Tests :

Dipicrylamine

The solubility of dipicrylamine in water was found to be less than 0.1 g. per litre and both the hydrogen and potassium forms are practically insoluble in the common organic solvents which are immiscible with water, namely, kerosene, xylene, benzene, carbon tetrachloride, n. hexane and Sec. octyl alcohol. Of the other solvents which were investigated, only ethyl acetate, pyridine and nitrobenzene dissolved the reagent to any extent. Pyridine is completely miscible with water, while nitrobenzene forms a complex with the dipicrylamine (16). Ethyl acetate is not a suitable solvent because it also is soluble in water (86 g. per litre).

p. Nitrophenol

The solubility characteristics are similar to those of dipicrylamine. It is practically insoluble in the common solvents immiscible with water and is soluble in ethyl acetate and nitrobenzene. The solubility of this reagent in water is 16 g. per litre.

o. Nitrophenol

The hydrogen form is soluble in kerosene, benzene, xylene and carbon tetrachloride but the potassium form is insoluble in these solvents. The reagent is slightly soluble in water.

2.4 Dinitrophenol

This reagent is soluble in water to the extent of 0.2g. per litre. The hydrogen form is soluble in kerosene, benzene, toluene, xylene and trichloro ethylene. The potassium form is not soluble to any extent in these solvents.

5.1.2 - Extraction Tests :

Although no suitable reagent was found, it was decided to examine the general principles of the extraction procedure. A solution of dipicrylamine in ethyl acetate was used in these tests. Difficulty was experienced in obtaining reliable extraction data because of the mutual solubilities of ethyl acetate and water; however, some useful information was obtained.

A negligible extraction was obtained unless the aqueous solution was kept at pH 7 or higher by the addition of alkali. The amount of alkali required was approximately equivalent to the amount of reagent present. The conversion of the hydrogen form reagent to the sodium or calcium form before the extraction stage was preferred to the addition of alkali during the extraction. In this case calcium hydroxide, the cheapest of the reagents available, could be used. The organic phase containing the extracted potassium was reconverted to the hydrogen form with sulphuric acid. More than the theoretical amount of acid was required to convert all of the potassium complex. Only 10 to 15 percent of the potassium was extracted. Most of the organic reagent was present in the aqueous solution after the extraction as soluble sodium and magnesium salts. It would be necessary to incorporate a recovery step because only a very small loss of such a costly reagent could be tolerated.

5.2 Discussion

No organic complexing agents with suitable solubility characteristics were found. More complex organic reagents might have greater solubilities in the common solvents but the reagent costs would be excessive. Assuming a recovery of 80 to 90 percent of the potassium, the cost of lime and sulphuric acid would amount to nearly one half of the value of the recovered potassium. Solvent and reagent losses which are normally major considerations in solvent extraction procedures would increase the cost of chemicals considerably. It is unlikely that any solvent extraction procedure would be economic.

6. RECOVERY OF POTASSIUM BY DIRECT PRECIPITATION.

A patented process for the recovery of potassium from sea water by precipitation with dipicrylamine has been reported in the literature (8, 9). An abstract of the patent is given below :-

> "Potassium-free sea water (24 cu.m. prepared by the process described below) is treated with 100 k.g. $Ca(OH)_2$ and 1.08 tons dipicrylamine (1), added with agitation and filtered to obtain the calcium salt of (1). This is added to 240 cu.m. of sea water. The potassium salt (2) of (1) is precipitated and separated by filtration. (2) is decomposed by adding 950 l. 14% HNO_3 and (1) is recovered by filtration and the filtrate is concentrated to yield 200 k.g. KNO_3. The filtrate from (2) is acidified with 750 l. 98% H_2SO_4 to pH 3.5 to recover (1) by filtering."

Several modifications would be required to adapt this process to the recovery of potassium from bitterns. The calcium salt of the reagent could not be prepared in potassium free bittern because the lime would react with the sulphate present in the bittern and an excessive consumption of lime would result. The high cost of nitric acid would preclude its use in recovering the potassium from the precipitate.

Precipitation tests were carried out using water for the preparation of the calcium salt and sulphuric acid to recover the potassium.

6.1 Experimental Procedure and Results

The required amount of freshly calcined lime was slaked with water and a weighed amount of dipicrylamine was added to the solution with stirring. The solution was filtered and the residue washed with water. The combined filtrate and washings were added to the bittern and the solution was stirred for at least a half an hour to allow complete formation of the potassium salt. The precipitate was filtered and washed with a small amount of water. The washings were added to the filtrate in tests 1 & 2 but were kept for chemical analysis in test 3. The amounts of potassium precipitated were calculated from the filtrate analyses. The precipitate was treated with 10 percent sulphuric acid to recover the potassium as the sulphate. In tests 1 and 3 a second treatment was carried out with nitric acid. Results of the precipitation tests are shown in Table 3 and the analyses of sulphate, nitrate and wash solutions from test 3 are given in Table 4.

TABLE 3.

RECOVERY OF POTASSIUM BY DIRECT PRECIPITATION.

Tests using dipicrylamine.

Test No.	1	2	3
Reagents			
Dipicrylamine, g.	22.3	22.3	46.6
Lime, g.	1.5	1.5	3.1
Volume after filtration, ml.	450	200	300
Bittern			
Volume, ml.	200	200	400
Potassium, g.	1.93	1.93	4.0
Ratio of reagent to K.	1.02 : 1	1.02 : 1	1.03 : 1
K precipitated, % (a)	69	66	66
Recovery from Precipitate			
K, g. (b)	1.25 (c)	0.79	2.08 (c)
Na, g.	0.49	0.23	0.23
Mg, g.	n.d.	0.18	0.10
Ca, g.	n.d.	n.d.	0.82

n.d. = not determined

(a) obtained from filtrate analyses.

(b) low results due to incomplete recovery.

(c) Total of nitric and sulphuric acid recoveries.

TABLE 4.

RECOVERY OF POTASSIUM BY DIRECT PRECIPITATION.

Chemical Composition of Solutions from Test 3.

Constituent	Solution		
	Wash	Sulphate	Nitrate
K, g.	0.06	0.42	1.66
Na, g.	0.72	0.14	0.09
Mg, g.	0.36	0.10	nil
Ca, g.	0.14	0.15	0.67

6.2 Discussion

Approximately two thirds of the potassium was precipitated by the dipicrylamine in all three tests. The constituents in the wash liquor were present in proportions similar to those of the bittern, showing that washing removed the entrained liquor without selectively removing the sodium and magnesium salts. Difficulty was experienced in converting the precipitate with sulphuric acid. Slightly more than one half of the potassium was recovered in the combined sulphuric and nitric acid solutions. Considerable amounts of sodium, magnesium and calcium were recovered with the potassium and reported in the final liquor. Because of the low recovery of potassium and the high reagent and filtration costs this method of recovering the potassium would not be economic.

7. RECOVERY OF POTASSIUM BY EVAPORATION.

Several references to the recovery of potassium by evaporation of brines which were practically free from either magnesium or sulphate, were noted (5, 6, 7). In such cases the number of double salts which could be formed on evaporation was limited and a high grade potassium salt could be obtained either directly by evaporation or by treatment of the carnallite which crystallized from the brine. Solar evaporation was used in each case; hence, evaporation costs were low and an economic recovery was possible.

When bitterns contain considerable quantities of both magnesium and sulphate, a large number of double salts is possible (1, 6, 17) and the recovery is more difficult. Two methods of treating the bittern were investigated, namely, evaporation of the bittern to produce a potassium-enriched product which could be given further treatment to upgrade the potassium and evaporation of the bittern after removal of the sulphate by precipitation with lime. Included in the first method were several evaporations which were carried out at near boiling point.

The production of a high grade potassium salt from the enriched product was investigated also. The enriched products were extracted at both room and elevated temperatures with varying amounts of water to dissolve sodium and magnesium salts. Mixed sodium and potassium chlorides were obtained by evaporation of a solution of the enriched product after the removal of magnesium and sulphate by precipitation with lime.

The recovery of the potassium would not be economic unless solar energy were used to evaporate the bitterns. Because the weather was unfavourable, evaporation tests could not be made out-of-doors. However, comparative evaporation rates were obtained by evaporating samples of sea water and bittern under conditions approximating to those of solar evaporation.

7.1 Experimental Procedure

Evaporation of Liquors

The evaporations were carried out by two different procedures. The first method involved the use of a "radiator" to simulate solar evaporation and in the second method the solution was heated by a gas flame and the evaporation took place at 100 to 110°C.

7.1.1 - Evaporation using a "Radiator" :

The bittern was placed in a porcelain evaporating dish over which was suspended a 1,000 watt. radiator. The radiator element was kept at a distance of 6 to 8 inches above the surface of the liquid and the evaporation rate was controlled by varying the applied voltage with a "variac" transformer. The solution was agitated continuously with a laboratory stirrer. When the required amount of water had been evaporated, the radiator was switched off and the solution was allowed to stand overnight. The product which had crystallized was filtered and washed sparingly with water to remove entrained liquor. The product after drying at 105°C was weighed and the volume and specific gravity of the filtrate liquor were determined. The filtrate liquor was returned to the porcelain dish and the procedure was repeated several times to give a series of products.

<u>7.1.2</u> - Evaporation at Elevated Temperatures :

A sample of the liquor contained in a glass beaker was agitated continuously during the evaporation. The solution was heated to boiling temperature with a gas burner and evaporated until the required amount of water had been removed. The hot solution was filtered through a preheated büchner funnel to recover the "first" product. The filtrate was allowed to cool slowly to room temperature and the "second" product which crystallized out was recovered by filtering. Neither of the products were washed but were sucked as dry as possible on the filter funnel.

7.2 <u>Results</u>

<u>7.2.1</u> - Recovery of Potassium-Enriched Products :

7.2.1.1 : <u>Direct Evaporation of the Bittern</u> -

A seven litre sample of bittern, B.1 was evaporated by the procedure in 7.1.1. The evaporation was carried out in four stages; hence, four products were recovered. The first two products consisted mainly of sodium chloride and the other two were complex salts containing most of the potassium. Samples of the products and liquors were analysed and the results are given in Tables 5 & 6. To simplify comparison with the other tests, the results were recalculated assuming that 10 l. of bittern had been evaporated. A chemical analysis of a sample of "salt" from Solar Salt Ltd. is included. From the analysis it was calculated that approximately 140 l. of sea water S.W.3 would be required to produce 10 l. of bittern B.1 and that about 4,000 g. of Sodium Chloride would be recovered during the evaporation.

TABLE 5.

DIRECT EVAPORATION OF THE BITTERN

First & Second Stages.

Sample	Bittern, B.1		Bittern, B.2			Bittern, B.3		
Volume, l.	10		7.257			5.123		
S.G.	1.248		1.268			1.300		
Temperature, °C.	29		27			28		
pH	7.0		6.7			-		
Chemical Composition	Liquor g/l.	Total Wt. g.	Liquor g/l.	Total Wt. g.	Recovery (c) %	Liquor g/l.	Total Wt. g.	Recovery (c) %
Na	71.0	710	56.8	412	60.7	32.5	167	24.5
K	10.3	103	13.6	99	105.5	19.0	97	104.0
Mg	36.5	365	49.6	360	103.4	68.5	351	100.8
Ca	nil	nil	nil	nil	nil	nil	nil	nil
Cl	186.2	1,862	186.4	1,353	74.6	197.0	1,009	55.6
SO_4	50.4	504	68.8	499	102.9	90.0	461	95.0
CO_3	0.5	5	0.6	4.4	103.5	-	-	-
Br	1.76	17.6	2.42	17.6	60.8	3.5	17.9	105.3
TOTAL	346.6	3,466	375.2	2,723	79.6	410.5	2,103	61.3

Sample	"Solar Salt"		Product 1.			Product 2.		
Weight, g.	approx. 3,800 (b)		817			628		
Chemical Composition	Wt. %	Total Wt. g.	Wt. %	Total Wt. g.	Recovery (c) %	Wt. %	Total Wt. g.	Recovery (c) %
Na	37.8	1,437	36.4	297	43.8	35.5	223	32.9
K	0.004	0.15	0.05	0.4	0.4	0.1	0.6	0.6
Mg	0.09	3.4	0.14	1.1	0.3	1.4	8.8	2.5
Ca	0.06	2.3	nil	nil	nil	nil	nil	nil
Cl	58.5	2,223	59.9	489	26.9	55.4	348	19.2
SO_4	0.27	10.3	0.4	3.3	0.7	4.9	31	6.3
CO_3	0.04	1.5	-	-	-	-	-	-
Br	0.015	0.57	0.02	0.2	1.2	0.03	0.2	1.2
TOTAL	96.78 (a)	3,678	97.1	793	23.2	97.3	611	17.8

(a) also H_2O^- 2.40% & H_2O^+ 0.66%
(b) Calculated
(c) % of total weight of the constituent which was recovered.

TABLE 6.

DIRECT EVAPORATION OF BITTERN.

Third and Fourth Stages

Sample	Bittern, B.4			Bittern, B.5		
Volume, l.	3.106			2.051		
S.G.	1.309			1.342		
Temperature °C.	29			23		
Chemical Composition	Liquor g/l.	Total Wt. g.	Recovery % (a)	Liquor g/l.	Total Wt. g.	Recovery % (a)
Na	11.5	35.7	5.3	2.8	5.6	0.8
K	15.0	46.6	49.8	1.3	2.7	2.9
Mg	90.0	280	80.3	112.5	231	66.3
Ca	nil	nil	nil	nil	nil	nil
Cl	242.5	753	41.6	299.5	614	34.0
SO_4	63.5	197	40.6	39.0	80	16.5
CO_3	-	-	-	-	-	-
Br	5.3	16.5	97.0	7.35	15.1	88.8
TOTAL	427.8	1,329	38.7	462.4	948	27.6

Sample	Product 3.			Product 4.		
Weight, g.	851			418		
Chemical Composition	Weight %	Total Wt. g.	Recovery % (a)	Weight %	Total Wt. g.	Recovery % (a)
Na	14.7	125	18.4	6.5	27.2	4.0
K	5.5	46.8	50.0	10.3	43.1	46.0
Mg	8.0	68.1	19.6	9.5	39.7	11.4
Ca	nil	nil	nil	nil	nil	nil
Cl	28.7	244	13.4	27.0	113	6.2
SO_4	30.3	258	53.1	27.1	113	23.3
CO_3	-	-	-	-	-	-
Br	0.08	0.7	4.1	0.19	0.8	4.7
TOTAL	87.3	743	21.7	80.6	337	9.8

(a) % of total weight of the constituent which was recovered.

7.2.1.2 : Evaporation at Elevated Temperatures -

The evaporation rate decreased in the final stages of the tests described in 7.2.1.1; hence, it might not be practicable to use solar evaporation to recover the potassium-enriched product. Therefore, the composition was determined of the potassium-enriched product which would be obtained by the evaporation, at elevated temperatures, of the bittern remaining after the separation of the sodium chloride-rich products 1 & 2.

Two synthetic solutions each containing salts equivalent to 500 ml. of bittern B.3, were prepared because the whole of that bittern had been used in the previous tests. The solutions were evaporated at 100 to 110°C by the procedure described in 7.1.2. Chemical analyses of the products and final filtrates are reported in Tables 7 & 8.

TABLE 7.

EVAPORATION AT ELEVATED TEMPERATURES.

500 ml. B.3 evaporated to approx. 320 ml.

Sample	"First" Product		"Second" Product.		Final Filtrate (b).	
Chemical Composition	Weight g.	Recovery % (a)	Weight g.	Recovery % (a)	Weight g.	Recovery % (a)
Na	10.6	66	3.62	22	1.85	12
K	6.4	70	0.11	1	2.61	29
Mg	5.7	17	1.70	5	26.7	78
Total Halides	19.2	20	6.65	7	72.7	73
SO_4	26.2	58	5.05	11	13.7	31
TOTAL	68.1	-	17.1	-	118	-

(a) % of the constituent in the original bittern B.3.
(b) approx. 275 ml.

TABLE 8.

EVAPORATION AT ELEVATED TEMPERATURES.

500 ml. B.3 evaporated to approx. 170 ml.

Sample	"First" Product		"Second" Product		Final Filtrate(b)	
Chemical Composition	Weight g.	Recovery % (a)	Weight g.	Recovery % (a)	Weight g.	Recovery % (a)
Na	15.2	97	0.34	2	0.16	1
K	7.68	86	1.13	13	0.05	1
Mg	14.9	44	8.15	24	11.1	32
Total Halides	42.8	43	25.05	25	31.0	32
SO_4	43.0	95	0.38	1	2.01	4
TOTAL	123.6	-	35.1	-	44.3	-

(a) % of constituent in the original bittern B.3.
(b) approx. 90 ml.

7.2.1.3 : Evaporation with Ammonium Chloride -

It was reported that a product suitable for the subsequent recovery of potassium could be obtained from salt bitterns by a cyclic treatment with ammonium chloride at elevated temperatures (18, 19). The following test was carried out using the suggested method to determine the composition of the salts produced.

Five grams of ammonium chloride were added to 500 g. (approx. 400 ml.) of bittern B.1 and the solution was evaporated by the procedure described in 7.1.2 until the boiling point of the solution had increased to 125°C. The "first" product was treated with approximately 130 ml. of water at room temperature and the undissolved salt was filtered. The chemical compositions of products and filtrates are shown in Tables 9 & 10.

TABLE 9.

EVAPORATION WITH AMMONIUM CHLORIDE.
500 g. B.1 evaporated to approx. 150 ml.

Sample	"First" Product		"Second" Product		Final Filtrate(b)	
Chemical Composition	Weight g.	Recovery % (a)	Weight g.	Recovery % (a)	Weight g.	Recovery % (a)
Na	27.6	97	0.45	1.5	0.42	1.5
K	2.95	73	0.86	21	0.21	5
Mg	7.12	48	2.15	15	5.52	37
NH_4	0.61	41	0.81	54	0.08	5
Cl	52.5	70	7.42	10	15.3	20
SO_4	18.0	89	0.22	1	1.9	10
Br	0.24	33	0.10	14	0.38	53
TOTAL	109	-	12.0	-	23.8	-

(a) % of constituent in the bittern
(b) approx. 120 ml.

TABLE 10.

EVAPORATION WITH AMMONIUM CHLORIDE.
"First" Product extracted with 130 ml. water.

Sample	"Third" Product		"Second" Filtrate	
Chemical Composition	Weight g.	Recovery % (a)	Weight g.	Recovery % (a)
Na	21.3	75	6.3	22
K	0.77	19	2.18	54
Mg	0.90	6	6.22	42
NH_4	0.19	13	0.42	28
Cl	33.3	44	19.2	26
SO_4	3.65	18	14.3	71
Br	0.03	4	0.21	29
TOTAL	60.0	-	48.8	-

(a) % of constituent in the bittern.

7.2.2 - Recovery of Potassium from Enriched Products :

Potassium-enriched products prepared in the evaporation tests contained more than 90 percent of the potassium but were not of a sufficiently high grade to be saleable. The following investigations were carried out to determine the possibility of removing some of the unwanted constituents.

7.2.2.1 : Treatment with Water at Room Temperature -

A "combined" product was prepared by mixing, in the correct proportions, products 3 and 4 which had been recovered in the direct evaporation tests. Samples of "combined" product (126.9 g.) were agitated with varying amounts of water at room temperature to dissolve sodium and magnesium salts. After several hours the undissolved material was filtered without washing. Chemical analyses of the undissolved products are shown in Table 11.

TABLE 11.

RECOVERY OF POTASSIUM FROM ENRICHED PRODUCTS.

Treatment with Water at Room Temperature.

Sample	"Combined" Product.	A		B		C	
Volume of water, ml.	-	100		150		200	
Chemical Composition	Weight g.	Weight g.	Recovery % (a)	Weight g.	Recovery % (a)	Weight g.	Recovery % (a)
Na	15.2	11.2	76	4.6	30	0.2	1
K	9.0	6.8	72	4.6	51	0.7	8
Mg	10.8	5.4	49	1.8	17	0.4	4
Total Halides	35.8	18.8	52	7.3	20	0.3	1
SO_4	37.1	27.4	74	12.7	34	2.3	6
TOTAL	117.9(b)	69.6	-	31.0	-	3.9	-

(a) % of the constituent in the "combined" product.
(b) 126.9 g. "combined" product.

7.2.2.2 : Treatment with Water at Elevated Temperatures -

Synthetic solutions each approximating the composition which would be obtained by dissolving 317 g. of "combined" products 3 & 4 in water were used in these tests. The solutions were evaporated at about 100°C using the procedure described in

7.1.2. The compositions of the products and final filtrates are reported in Tables 12 & 13.

TABLE 12.

RECOVERY OF POTASSIUM FROM ENRICHED PRODUCTS.
Treatment with Water at Elevated Temperatures - (approx. 100°C) Volume of liquor 180 ml.

Sample	"First" Product		"Second" Product		Final Filtrate[(b)]	
Chemical Composition	Weight g.	Recovery % (a)	Weight g.	Recovery % (a)	Weight g.	Recovery % (a)
Na	34.6	91	1.28	3	1.93	5
K	16.2	75	2.13	10	3.32	15
Mg	16.8	62	0.29	1	10.1	37
Total Halides	53.2	60	4.62	5	31.4	35
SO_4	87.0	94	0.14	0.2	5.2	6
TOTAL	208	-	8.5	-	52	-

(a) % of constituent originally present
(b) Volume = 120 ml.

TABLE 13.

RECOVERY OF POTASSIUM FROM ENRICHED PRODUCTS.
Treatment with Water at Elevated Temperatures (Approx. 100°C). Volume of liquor 270 ml.

Sample	"First" Product		"Second" Product		Final Filtrate[(b)]	
Chemical Composition	Weight g.	Recovery % (a)	Weight g.	Recovery % (a)	Weight g.	Recovery % (a)
Na	27.6	75	3.38	9	5.94	16
K	5.82	26	8.75	39	7.68	35
Mg	12.5	46	0.56	2	13.9	52
Total Halides	28.7	32	13.9	16	46.1	52
SO_4	76.8	84	0.90	1	14.3	15
TOTAL	151	-	27.5	-	87.9	-

(a) % of constituent originally present
(b) Volume = 210 ml.

7.2.2.3 : Treatment with Lime -

A synthetic solution, which contained salts equivalent to those present in the "combined" product, was prepared from laboratory reagents. The solution was treated with a lime slurry containing 60 g. of freshly prepared calcium oxide. The weight of lime was 1.1 times the equivalent of the sulphate in solution. The precipitate which formed was filtered and washed with water. The composition of the precipitate, which was obtained by difference from the chemical analysis of the combined filtrate and washings, is shown in Table 14.

TABLE 14.

RECOVERY OF POTASSIUM FROM ENRICHED PRODUCTS.
Treatment with lime - precipitation.

Sample	Synthetic Solution.	Filtrate		Precipitate[(b)]
Volume, ml.	1450	1700		-
Chemical Composition	Weight g.	Weight g.	Recovery % (a)	Weight g.
Na	36.2	33.6	93	2.6
K	20.6	18.7	91	1.9
Mg	26.0	0.03	0.2	26.0
Ca	nil	6.63	-	36.0 (c)
Total Halides	85.5	75.8	89	9.7
SO_4	90.6	4.51	5	86.1
TOTAL	259	139	-	163

(a) % of constituent in synthetic solution
(b) by difference
(c) calculated.

One litre of the filtrate was evaporated to 30 ml. The salts which crystallized were filtered without washing. The composition of the product was determined by difference from the chemical analysis of the filtrate. The results are reported in Table 15.

TABLE 15.

RECOVERY OF POTASSIUM FROM ENRICHED PRODUCTS.
Treatment with Lime - Evaporation of Filtrate.

Sample	Final Liquor	Final Product	
Chemical Composition	Weight g.	Weight g.	Recovery % (a)
Na	1.29	18.46	93
K	1.24	9.76	89
Mg	trace	0.02	100
Ca	2.14	1.76	45
Total Halides	6.80	37.8	85
SO_4	0.03	2.62	98
TOTAL	11.5	70.4	-

(a) % of constituent present in 1 l. of filtrate.

7.2.3 - Evaporation of Bittern After Removal of Sulphate :

A lime slurry containing 59 g. of freshly prepared quicklime was added to 2 l. of bittern B.1. The solution was agitated for several hours and allowed to stand overnight. The precipitate was filtered and washed with water and the filtrate and washings were combined to give a volume of 2,520 ml. This solution was evaporated with a "radiator" using the procedure described in 7.1.1. Samples of the products and liquors were analysed and the results were recalculated, for ease of comparison, assuming that 10 l. of B.1 had been used. The results of the precipitation and evaporation tests are shown in Tables 16, 17, and 18.

TABLE 16.

PRECIPITATION OF SULPHATE FROM BITTERN B.1 WITH LIME.
Lime ≡ SO_4.

Sample	Bittern B.1		Treated Bittern B.1A			Precipitate
Volume, l.	10		12.6			–
Chemical Composition	Liquor g/l.	Total Wt. g.	Liquor g/l.	Total Wt. g.	Recovery % (a)	Wt. g. by difference.
Na	71.0	710	55.0	693	98	17
K	10.3	103	8.0	101	98	1.5
Mg	36.5	365	19.0	239	66	126
Ca	nil	nil	1.7	21	–	190
Cl	186.2	1862	146.0	1840	99	22
SO_4	50.4	504	4.6	58	12	446
CO_3	0.5	5	0.1	1.3	26	3.7
Br	1.76	17.6	1.5	18.9	107	nil
TOTAL	346.6	3,466	235.9	2,972	86	806.2

(a) % of constituent in B.1.

TABLE 17.

EVAPORATION AFTER REMOVAL OF SULPHATE .. First and Second Salts.

SAMPLE	Bittern B.1B			Bittern B.1C		
Volume, l.		6.887			3.841	
S.G.		1.223			1.252	
Temperature, °C.		21			21	
Chemical Composition	Liquor g/l.	Total Wt. g.	Recovery % (a)	Liquor g/l.	Total Wt. g.	Recovery % (a)
Na	62.3	429	60.4	27.5	105	14.8
K	15.1	104	101	26.5	102	99
Mg	34.0	234	64.1	59.5	229	62.7
Ca	1.7	11.7	-	1.5	5.8	-
Cl	206.0	1,419	76.2	238.0	914	49.1
SO_4	3.6	24.8	4.9	2.5	9.6	1.9
CO_3	0.3	2.1	42	0.5	1.9	38.0
Br	2.7	18.6	106	4.5	17.3	98.3
TOTAL	325.7	2,243	64.7	360.5	1,385	40.0

SAMPLE	Product B.1B			Product B.1C		
Weight, g.		704			843	
Chemical Composition	Weight %	Total Wt. g.	Recovery % (a)	Weight %	Total Wt. g.	Recovery % (a)
Na	35.6	251	35.3	37.6	317	44.6
K	0.02	0.14	0.14	0.08	0.67	0.65
Mg	0.06	0.42	0.12	0.17	1.43	0.39
Ca	1.76	12.4	-	0.64	5.4	-
Cl	56.2	396	21.2	58.5	493	26.5
SO_4	3.86	27.2	5.4	1.49	12.6	2.5
CO_3	nil	nil	nil	0.01	0.08	1.6
Br	0.06	0.42	2.4	0.07	0.59	3.4
TOTAL	97.6	687	19.8	98.6	831	24.0

(a) % of constituent present in B.1.

TABLE 18.

EVAPORATION AFTER REMOVAL OF SULPHATE.
Third and Fourth Salts.

SAMPLE	Bittern B.1D			Bittern B.1E		
Volume, l.		1.992			1.355	
S.G.		1.293			1.341	
Temperature, °C.		22			20	
Chemical Composition	Liquor g/l.	Total Wt. g.	Recovery % (a)	Liquor g/l.	Total Wt. g.	Recovery % (a)
Na	8.0	15.9	2.2	1.60	2.2	0.3
K	9.95	19.8	19.3	0.65	0.9	0.9
Mg	89.5	178	48.8	119.5	162	44.4
Ca	3.0	6.0	-	1.2	1.6	-
Cl	283.5	565	30.3	345.0	467	25.1
SO$_4$	1.75	3.5	0.7	0.55	0.8	0.2
CO$_3$	0.85	1.7	34.0	1.2	1.6	32.0
Br	7.95	15.8	89.8	10.0	13.6	77.3
TOTAL	404.5	806	23.2	479.7	650	18.8

SAMPLE	Product B.1D			Product B.1E		
Weight, g.		740			193	
Chemical Composition	Weight %.	Total Wt. g.	Recovery % (a)	Weight %	Total Wt. g.	Recovery % (a)
Na	13.2	97.7	13.8	5.7	11.0	1.6
K	10.4	77.0	75.1	9.1	17.6	17.2
Mg	5.6	41.4	11.3	9.5	18.3	5.0
Ca	0.34	2.5	-	0.07	0.14	-
Cl	45.8	339	18.2	44.5	85.9	4.6
SO$_4$	0.88	6.5	1.3	0.24	0.46	0.1
CO$_3$	0.04	0.3	6.0	0.07	0.14	2.8
Br	0.28	2.1	11.9	0.52	1.00	5.7
TOTAL	76.5	567	16.4	69.7	135	3.9

(a) % of constituent present in B.1.

7.2.4 - "Solar" Evaporation :

Comparative evaporation rates were obtained for sea water S.W.1 and Bittern B.1, by evaporating 1 l. samples of each with a "radiator" as described in 7.1.1. In these tests the solutions were not agitated and the voltage applied to the radiator was adjusted to give a surface temperature of 30°C. As the volume of the solutions was reduced the surface temperature increased to 40°C. The amount of water in each sample was calculated from the specific gravity and the chemical analysis. The weight of water lost during the evaporation was obtained by weighing the dishes at regular intervals. The bittern was evaporated in two stages. At the end of the first stage the solution was filtered to remove the impure sodium chloride (equivalent to products 1 & 2 in the direct evaporation of sea water). A small portion of the liquor was held in the crystallized salts and was lost. Corrections were made to the weights obtained in the second stage of the evaporation to allow for this loss. The results are shown graphically in Figures 1, 2 and 3.

When the solution from the second stage of the evaporation was allowed to stand for several days at ambient temperature an increase in weight due to the absorption of atmospheric moisture was found. The final liquor, after the completion of the evaporation tests was allowed to stand for several days and the increase in weight was determined at regular intervals. The results are shown in Figure 4.

7.3 Discussion

7.3.1 - Recovery of Potassium-enriched Products :

7.3.1.1 : Direct Evaporation of the Bittern -

The bittern received from Solar Salt Ltd. contained about 30 percent of the sodium chloride originally present in the sea water. A further twenty percent of the sodium chloride was recovered in products 1 & 2 which contained 36 percent of sodium, mainly as the chloride.

More than 90 percent of the potassium reported in products 3 & 4. Although some enrichment was obtained the "combined" products contained only 7 percent of potassium. The final bittern B.5 contained mainly magnesium chloride with small amounts of the other salts. Nearly 90 percent of the bromine remained in this liquor.

7.3.1.2 : Evaporation at Elevated Temperatures -

The products recovered in these tests were of similar composition to those obtained by evaporation of the bittern at lower temperatures. Both treatments resulted in the removal of some of the magnesium as chloride. For comparable recoveries of potassium, the products were of no better grade than those produced in the previous tests.

7.3.1.3 : <u>Evaporation with Ammonium Chloride</u> -

Three quarters of the potassium reported in the "first" product together with nearly all of the sodium and about one half of the magnesium. The "second" product would be recycled to supply one half of the ammonium chloride needed for the next evaporation, without introducing large amounts of either sodium or magnesium. The final filtrate containing mainly magnesium chloride would be discarded. Treatment of the "first" product with water removed most of the sodium salts but only one half of the potassium was recovered in the filtrate. This method of recovery had no advantages over direct evaporation of the bittern and would be more costly.

7.3.2 - Recovery of Potassium from Enriched Products :

7.3.2.1 : <u>Treatment with Water at Room Temperature</u> -

It was evident that this method of recovery could not be used to produce a high grade potassium salt. Under conditions which gave a reasonable recovery of the potassium, large amounts of sodium and magnesium salts were present.

7.3.2.2 : <u>Treatment with Water at Elevated Temperatures</u> -

The products were very similar to those obtained in the room temperature tests. Neither would be saleable without further treatment.

7.3.2.3 : <u>Treatment with Lime</u> -

The addition of 1.1 times the theoretical amount of lime required to combine with the sulphate resulted in the precipitation of 99 percent of the magnesium and 95 percent of the sulphate. The precipitate was difficult to filter and retained about 10 percent of the other constituents, including potassium. The product obtained by evaporation of the filtrate was a mixture of sodium and potassium chlorides contaminated with gypsum. Approximately 80 percent of the potassium reported in this salt. The potassium chloride might be separated by a flotation treatment similar to that used at Lake Bonneville, U.S.A. (4, 7). At this plant potassium chloride is separated by flotation from a mixture of sodium and potassium chlorides which are produced by solar evaporation of a natural brine. Microscopic examination of the salt obtained in this test showed that the crystals were intergrown and could not be liberated to any extent by crushing. This may have been due to the use of artificial means to evaporate the solution.

7.3.3 - Evaporation of the Bittern after the Removal of Sulphate :

Nearly 90 percent of the sulphate and one third of the magnesium were precipitated by the lime. Because of difficulty in filtering and washing, 2 to 3 percent of the other salts remained in the precipitate.

Three quarters of the sodium chloride in the bittern crystallized out in products B.1B and B.1C. Calcium sulphate was the major contaminant of these products.

The potassium-enriched products B.1E and B.1D contained less sulphate than the corresponding products obtained by direct evaporation but the ratio of potassium to sodium and magnesium was almost unaltered. Approximately 90 percent of the potassium reported in these products.

7.3.4 - "Solar" Evaporation :

7.3.4.1 : Evaporation of Sea Water -

Under the conditions of the experiment 70 hours were required to evaporate the sea water to the bittern stage. The average evaporation rate was therefore 13.5 g. water per hour.

7.3.4.2 : Evaporation of Bittern -

The evaporation was retarded by the formation of salt crusts on the surface of the bittern. The end of the first stage was reached in 57 hours, giving an evaporation rate of

7.8 g. water per hour. As the concentration of salts increased in the supernatant liquor, the evaporation rate fell considerably and only 13 g. of water were lost in 70 hours in the final stages of the evaporation. The evaporated bittern gained in weight when the artificial heating was discontinued due to absorption of atmospheric moisture. The evaporation was continued until the amount of water left had been reduced to 192 g. The resulting bittern was allowed to stand at room temperature for several days to determine the amount of water which would be absorbed. An increase of 36 g. was found during the first 50 hours but little change occurred in the next 30 hours. This would be the practical limit of evaporation under these conditions, although, in the summer months when the evaporation would normally take place a lower limit might be reached. The concentration of potassium in the liquor at this stage was 3.5 g. per litre corresponding to about 8 percent of the total potassium.

The amount of water in the bittern was reduced to the limit of 228 g. in 40 hours giving an average evaporation rate of 5.7 g. water per hour. The total time required to evaporate the bittern was, therefore, 97 hours. This was not excessively longer than the time required to evaporate the sea water, when it is considered that, in practice, the volume of sea water is about 14 times that of the bittern produced from it. Under natural conditions of intermittent evaporation, more time would be required to evaporate both the sea water and the bittern. It is probable that the increase would be greater for the bittern, because higher temperatures are required to give efficient evaporation. Solar evaporation could be used to recover the potassium-enriched product but lower recoveries of the potassium would be obtained. Some difficulties might be experienced in separating the salts from the supernatant liquor but this might be overcome by a suitable design of evaporating pond.

8. CONCLUSIONS.

Although several procedures gave promising results it is unlikely that potassium salts could be produced by any of the methods investigated at a sufficiently low cost to compete with overseas prices.

The use of conventional ion exchange procedures was not practicable because of the inefficient separation of the potassium and the difficulty of adapting the procedure to large scale production.

No suitable organic reagents were found for the solvent extraction procedure. Further investigations were not carried out because the cost of chemicals would make the recovery uneconomic even if a suitable reagent were found.

Only one half of the potassium was recovered in the direct precipitation tests with dipicrylamine. Difficulty was experienced in recovering the potassium from the precipitate with sulphuric acid and the final solution was contaminated with considerable amounts of sodium, magnesium and calcium salts. The high costs of reagents and filtration would make the recovery uneconomic.

Evaporation of the bittern gave the best recovery of the potassium. The two evaporations which were made at near boiling temperatures would be too costly and the products produced were of no higher grade than those obtained at lower temperatures. None of the potassium-enriched products were of sufficiently high grade to be saleable without further treatment. Little improvement was found when the products were treated with water at either room or elevated temperatures. Both the magnesium and sulphate were almost completely precipitated from a solution of the potassium-enriched products by the addition of lime. Evaporation of the remaining solution yielded a mixture of sodium and potassium chlorides with some gypsum. The potassium chloride might be separated from the mixture by flotation. The alternative treatment in which the sulphate was removed from the bittern before evaporation, gave a low grade potassium-enriched product. This product was similar to that produced by direct evaporation of the bittern except that it contained little sulphate. The first procedure, therefore, is preferred although it involves the resolution of the whole of the potassium-enriched products.

If solar evaporation were used to evaporate the bittern 75 to 80 percent of the potassium would be recovered in the mixed sodium and potassium chlorides. It is unlikely that such a process would be economical even if the crude salt produced in the initial stages of the evaporation could be marketed unless the magnesium salts could be sold also.

Preliminary tests showed that bromine could be recovered from the bitterns by displacement with chlorine. Although similar methods of recovery are in use in other countries the cost of chlorine gas is much higher in Australia. The economic recovery of bromine would depend mainly on two factors; the availability and cost of large quantities of chlorine and the extent of the local market for bromine.

APPENDIX

RECOVERY OF BROMINE FROM BITTERNS.

1. RECOVERY BY ION EXCHANGE.

An ion exchange procedure for recovering iodine from sea water has been patented (20). This involved :-

(1) the adsorption of iodide by the resin until equilibrium was reached.

(2) the liberation of iodine, which was then molecularly adsorbed in situ, by passing ferric chloride solution through the resin.

(3) a repetition of steps (1) & (2) until the resin was saturated (about 50 cycles).

(4) the elution of the iodine with alkaline sulphite solution.

The method cannot be readily adapted to the recovery of bromine because stronger oxidizing agents than ferric chloride are required to release bromine. Chlorine was found to be the most suitable of the common reagents capable of oxidizing bromides.

1.1 Experimental Procedure and Results

Bittern B.1, containing 1.67 g. bromine per litre, was passed through 50 ml. wet settled chloride form anion exchange resin at 2 ml. per minute. The effluent was spot tested for bromine after 2 and 3 column volumes had passed through the resin. A bulk sample of the first 10 column volumes of effluent and samples of the eleventh and twelfth column volumes were analysed for bromine. The results are shown in Table 19.

TABLE 19.

RECOVERY OF BROMINE BY ION EXCHANGE.
Absorption Test.

Effluent Samples	Bromine, g/l.
2 column volumes	not detected
3 " "	trace
First 10 " "	1.42
11 " "	1.76
12 " "	1.74
Resin loading	0.1 m.eq./g.

The loaded column, after a water wash, was treated with chlorine water. The solution contained twice the theoretical amount of chlorine necessary to oxidize all of the bromine to the elemental form. The top 1.5 inches of resin were bleached by the chlorine. Subsequent washing with 2 column volumes of water removed less than 1 milligram of bromine. Bittern was then passed through the treated column and the resin loading was calculated from the concentration of bromine in the bulk effluent sample.

Calculated resin loading = 0.08 m.eq./g.

1.2 Discussion

Due to the presence of large quantities of chloride ions in solution, bromine loadings of the order of only 0.1 m.eq. per gram were obtained for the bittern. Breakthrough occurred after 2 column volumes of bittern had passed through the resin. The final effluent samples contained a greater concentration of bromine than the head solution indicating that some of the bromine which had been loaded onto the resin was being displaced. The elemental bromine produced by the treatment with chlorine appeared to be adsorbed in situ because very little bromine was removed on washing and a second absorption test gave a similar resin loading. No further tests were carried out since this method appeared to have no advantages over the conventional procedure of displacing the bromine with chlorine.

2. RECOVERY BY DISPLACEMENT WITH CHLORINE.

Two bromine extraction processes are commonly used in the recovery of bromine from sea water and bitterns (21). Both processes involve the removal of the bromine from the liquors by displacement with chlorine (22). In the first process, the bromine vapour displaced with the chlorine is absorbed in sodium carbonate solution. When the carbonate solution can absorb no more bromine a measured excess of sulphuric acid is added and the bromine is steam distilled from the solution and collected in condensers. In the second process the bromine vapour is reacted with sulphur dioxide gas producing a mixture of hydrobromic and sulphuric acids which are absorbed in water. The bromine is recovered from this solution by displacement with chlorine and steam distillation. Only a few tests were carried out as the processes are both well known. The recoveries of bromine obtained by treatment of sea water and bitterns B.1 and B.5 were compared. The first stage of the recovery only was investigated because this was common to both processes and the subsequent treatment would not be significantly affected by using differing starting solutions. The bromine was absorbed in sodium carbonate solution since this could be carried out most easily in the laboratory.

2.1 Experimental Procedure and Results

In practice the bromine containing liquid, after the addition of the acid and chlorine, flows down a baffled "blowing out tower". A current of air passes up the tower carrying with it the displaced bromine. The preparation of a tower suitable for use with small amounts of liquor was not warranted. Comparative figures were obtained by blowing air through the solutions via a sintered glass diffuser.

A measured volume of the bromine containing liquor (600 ml. of sea water and 100 ml. of bitterns) was adjusted to pH 3.5 with sulphuric acid and transferred to the reaction vessel. Chlorine equivalent to approximately 110 percent of the theoretical amount necessary to displace the bromine was added and air was passed through the apparatus for 4 hours. In most cases the reaction vessel was a measuring cylinder sealed with a rubber stopper through which passed two pieces of glass tubing. Air entered through one glass tube which was connected to the diffuser and the bromine vapour was carried out through the other into a series of bubblers containing 5 percent sodium carbonate solution.

The chlorine was added in an aqueous solution. The concentration of the solution was adjusted to give approximately proportional dilutions of the various liquors. Bromine recoveries are reported in Table 20.

TABLE 20.

SAMPLE	Sea Water	Bittern B.1	Bittern B.5
Bromine Content g/l.	0.065	1.76	7.35
Chlorine Addition (a)	1.1	1.15	1.3
Bromine Recovery, %	84	87	84
Acid Addition, g./g.Br.	1.86	0.44	0.4

(a) times theoretical requirements.

2.2 Discussion

A considerable reduction in the amount of sulphuric acid required to bring the pH value to 3.5 was found for the more concentrated solutions (23). Bromine recoveries of approximately 85 percent were obtained for all three samples. No further work was carried out as the process has been fully developed in other parts of the world.

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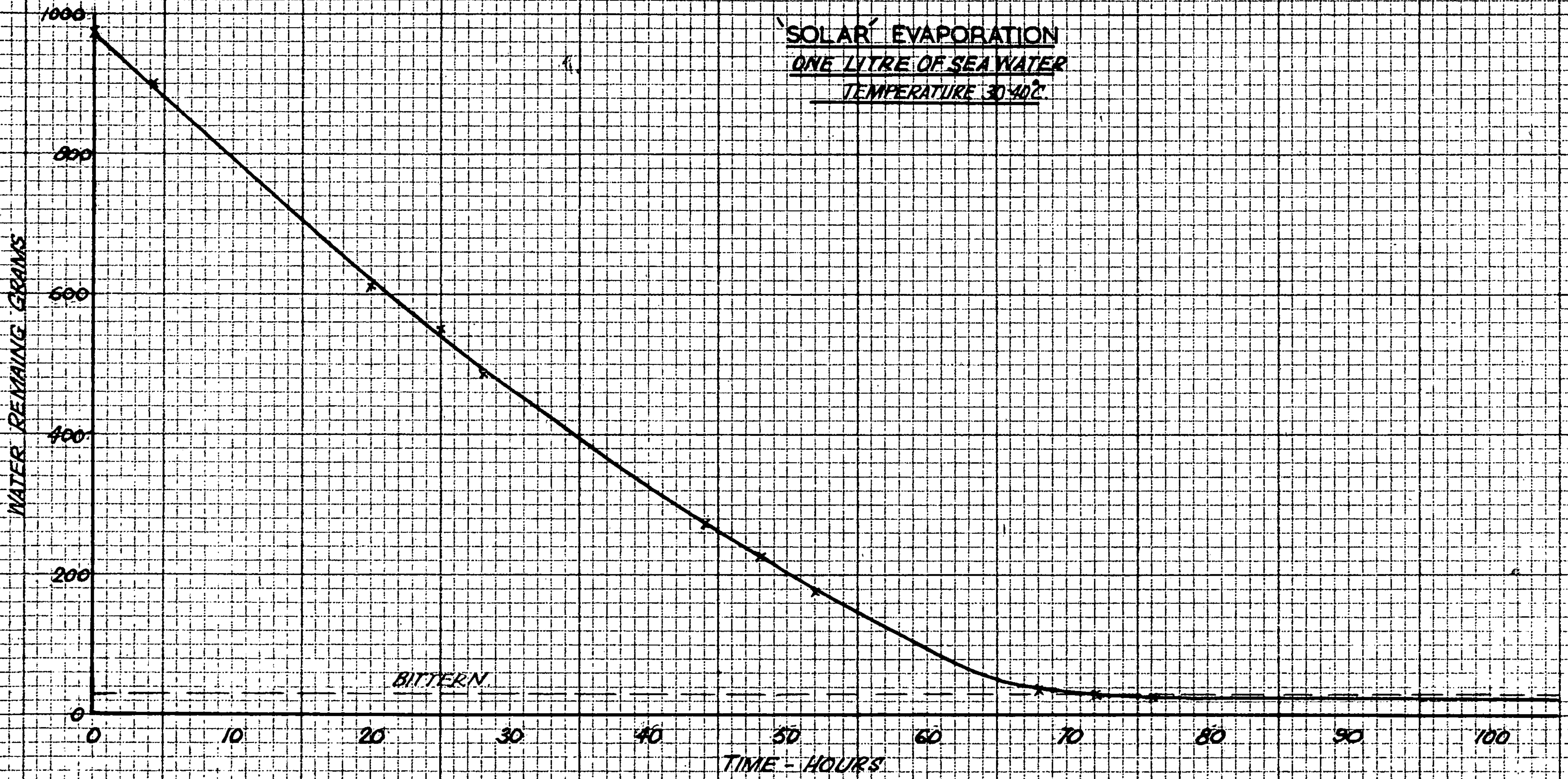
FIGURE. — 1.

'SOLAR' EVAPORATION

ONE LITRE OF SEA WATER

TEMPERATURE 30-40°C.



R.G.564.

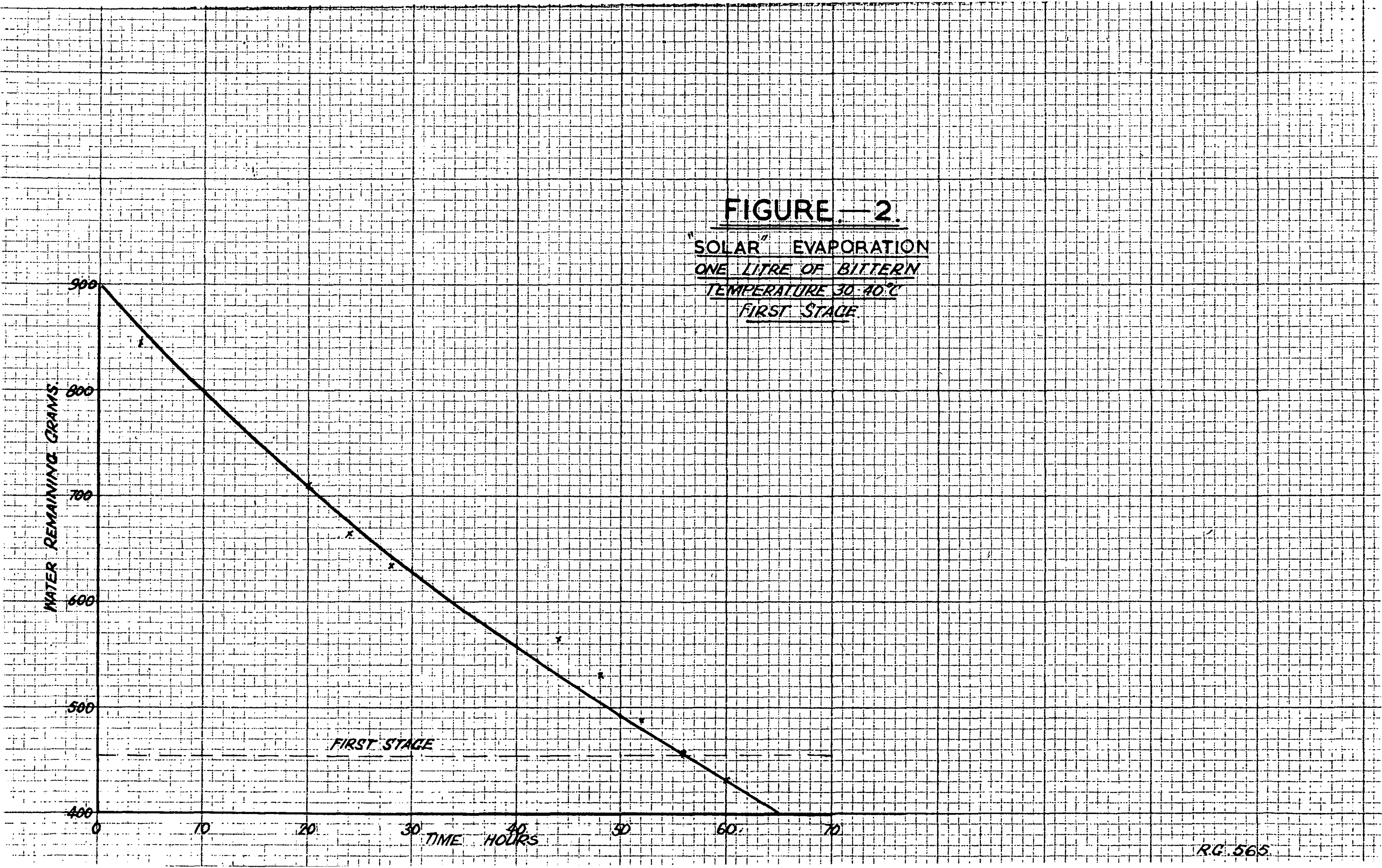


FIGURE — 2.

"SOLAR" EVAPORATION

ONE LITRE OF BITTERN

TEMPERATURE 30–40°C

FIRST STAGE

R.G. 565

FIGURE – 3.

SOLAR' EVAPORATION
ONE LITRE OF BITTERN
TEMPERATURE 30 - 40° C.
SECOND STAGE

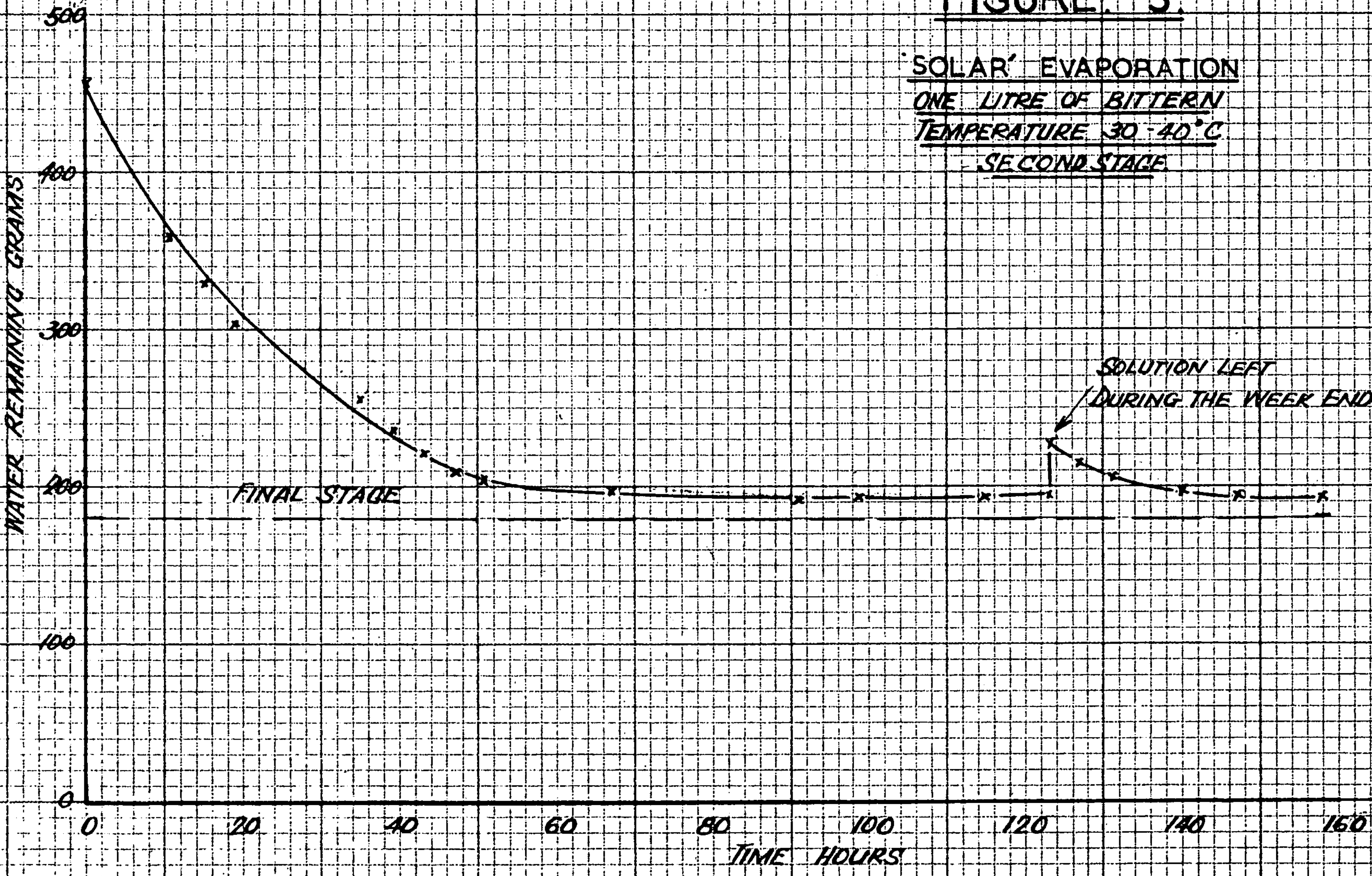
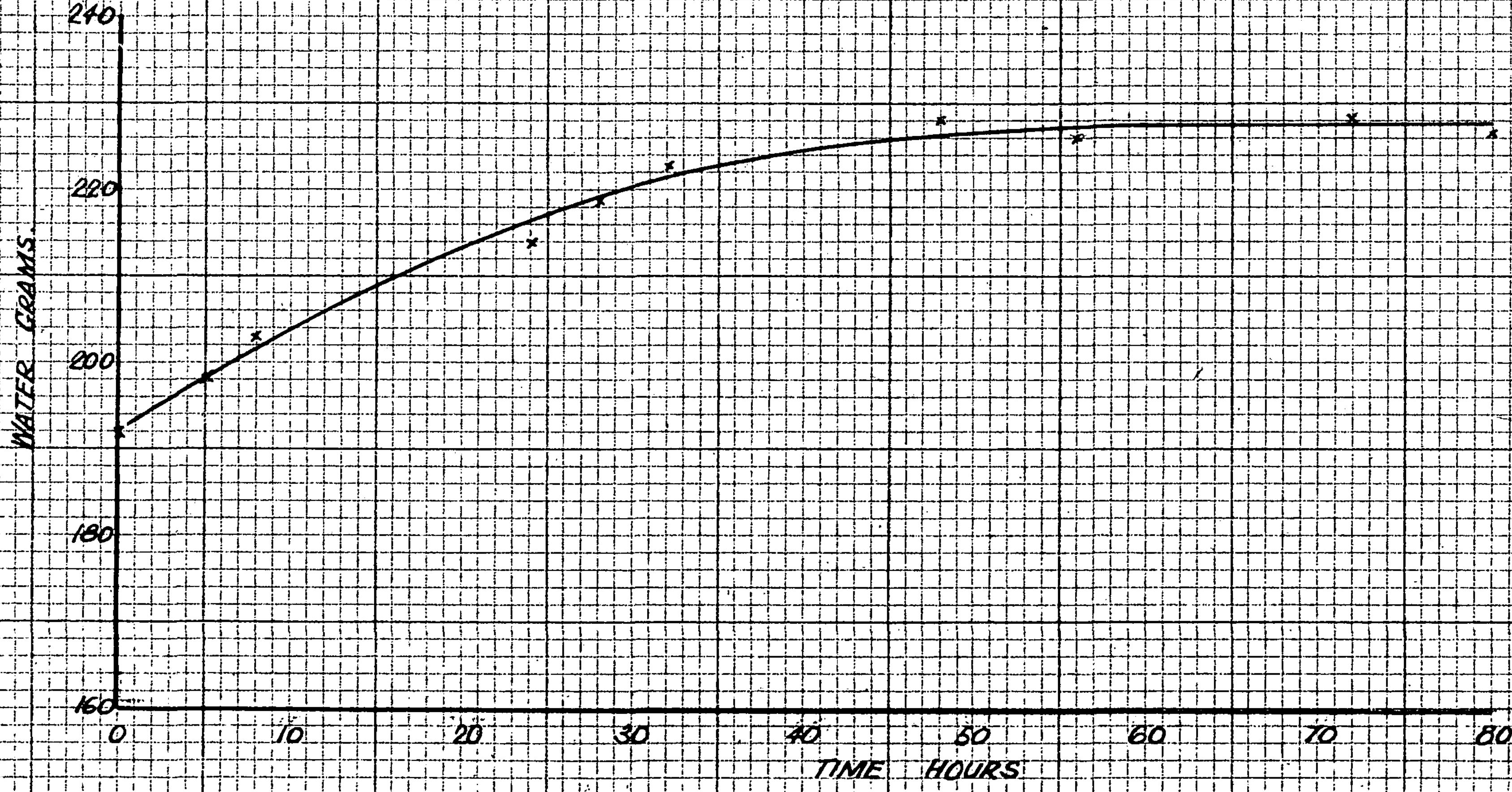


FIGURE. 4.

'SOLAR' EVAPORATION
ABSORPTION OF WATER BY
EVAPORATED BITTERN
TEMPERATURE 18°C APPROX



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DEPARTMENT OF MINES

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RESEARCH AND DEVELOPMENT BRANCH

R.D. 69

"SALT INVESTIGATIONS .. RECOVERY OF POTASSIUM FROM SALT BITTERNS

PART TWO

by

F. J. Moyle.

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This document consists of 35 pages. DATE : April, 1958.

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CONTENTS

ABSTRACT

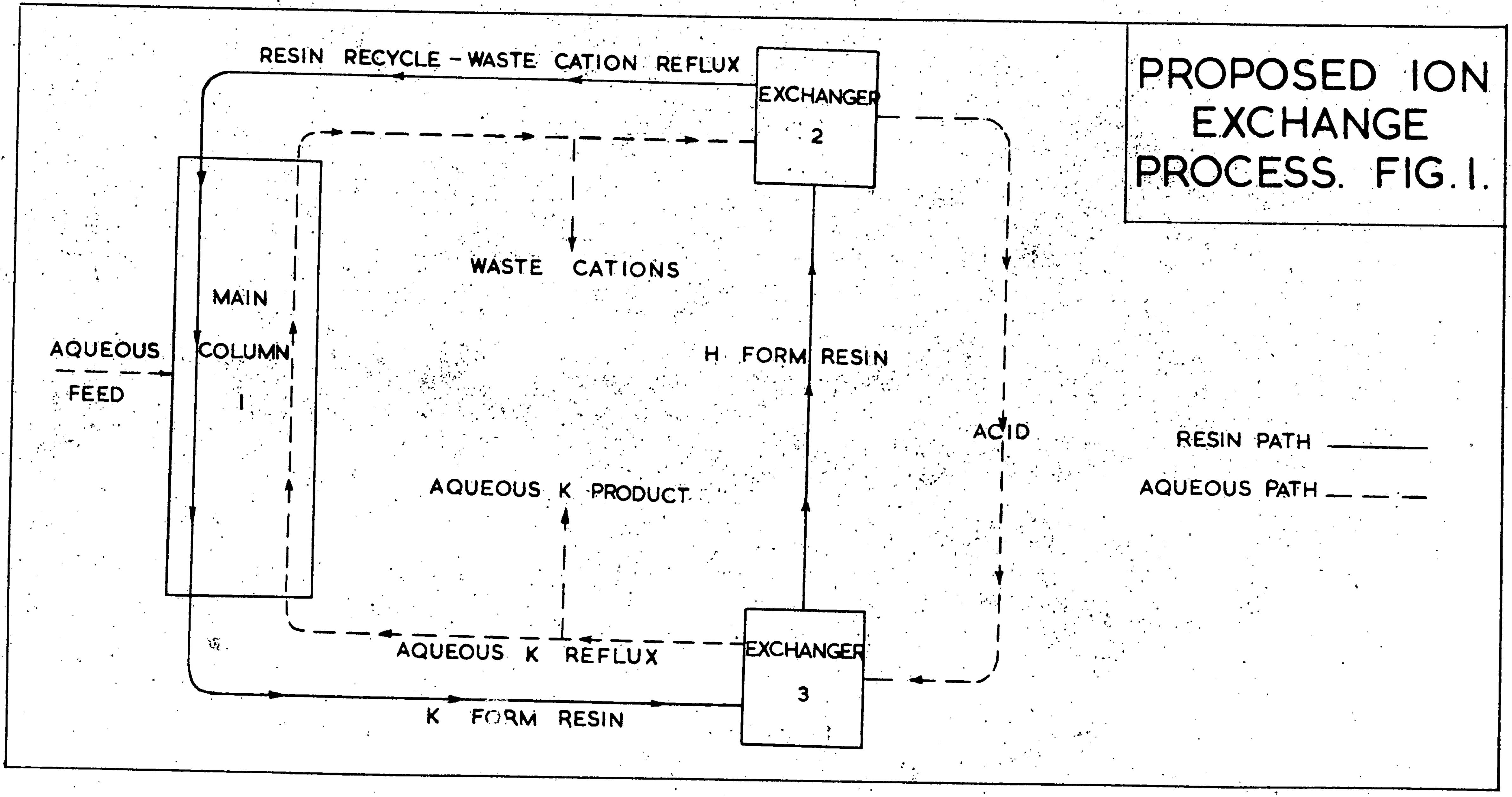
The distribution of potassium between Dowex 50 resin and aqueous solutions containing salts of potassium and either sodium or magnesium was determined. Equilibrium curves, which were drawn from the data, showed that potassium could possibly be separated from either sodium or magnesium by an ion exchange procedure analagous to fractional distillation. The operating conditions necessary for the separations were determined graphically from the equilibrium curves and the results indicated that the separation of potassium from bitterns would be feasible. Investigation of the mechanics of resin transfer and consideration of cost factors would be necessary to enable the possibility of economic recovery of the potassium from bitterns to be determined.

1. INTRODUCTION.

Previous investigations of the ion exchange recovery of potassium from bitterns, Moyle 1957$^{(1)}$, showed that potassium was adsorbed by a cation exchange resin more strongly than sodium and magnesium. Conventional fixed bed ion exchange procedures could not be applied easily to the recovery of the potassium because of the high concentration of salts in the bittern and the relatively low concentration of the potassium.

It was thought that the potassium might be separated from the other cations by an ion exchange procedure analagous to fractional distillation. This procedure would involve the use of a continuous countercurrent ion exchange column with reflux of both the potassium in aqueous solution and waste cations adsorbed on recycled resin. A diagram of the proposed scheme, showing the main exchange column and the two ancillary countercurrent exchangers necessary to obtain continuous reflux of product and waste streams, is given in Fig. 1.

The investigation was confined to the exchange of ions in the main column. The operating conditions necessary for the separation of potassium from sodium and from magnesium were determined graphically from potassium equilibrium curves. Since the behaviour of all three cations could not be predicted, the conditions required for the separation of potassium from bitterns were estimated from the values obtained for the simpler separations.



PROPOSED ION EXCHANGE PROCESS. FIG. I.

2. MATERIAL EXAMINED.

Salt Bittern

A sample of salt bittern, B.1, was obtained from Solar Salt Ltd., in January, 1957. This sample was not used in the actual tests but the chemical analysis of the solution was used in determining the composition of synthetic solutions and in calculating results.

CHEMICAL ANALYSIS - Bittern B.1

Constituent		g/l.	g.eq/l. (a)
Sodium,	Na	71.0	3.09
Potassium,	K	10.25	0.262
Magnesium,	Mg	36.5	3.00
Calcium,	Ca	nil	nil
Carbonate,	CO_3	0.5	0.008
Total halides, as	Cl	187.0	5.27
Sulphate,	SO_4	50.4	1.05

Specific Gravity at 29°C = 1.248

pH = 6.95

(a) = gram equivalents per litre.

3. ANCILLARY MATERIALS.

3.1 Dowex 50 Resin

The sample of this resin contained few broken beads and was uniformly sized as shown by the following wet screen analysis :-

WET SCREEN ANALYSIS - Dowex 50 Resin

Mesh	Weight, %	Cum. Weight, %
+ 10	0	0
- 10 + 18	6.0	6.0
- 18 + 25	75.4	81.4
- 25 + 30	15.4	96.8
- 30 + 60	3.1	99.9
- 60 + 100	0.1	100.0
	100.0	

Effective size = 0.02 inches diameter.
Uniformity Coefficient = approx. 1.3

The - 18, + 25 mesh fraction was used in all the equilibrium tests. The total capacity of this fraction, determined by the method of Kunin and Myers (2), was 5.16 milliequivalents per gram of dry hydrogen form resin. Both sodium and potassium forms of the resin were used in the tests. These were prepared by soaking screened resin in sodium or potassium chloride solutions. The converted resin was washed with water until the washings were chloride free, then air dried and stored in glass bottles. The amounts of various cations adsorbed on the resin were obtained by eluting a weighed sample of the resin with nitric acid and analysing the eluate.

3.2 Chemical Reagents

"AnalaR" grade reagents were used in preparing the solutions for the equilibrium tests. Impurity limits quoted on the labels were generally accepted but where limits were not given, chemical analyses were obtained. In all cases impurities were present in sufficiently small amounts to be neglected in the calculations.

4. EXPERIMENTAL PROCEDURE.

Since the cations exchange between resin and aqueous solutions on an equivalent basis, the aqueous concentration expressed in gram equivalents of total cations per litre should be relatively constant in all stages of the proposed separation scheme.

A saturated solution of potassium salts in which chloride and sulphate ions were in similar proportion to that of the original bittern contained approximately 2.1 gram equivalents potassium per litre. Hence the maximum product and feed concentrations could not exceed 2.1 gram equivalents total cations per litre.

The equilibrium tests were carried out at room temperature (approx. 22°C) and at total cation concentrations of 1.2 and 2.1 gram equivalents of total cations per litre.

4.1 Aqueous Solutions

With the exception of a few preliminary tests all solutions contained both chloride and sulphate ions in the proportion found in the original bittern, namely, 5 gram equivalents of chloride for every gram equivalent of sulphate. 500 Ml. of aqueous solution were used in each test.

The preliminary test solutions, which contained 1.2 gram equivalents total cations per litre were prepared by dissolving weighed amounts of "AnalaR" grade reagents in water. The cation concentration of the solutions was checked by chemical analysis in most instances. The equilibrium concentrations were obtained by correcting for the cations adsorbed on the resin and for the cations introduced with the resin.

The aqueous solutions for each series of equilibrium tests were prepared by mixing various amounts of two stock solutions, e.g. for the sodium-potassium separation at 2.1 gram equivalents total cations per litre, the stock solutions contained 2.1 gram equivalents of sodium and potassium respectively per litre. The concentration of the cations in the mixed solutions was obtained by calculation from the chemical analysis of the stock solutions. Equilibrium liquor concentrations were obtained by correcting these concentrations for the cations introduced with the resin and for the cations adsorbed on the resin after equilibration with the liquor.

4.2 Resin

Approximately seven grams of air dried resin were added to each of the prepared solutions and allowed to equilibrate with occasional stirring for several days. The moisture content of the resin used in each series of tests was obtained by drying a weighed sample for 16 hours at 105°C. The weight of resin used for each test was expressed as grams of dry hydrogen form resin by correcting the air dry weight for the moisture content and for the amounts of the various cations adsorbed on the resin.

After equilibration, the solutions were filtered on a small buchner funnel and the resin sucked as dry as possible to remove surplus liquor. The resin was transferred to a half inch glass column and eluted with one litre of 4 per cent nitric acid ($^{v}/_{v}$) at a flowrate of approximately one ml. per minute. Two aliquots, each of 200 ml., were removed from the eluate for determination of chloride and sulphate. The remaining 600 ml. of eluate was evaporated to dryness and then made to 200 ml. with distilled water. Potassium, sodium and/or magnesium were determined in this solution. Both the anion and cation loadings were calculated as milli-equivalents per gram of dry hydrogen form resin.

5. INTERPRETATION OF DATA.

5.1 Neutral Salt Adsorption

When a cation exchange resin is immersed in a solution of a salt some anions diffuse into the resin beads. If it is assumed that the outer surface of the beads is a semipermeable membrane, the effect may be explained by the Donnan Membrane Theory (2,3,4). According to this theory, at equilibrium the activities of the diffusible salts on both sides of the membrane must be equal and electrical neutrality of both solutions must be maintained. Since the resin matrix, R^-, is a non diffusible anion, there is a diffusion of anions into the resin beads.

In the simplest case, when sodium form resin is immersed in a very dilute sodium chloride solution, the following equations apply.

$$[Na_1^+]\ [Cl_1^-] = [Na_2^+]\ [Cl_2^-]$$

$$[Na_1^+] = [Cl_1^-] \quad \text{and} \quad [Na_2^+] = [Cl_2^-] + [R^-]$$

where $[Na_1^+]$ and $[Cl_1^-]$ = concentrations in the outside solution

$[Na_2^+]$ and $[Cl_2^-]$ = concentrations inside the resin beads

$[R^-]$ = concentration of exchange sites in the resin.

Combining the equations

$$[Cl_1^-]^2 = [Cl_2^-]^2 + [Cl_2^-] \cdot [R^-]$$

For strong cation exchangers the value of $[R^-]$ is relatively high. The concentration of chloride ions, and therefore the concentration of neutral salts, in the resin beads is less than that of the outside solution.

In the above case the amount of sodium in the resin beads in excess of the exchange capacity, could be obtained from the chloride content of the resin. When more than one cation is involved the amounts of each which are held as neutral salts are not easily determined.

For the purpose of evaluating the process, only the total cation loading was important because both the exchange and neutral salt cations would be carried by the resin in the exchange columns. The extent of the neutral salt adsorption was shown in the preliminary tests. Although anion loadings were determined for most of the equilibrium tests only the total cation loading was used in plotting the equilibrium curves.

5.2 Equilibrium Curves

To determine the operating conditions of the exchange column it was necessary to draw accurate equilibrium curves. The concentrations of the cations in both the aqueous and resin phases were plotted as equivalent fractions to enable comparison of exchange data for both divalent and monovalent ions and to eliminate difficulties due to variations in the total cation loadings.

The drawing of a smooth curve through the points was difficult owing to variations in the data due to experimental errors. Attempts were made to obtain a linear plot of the data so that errors might be averaged by drawing a straight line of best fit through the points.

According to Walton⁽⁵⁾, almost all data on ion exchange distributions fit the following equation of Rothmund and Kornfeld.

$$\frac{X_R^{A^+}}{X_R^{B^+}} \cdot \left(\frac{C_S^{B^+}}{C_S^{A^+}}\right)^p = k$$

where A^+ and B^+ are the two ions

$X_R^{A^+}$ & $X_R^{B^+}$ = equivalent fractions of A^+ & B^+ in the resin

$C_S^{A^+}$ & $C_S^{B^+}$ = concentrations of A^+ & B^+ in solution

k & p = empirical parameters

The plot of log $\left(\frac{X_R^{A^+}}{X_R^{B^+}}\right)$ against log $\left(\frac{C_S^{A^+}}{C_S^{B^+}}\right)$ is a straight line.

This type of plot was tried for each series of tests with the exception that the equivalent fractions of the cations in the aqueous phase were plotted instead of concentrations

i.e. log $\left(\frac{X_R^{A^+}}{X_R^{B^+}}\right)$ was plotted against log $\left(\frac{X_S^{A^+}}{X_S^{B^+}}\right)$

In all cases the logarithmic plot was linear and a straight line of best fit was drawn through the points. The equilibrium curves were drawn from the equations of the straight lines by calculating the equivalent fractions of potassium in the resin corresponding to various liquer concentrations.

For exchanges between a monovalent cation A^+ and a divalent cation B^{++}

log $\left(\frac{\left(X_R^{A^+}\right)^2}{X_R^{B^{++}}}\right)$ was also plotted against log $\left(\frac{\left(X_S^{A^+}\right)^2}{X_S^{B^{++}}}\right)$

This plot was also linear and gave equilibrium curves identical with those obtained from the previous plot.

5.3 Graphical Interpretation of Results

Two variations of the proposed scheme were considered. In the first it was assumed that no resin was introduced with the feed solution and in the second that resin equivalent to the potassium in the feed was added with the feed solution. Only the first method was investigated because of the disadvantages of the second variation, namely,

(a) the transfer of resin would be made more difficult by having to recycle a constant fraction with the feed solution.

(b) extra acid, equivalent to the potassium recovered in the product, would be required.

The operating conditions of the column were obtained graphically from the equilibrium curves by a method similar to that used by McCabe and Thiele for analagous fractional distillation separations (6,7,8,9,10). The graphical determinations were limited to separations in which the aqueous and resin concentrations could be each represented by a single variable, e.g. the separation of potassium from either sodium or magnesium and the separation of potassium from sodium and magnesium at a constant sodium to magnesium ratio.

5.3.1 - Equations of the Operating Lines :

Two operating lines were used in conjunction with the equilibrium curves to determine the operating conditions. In calculating the equations of these lines the following assumptions were made :-

(a) the amount of resin in the main column was just equivalent to the potassium.

(b) the flowrate of the resin was constant.

(c) one gram equivalent of product was obtained in unit time.

(d) the product and waste reflux ratios were related so that no extra acid was needed.

The proposed scheme is shown in Figure 2, where

F = feed in gram equivalents of total cations per unit time.

W = waste " " " " " cations per unit time.

P = 1(one) product in gram equivalents of total cations per unit time.

V = gram equivalents of total cations carried by the resin in unit time.

O = gram equivalents of total cations carried by the aqueous solution in the enriching section in unit time.

$\bar{O}$ = gram equivalents of total cations carried by the aqueous solution in the stripping section in unit time.

R = reflux ratio of the enriching section.

x = equivalent fraction of potassium in the aqueous solution.

y = equivalent fraction of potassium in the resin.

a = " " " " " " feed.

b = " " " " " " waste.

c = " " " " " " product.

n & m refer to the theoretical stage numbers for the enriching and stripping sections respectively.

<u>Considering the Enriching Section of the Main Column</u>

Assume the column is in continuous operation and consider the n^{th} stage and the section below it.

A material balance in unit time gives

$$V_{n+1} = O_n + 1$$

A potassium balance gives

$$V_{n+1} \cdot y_{n+1} = O_n \cdot x_n + c$$

$$\text{or } y_{n+1} = \frac{O_n}{V_{n+1}} \cdot x_n + \frac{c}{V_{n+1}}$$

Since the exchanges take place by equivalents, O and V are constant for this section and $O = R$ since 1 gram equivalent of product is obtained in unit time.

$$\therefore y_{n+1} = \frac{R}{V} \cdot x_n + \frac{c}{V}$$

but $V = O + 1 = R + 1$

$$\therefore y_{n+1} = \frac{R}{R+1} \cdot x_n + \frac{1}{R+1} \cdot c \qquad \ldots\ldots\ldots \text{(a)}$$

This is the equation of the operating line for the enriching section.

Considering the Stripping Section of the main column.

Consider the m^{th} stage and the section above it.

A material balance in unit time gives

$$\bar{O}_{m+1} = V_m + W$$

A potassium balance gives

$$\bar{O}_{m+1} \cdot x_{m+1} = V_m \cdot y_m + Wb$$

$\bar{O}$ and V are constant in all stages of this section

$$\therefore \bar{O} \cdot x_{m+1} = V \cdot y_m + Wb$$

but $\bar{O} = O + F$ and $O = R$

$$\therefore \bar{O} = R + F$$

$$\therefore (R + F) \cdot x_{m+1} = V \cdot y_m + Wb$$

$$\text{or} \quad y_m = \frac{R + F}{V} \cdot x_{m+1} - \frac{Wb}{V}$$

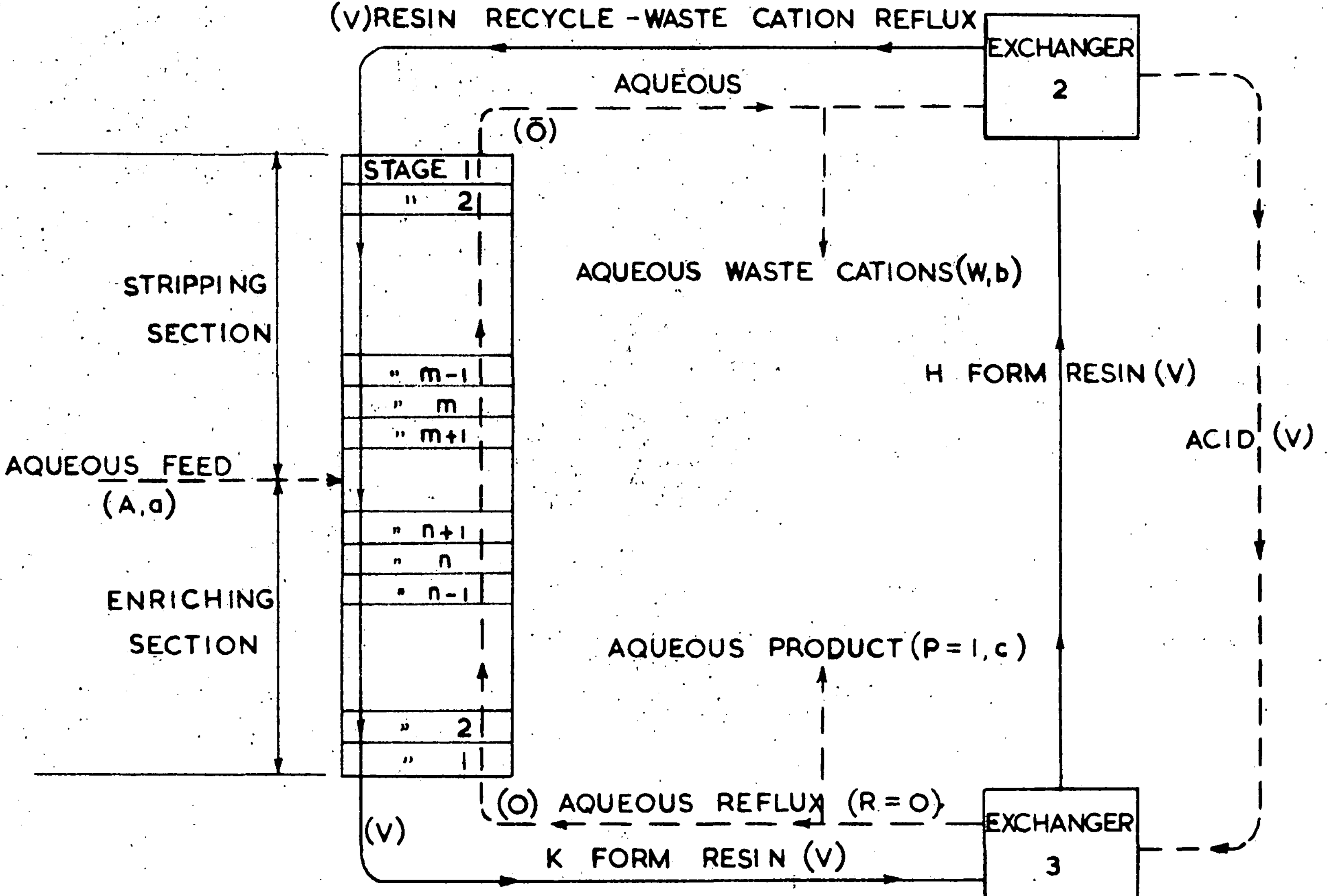
but $V = R + 1$

$$\therefore y_m = \frac{R + F}{R + 1} \cdot x_{m+1} - \frac{W}{R + 1} \cdot b \qquad \ldots\ldots\ldots\ldots\ldots \text{(b)}$$

This is the equation of the operating line for the stripping section.

Both equations give the relationship between the concentrations of potassium in the aqueous and resin

SEPARATION SCHEME
FIG. 2



NOTE: MATERIAL BALANCE IN UNIT TIME

phases with the reflux ratio of the enriching section as the only other variable. The equations represent straight lines with slopes of $^R/_{R+1}$ and $\frac{R+F}{R+1}$ respectively.

5.3.2 - Determination of the Operating Conditions :

Theoretical Stages

The number of theoretical stages required at a given reflux ratio was found by tracing down the equilibrium curve from the point (c,c.) on the $X = y$ line, alternate horizontal and vertical lines between the equilibrium curve and the operating lines as shown in Fig. 3. Each horizontal line was equivalent to one theoretical stage. The stage which corresponded most closely to the intersection of the operating lines was the feed stage. Since steps were drawn from the product end of the equilibrium curve the number of theoretical stages in the enriching section, i.e. above the feed stage on the graph, was always a whole number.

Minimum Number of Theoretical Stages

The minimum of theoretical stages are required when the reflux of both the enriching and stripping sections equal 100 per cent. Under these conditions, R, the reflux ratio of the enriching section becomes infinitely large and the equations of both operating lines reduce to $x = y$. The new operating lines are coincident with the $x = y$ line. The minimum number of stages was found by drawing the horizontal and vertical steps between the equilibrium curve and the $x=y$ line.

Minimum Reflux

The minimum reflux for any given separation can be used only when the column contains an infinite number of theoretical stages. Graphically this occurs when the operating lines intersect on the equilibrium curve and an infinite number of stages can be drawn in the pinches which occur on each side of the intersection point. (Figure 4). The equation for the locus of the intersection of the operating lines can be derived from equations (a) and (b). The equations may be written

$$y_{n+1} = \frac{R}{R+1} \cdot x_n + \frac{1}{R+1} \cdot c \qquad \ldots\ldots\ldots\ldots \text{(a)}$$

$$y_{n+1} = \frac{R+F}{R+1} \cdot x_n - \frac{W}{R+1} \cdot c \qquad \ldots\ldots\ldots\ldots \text{(c)}$$

Since stages n + 1 and n of the enriching section correspond to stages m and m + 1 respectively of the stripping section. Multiplying by R + 1 and subtracting (c) from (a)

$$F \cdot x_n = Wb + c$$

But the overall potassium balance of the main column is

$$F \cdot a = Wb + c$$

$$\therefore \underline{x_n = a}$$

The locus of the intersection of the operating lines is $x = a$, a straight line parallel to the y axis at a distance equal to the equivalent fraction of potassium in the feed. The minimum reflux was obtained from the intersection of the line $x = a$ and the equilibrium curve.

5.3.3 - Product, Waste and Feed Compositions :

For the purpose of obtaining numerical values for the number of theoretical stages, etc., it was necessary to assume a product grade and an overall potassium recovery.

It was assumed that 90 per cent. of the potassium was recovered in the product, and the potassium would comprise 96 per cent. by weight of the cations in the product.

Product Composition

Assuming the ratio of sodium to magnesium in the product to be similar to that of the original bittern, the equivalent fractions of the three cations necessary to give the required product grade would be as follows :-

Potassium, K = 0.909
Sodium, Na = 0.046
Magnesium, Mg = 0.045

The equivalent fraction of potassium in the product, c, was assumed to be equal to 0.91.

Feed Composition

The composition of the feed solution obtained by diluting the bitterns to a total cation concentration of 2.1 gram equivalents per litre would be

		g/l.	g.eq/l.	Eq. Fraction
Sodium,	Na	23.5	1.02	0.49
Potassium,	K	3.39	0.087	0.041
Magnesium,	Mg	12.1	0.99	0.47

The equivalent fraction of potassium in the feed, a, therefore equals 0.041.

Assuming a 90 per cent. recovery of the potassium, $\frac{100}{90}$ x 0.91 gram equivalents of potassium will enter the column in unit time. The feed flowrate, F,

$$= \frac{100}{90} \times \frac{0.91}{0.041}$$

= 24.4 gram equivalents of total cations per unit time. The operating conditions for all separations were determined by assuming that the concentration of potassium in the feed was equal to that of the bittern, namely, 0.041 equivalent fraction potassium. For example, in the separation of potassium from sodium, it was assumed that all of the magnesium had been replaced by an equivalent amount of sodium.

Waste Composition

The number of gram equivalents of total cations leaving the column in the waste, W, equals F − 1.

i.e. W = 23.4 gram equivalents of total cations per unit time.

Since this solution contains 10 per cent. of the potassium added in the feed, the concentration of the potassium in the waste liquor, b, equals

$$\frac{10}{90} \times \frac{0.91}{23.4} = \underline{0.004\ (3)} \text{ equivalent fraction potassium.}$$

6. RESULTS.

6.1 Preliminary Investigations

Preliminary equilibrium tests showed the extent of the neutral salt adsorption and gave an indication of the affinities of the various cations for the resin. The tests were carried out at a total cation concentration of 1.2 gram equivalents per litre. The exchange loadings were obtained by subtracting from the total cation loadings, cations equivalent to the total anion loadings. The results are given in Table 1.

TABLE 1.

PRELIMINARY INVESTIGATIONS

TOTAL CATION CONCENTRATION = 1.2 g.eq./l.

AQUEOUS						RESIN							
TEST	EQ. FRACTION			G.EQ./L.		M. EQ. PER G. DRY HYDROGEN FORM RESIN					EQ. FRACTION		
	Na	K	Mg	Cl	SO_4	Cl	SO_4	Total Anions	Total Cations	Exchange Cations	Na	K	Mg
D.1	0.503	0.497	-	1.20	-	0.27	-	0.27	5.34	5.07	0.388	0.612	-
D.2	0.503	0.497	-	-	1.20	-	0.51	0.51	5.48	4.97	0.396	0.604	-
D.5	0.505	0.495	-	1.00	0.20	0.23	0.17	0.40	5.13	4.91	0.388	0.612	-
D.3	-	-	1.000	1.20	-	0.26	-	0.26	5.42	5.16	-	-	1.000
D.4	-	-	1.000	-	1.20	-	0.36	0.36	5.42	5.06	-	-	1.000
D.6	-	-	1.000	1.00	0.20	0.24	0.20	0.44	5.52	5.08	-	-	1.000
D.8	-	0.499	0.501	1.20	-	0.26	-	0.26	5.49	5.23	-	0.534	0.466
D.10	-	0.500	0.500	1.20	-	0.28	-	0.28	5.55	5.27	-	0.524	0.476
D.9	-	0.498	0.502	-	1.20	-	0.37	0.37	5.48	5.11	-	0.602	0.398
D.11	-	0.497	0.503	-	1.20	-	0.32	0.32	5.48	5.16	-	0.593	0.407
D.7	0.338	0.330	0.332	1.00	0.20	0.16	0.19	0.35	5.45	5.10	0.233	0.405	0.362
D.12	0.505	-	0.495	1.00	0.20	0.21	0.11	0.32	5.44	5.12	0.408	-	0.592

6.2 Separation of Potassium from Sodium

This separation was investigated at two concentration levels, namely, 1.2 and 2.1 gram equivalents of total cations per litre. Sodium form resin was used in both series of tests and the results are shown in Tables 2 and 3. The experimental data were plotted and empirical formulae determined for each series. The formulae obtained were

$$\frac{X_R^{K^+}}{X_R^{Na^+}} = 1.54 \left(\frac{X_S^{K^+}}{X_S^{Na^+}} \right)^{0.966} \quad \text{at 1.2 g.eq./l.}$$

and $$\frac{X_R^{K^+}}{X_R^{Na^+}} = 1.46 \left(\frac{X_S^{K^+}}{X_S^{Na^+}} \right)^{0.948} \quad \text{at 2.1 g.eq./l.}$$

Calculated values for the equivalent fraction of potassium in the resin for each aqueous concentration were obtained from the formulae and are shown in the tables together with the differences between the calculated and experimental values. The equilibrium curves drawn from the respective formulae are shown in Figure 5. The graphically determined operating conditions necessary for the separation of potassium from sodium are shown in Tables 4 and 5. In each case the feed solution was assumed to have a composition similar to that of the original bittern but with the magnesium replaced by an equivalent amount of sodium.

TABLE 2.

SEPARATION OF POTASSIUM FROM SODIUM.

Total Cations = 1.2 g.eq./l. Cl = 1.00 g.eq./l. SO_4 = 0.20 g.eq./l.

	AQUEOUS		RESIN								
TEST	EQ. FRACTION		M. EQ. PER G. DRY HYDROGEN FORM RESIN					EQ. FRACTION			
	Na	K	Cl	SO_4	Total Anions	Total Cations	Exchange Cations	Na	K	Calculated K	Difference
1	0.005	0.995	0.22	0.11	0.33	5.61	5.28	0.007	0.993	0.996	- 0.003
2	0.043	0.957	0.22	0.12	0.34	5.50	5.16	0.031	0.969	0.969	0
3	0.084	0.916	0.22	0.11	0.33	5.43	5.10	0.063	0.937	0.939	- 0.002
4	0.154	0.846	0.22	0.10	0.32	5.41	5.09	0.118	0.882	0.889	- 0.007
19	0.253	0.747	n.d.	n.d.	n.d.	5.27	n.d.	0.184	0.816	0.814	+ 0.002
5	0.303	0.697	0.24	0.08?	0.32	5.74	5.42	0.249	0.751	0.775	- 0.024?
18	0.303	0.697	n.d.	n.d.	n.d.	5.30	n.d.	0.225	0.775	0.775	0
6	0.404	0.596	0.22	0.09?	0.31	5.59	5.28	0.313	0.687	0.691	- 0.004
7	0.503	0.497	0.20	0.11	0.31	5.56	5.25	0.403	0.597	0.603	- 0.006
17	0.553	0.447	n.d.	n.d.	n.d.	5.15	n.d.	0.437	0.563	0.556	+ 0.007
8	0.603	0.397	0.23	0.11	0.34	5.46	5.12	0.484	0.516	0.506	+ 0.010
9	0.703	0.297	0.24	0.11	0.35	5.44	5.09	0.590	0.410	0.401	+ 0.009
16	0.752	0.248	n.d.	n.d.	n.d.	5.39	n.d.	0.666	0.334	0.345	- 0.011
10	0.852	0.148	0.22	0.11	0.33	5.55	5.22	0.766	0.234	0.220	+ 0.014
15	0.852	0.148	n.d.	n.d.	n.d.	5.42	n.d.	0.780	0.220	0.221	- 0.001
11	0.919	0.081	0.22	0.11	0.33	5.48	5.15	0.872	0.128	0.128	0
12	0.960	0.040	0.22	0.12	0.34	5.52	5.18	0.933	0.067	0.067	0
14	0.980	0.020	n.d.	n.d.	n.d.	5.73	n.d.	0.967	0.033	0.035	- 0.002
13	1.000	--	0.23	0.10	0.33	5.41	5.08	1.000	--	--	--
		AVGE.	0.22	0.11	0.33	5.47	5.19			R.M.S. DIFFCE	± 0.009

n.d. = not determined

TABLE 3.
SEPARATION OF POTASSIUM FROM SODIUM.

Total Cations = 2.1 g.eq./l.   Cl = 1.75 g.eq./l. SO_4 = 0.35 g.eq./l.

	AQUEOUS		RESIN								
TEST	EQ. FRACTION		M. EQ. PER G. DRY HYDROGEN FORM RESIN					EQ. FRACTION			
	Na	K	Cl	SO_4	Total Anions	Total Cations	Exchange Cations	Na	K	Calculated K	Difference
20	0.900	0.100	0.42	0.22	0.64	5.60	4.96	0.846	0.154	0.165	- 0.011
21	0.801	0.199	0.42	0.18	0.60	5.54	4.94	0.715	0.285	0.281	+ 0.004
22	0.702	0.298	0.43	0.28?	0.71?	5.64	5.03	0.605	0.395	0.394	+ 0.001
23	0.553	0.447	0.45	0.16	0.61	5.61	5.00	0.449	0.551	0.545	+ 0.006
24	0.454	0.546	0.43	0.18	0.61	5.71	5.10	0.366	0.634	0.635	- 0.001
25	0.307	0.693	0.44	0.15	0.59	5.73	5.14	0.243	0.757	0.760	- 0.003
26	0.210	0.790	0.44	0.17	0.61	5.64	5.03	0.163	0.837	0.837	0
27	0.113	0.887	0.44	0.15	0.59	5.63	5.04	0.087	0.913	0.912	+ 0.001
		AVGE.	0.44	0.17	0.61	5.64	5.03			R.M.S. DIFFERENCE	± 0.005

TABLE 4.
SEPARATION OF POTASSIUM FROM SODIUM. OPERATING CONDITIONS

1.2 g.eq. Total Cations per litre.

Enriching Section			Stripping Section		
Reflux, %	R	Theoretical Stages below Feed Stage	Reflux, %	Theoretical Stages above Feed Stage	Total No. Theoretical Stages
96.8(a)	30.5	infinite	57.3	infinite	infinite
97.5	39	16	63.1	10.4	27.4
98.0	49	14	68.1	8.0	23.0
99.0	99	13	81.0	4.6	18.6
100.0	infinite	12	100.0	3.1	16.1(b)

(a) = minimum reflux (b) = minimum no. theoretical stages.

TABLE 5.
SEPARATION OF POTASSIUM FROM SODIUM. OPERATING CONDITIONS

2.1 g.eq. Total Cations per litre

Enriching Section			Stripping Section		
Reflux, %	R	Theoretical Stages below Feed Stage	Reflux, %	Theoretical Stages above Feed Stage	Total No. Theoretical Stages
96.8(a)	30.3	infinite	57.1	infinite	infinite
97.5	39	17	63.1	9.7	27.7
98.0	49	16	68.1	6.8	23.8
99.0	99	14	81.0	4.7	19.7
100.0	infinite	13	100.0	3.3	17.3(b)

(a) = minimum reflux (b) = minimum no. theoretical stages.

6.3 Separation of Potassium from Magnesium

These tests were carried out at concentrations of 1.2 and 2.1 gram equivalents of total cations per litre. Both types of logarithmic plot were used to obtain the following empirical equations :-

$$\frac{x_R^{K^+}}{x_R^{Mg^{++}}} = 1.18\left(\frac{x_S^{K^+}}{x_S^{Mg^{++}}}\right)^{0.855}$$

and

$$\frac{{x_R^{K^+}}^{2}}{x_R^{Mg^{++}}} = 1.15\left(\frac{\left(x_S^{K^+}\right)^{2}}{x_S^{Mg^{++}}}\right)^{0.853} \quad \text{at 1.2 g.eq./l.}$$

$$\frac{x_R^{K^+}}{x_R^{Mg^{++}}} = 1.49\left(\frac{x_S^{K^+}}{x_S^{Mg^{++}}}\right)^{0.894}$$

and

$$\frac{{x_R^{K^+}}^{2}}{x_R^{Mg^{++}}} = 1.62\left(\frac{\left(x_S^{K^+}\right)^{2}}{x_S^{Mg^{++}}}\right)^{0.843} \quad \text{at 2.1 g.eq./l.}$$

The results of the tests and the calculated values for the equivalent fractions of potassium for each aqueous concentration are shown in Tables 6 and 7. The corresponding equilibrium curves are given in Figure 6. The operating conditions necessary to separate potassium from magnesium at a total cation concentration of 2.1 gram equivalents per litre are recorded in Table 8. These values were obtained by assuming that all of the sodium in the bittern had been replaced by an equivalent amount of magnesium. The operating conditions could not be determined for the tests at 1.2 gram equivalents per litre because the equilibrium curve crossed the x = y line at 0.757. Hence, it would not be possible to obtain the required product grade corresponding to a potassium equivalent fraction of 0.91.

TABLE 6.

SEPARATION OF POTASSIUM FROM MAGNESIUM.

Total Cations = 1.2 g.eq./l. Cl = 1.0 g.eq./l. SO_4 = 0.20 g.eq./l.

	AQUEOUS		RESIN								
TEST	Eq. FRACTION		M. Eq. PER G. DRY HYDROGEN FORM RESIN					Eq. FRACTION			
	K	Mg	Cl	SO_4	Total Anions	Total Cations	Exchange Cations	K	Mg	Calculated K	Difference
1	0.961	0.039	0.23	0.11	0.34	5.55	5.21	0.948	0.052	0.948	0
2	0.922	0.078	0.23	0.12	0.35	5.53	5.18	0.899	0.101	0.907	- 0.008
3	0.854	0.146	0.22	0.11	0.33	5.35	5.02	0.834	0.166	0.842	- 0.008
16	0.749	0.251	n.d.	n.d.	n.d.	5.91	n.d.	0.756	0.244	0.750	+ 0.006
4	0.705	0.295	0.22	0.11	0.33	5.51	5.18	0.710	0.290	0.713	- 0.003
5	0.606	0.394	0.23	0.11	0.34	5.53	5.19	0.626	0.374	0.630	- 0.004
6	0.506	0.494	0.23	0.11	0.34	5.57	5.23	0.549	0.451	0.546	+ 0.003
7	0.405	0.595	0.21	0.11	0.32	5.44	5.12	0.463	0.537	0.459	+ 0.004
15	0.298	0.702	n.d.	n.d.	n.d.	5.38	n.d.	0.372	0.628	0.361	+ 0.011
8	0.304	0.696	0.22	0.12	0.34	5.50	5.16	0.373	0.627	0.368	+ 0.005
14	0.248	0.752	n.d.	n.d.	n.d.	5.49	n.d.	0.313	0.687	0.313	0
9	0.151	0.849	0.21	0.12	0.33	5.52	5.19	0.217	0.783	0.212	+ 0.005
10	0.081	0.919	0.21	0.12	0.33	5.50	5.17	0.125	0.875	0.129	+ 0.004
11	0.040	0.960	0.21	0.12	0.33	5.46	5.13	0.066	0.934	0.072	- 0.006
13	0.020	0.980	n.d.	n.d.	n.d.	5.57	n.d.	0.032	0.968	0.040	- 0.008
12	--	1.000	0.20	0.13	0.33	5.48	5.15	--	1.000	1.000	--
	AVGE.		0.22	0.12	0.33	5.54	5.17			**R.M.S. DIFFCE.**	± 0.006

TABLE 7.
SEPARATION OF POTASSIUM FROM MAGNESIUM.

Total Cations = 2.1 g.eq./l. Cl = 1.75 g.eq./l. SO_4 = 0.35 g.eq./l.

AQUEOUS —— RESIN ——

TEST	EQ. FRACTION		M. EQ. PER G. DRY HYDROGEN FORM RESIN					EQ. FRACTION			
	K	Mg	Cl	SO_4	Total Anions	Total Cations	Exchange Cations	K	Mg	Calculated K	Difference
17	0.949	0.051	0.40	0.15	0.55	5.76	5.21	0.932	0.068	0.953	- 0.021?
18	0.848	0.152	0.44	0.18	0.62	5.65	5.03	0.874	0.126	0.874	0
19	0.797	0.203	0.42	0.16	0.58	5.66	5.08	0.829	0.171	0.835	- 0.006
20	0.696	0.304	0.42	0.20	0.62	5.60	4.98	0.761	0.239	0.758	+ 0.003
21	0.496	0.504	0.41	0.21	0.62	5.55	4.93	0.584	0.416	0.595	- 0.011
22	0.346	0.654	0.41	0.20	0.61	5.59	4.98	0.456	0.544	0.457	- 0.001
23	0.197	0.803	0.43	0.18	0.61	5.67	5.06	0.296	0.704	0.298	- 0.002
24	0.098	0.902	0.41	0.19	0.60	5.59	4.99	0.170	0.830	0.170	0
	AVGE.		0.42	0.18	0.60	5.63	5.03			R.M.S. DIFFCE. =	± 0.008

TABLE 8.
SEPARATION OF POTASSIUM FROM MAGNESIUM, OPERATING CONDITIONS

2.1 g.eq. Total Cations per litre.

Enriching Section			Stripping Section		
Reflux, %	R	Theoretical Stages below Feed Stage	Reflux, %	Theoretical Stages above Feed Stage	Total No. Theoretical Stages
95.3[(a)]	20.2	infinite	47.5	infinite	infinite
96	24	18	51.6	7.9	26.9
97	32.3	16	58.7	4.7	21.7
98	49	15	68.1	3.2	19.2
99	99	14	81.0	2.6	17.6
100	infinite	13	100.0	2.4	16.4[(b)]

(a) minimum reflux (b) minimum no. theoretical stages.

6.4 Separation of Potassium from Sodium and Magnesium

Since the behaviour of all three cations could not be determined graphically, it was necessary to keep the ratio of sodium to magnesium constant. The first tests were carried out at 1.2 gram equivalents of total cations per litre, using resin which was partly in the sodium form. The ratio of sodium to magnesium in the aqueous solutions was approximately 1.1 to 1, but at high potassium concentrations the sodium introduced with the resin increased the ratio. The following empirical formula for the exchange was obtained from the logarithmic plot of the data :-

$$\frac{x_R^{K^+}}{x_R^{(Na^+ + Mg^{++})}} = 1.32 \left(\frac{x_S^{K^+}}{x_S^{(Na^+ + Mg^{++})}} \right)^{0.897}$$

Potassium form resin was used in the tests at 2.1 gram equivalents per litre and the sodium to magnesium ratio was held constant at 1:1. The empirical formula found for this exchange was :-

$$\frac{x_R^{K^+}}{x_R^{(Na^+ + Mg^{++})}} = 1.45 \left(\frac{x_S^{K^+}}{x_S^{(Na^+ + Mg^{++})}} \right)^{0.912}$$

The results of both series of tests are shown in Tables 9 and 10 respectively. Figure 7 shows the two equilibrium curves and Figure 8 is a plot of the sodium and magnesium concentrations in the resin and aqueous phases.

The operating conditions necessary for the separation of potassium, assuming constant sodium to magnesium ratios in the aqueous phase of the exchange columns are given in Tables 11 and 12.

TABLE 9.
SEPARATION OF POTASSIUM FROM SODIUM AND MAGNESIUM.

Total Cations = 1.2 g.eq./l. Aqueous Na to Mg ratio 1.1 : 1 (approx.) Cl = 1.0 g.eq./l. SO_4 = 0.20 g.eq./l.

AQUEOUS				RESIN									
TEST	EQ. FRACTION			M. EQ. PER G. DRY HYDROGEN FORM RESIN					EQ. FRACTION				
	Na	K	Mg	Cl	SO_4	Total Anions	Total Cations	Exchange Cations	Na	K	Mg	Calculated K	Difference
1	0.519	0.021	0.460	0.20	0.09	0.29	5.49	5.20	0.430	0.031	0.539	0.041	- 0.010
2	0.505	0.046	0.449	0.21	0.11	0.32	5.58	5.26	0.414	0.077	0.509	0.080	- 0.003
3	0.483	0.092	0.425	0.21	0.10	0.31	5.48	5.17	0.376	0.146	0.478	0.145	+ 0.001
4	0.458	0.139	0.403	0.22	0.11	0.33	5.50	5.17	0.342	0.207	0.451	0.205	+ 0.002
5	0.410	0.233	0.357	0.22	0.10	0.32	5.33	5.01	0.276	0.325	0.399	0.313	+ 0.012
6	0.360	0.329	0.311	0.21	0.10	0.31	5.45	5.14	0.248	0.411	0.341	0.411	0
7	0.312	0.424	0.264	0.21	0.09	0.30	5.37	5.07	0.203	0.505	0.292	0.502	+ 0.003
8	0.262	0.522	0.216	0.22	0.11	0.33	5.47	5.14	0.172	0.578	0.250	0.589	- 0.011
9	0.209	0.621	0.170	0.21	0.10	0.31	5.44	5.13	0.138	0.665	0.197	0.673	- 0.008
10	0.160	0.718	0.122	0.21	0.11	0.32	5.40	5.08	0.106	0.742	0.152	0.754	- 0.012
11	0.106	0.819	0.075	0.21	0.11	0.32	5.41	5.09	0.076	0.833	0.091	0.837	- 0.004
12	0.082	0.869	0.049	0.21	0.11	0.32	5.56	5.24	0.054	0.881	0.065	0.879	+ 0.002
13	0.055	0.919	0.026	0.21	0.11	0.32	5.54	5.22	0.038	0.929	0.033	0.921	+ 0.008
14	0.040	0.950	0.010	0.20	0.11	0.31	5.41	5.10	0.028	0.948	0.024	0.949	- 0.001
		AVGE.		0.21	0.11	0.31	5.46	5.14				R.M.S. DIFFCE. =	± 0.007

TABLE 10.
SEPARATION OF POTASSIUM FROM SODIUM AND MAGNESIUM.

Total Cations = 2.1 g.eq./l. Aqueous Na to Mg ratio = 1 : 1 Cl = 1.75 g.eq./l. SO_4 = 0.35 g.eq./l.

	AQUEOUS			RESIN									
TEST	EQ. FRACTION			M. EQ. PER G. DRY HYDROGEN FORM RESIN					EQ. FRACTION				
	Na	K	Mg	Cl	SO_4	Total Anions	Total Cations	Exchange Cations	Na	K	Mg	Calculated K	Difference
15	0.442	0.115	0.443	0.43	0.17	0.60	5.79	5.19	0.400	0.180	0.420	0.184	- 0.004
16	0.393	0.214	0.393	0.43	0.20	0.63	5.68	5.05	0.327	0.310	0.363	0.307	+ 0.003
17	0.343	0.312	0.345	0.42	0.15	0.57	5.74	5.17	0.284	0.408	0.308	0.413	- 0.005
18	0.270	0.460	0.270	0.42	0.18	0.60	5.79	5.19	0.212	0.548	0.240	0.556	- 0.008
19	0.220	0.559	0.221	0.43	0.16	0.59	5.66	5.07	0.164	0.647	0.189	0.643	+ 0.004
20	0.147	0.706	0.147	0.43	0.16	0.59	5.75	5.16	0.111	0.757	0.132	0.763	- 0.006
21	0.098	0.804	0.098	0.43	0.17	0.60	5.80	5.20	0.071	0.836	0.093	0.840	- 0.004
22	0.049	0.902	0.049	0.41	0.15	0.56	5.62	5.06	0.036	0.923	0.041	0.917	+ 0.006
			AVGE.	0.42	0.17	0.59	5.73	5.14				R.M.S. DIFFCE.	± 0.006

TABLE 11.
SEPARATION OF POTASSIUM FROM SODIUM AND MAGNESIUM OPERATING CONDITIONS.

1.2 g.eq. total Cations per litre.

Na to Mg Ratio 1.1 : 1 (approx.)

ENRICHING SECTION			STRIPPING SECTION		TOTAL No. Theoretical Stages
Reflux, %	R	Theoretical Stages below feed stage.	Reflux, %	Theoretical Stages above feed stage.	
96.3(a)	26.2	infinite	53.7	infinite	infinite
97	32.3	28	58.7	8.2	37.2
98	49	25	68.1	5.1	31.1
99	99	23	81.0	3.8	27.8
100	infinite	22	100.0	2.3	25.3(b)

(a) Minimum reflux. (b) Minimum no. theoretical stages.

TABLE 12.
SEPARATION OF POTASSIUM FROM SODIUM AND MAGNESIUM OPERATING CONDITIONS.

2.1 g.eq. Total Cations per litre.

Na to Mg ratio 1 : 1.

ENRICHING SECTION			STRIPPING SECTION		TOTAL No. Theoretical Stages
Reflux, %	R	Theoretical Stages below feed stage.	Reflux, %	Theoretical Stages above feed stage.	
95.9(a)	23.7	infinite	51.3	infinite	infinite
97	32.3	18	58.7	6.7	25.7
98	49.0	16	68.1	4.6	21.6
99	99	15	81.0	3.2	19.2
100	infinite	14	100.0	2.5	17.5(b)

(a) Minimum reflux. (b) Minimum no. theoretical stages.

6.5 Separation of Sodium from Magnesium

The tests were carried out at a total cation concentration of 1.2 gram equivalents per litre. Both logarithmic plots were made and the following two empirical equations were derived from the straight lines of best fit :-

$$\frac{x_R^{Na^+}}{x_R^{Mg^{++}}} = 0.692 \left(\frac{x_S^{Na^+}}{x_S^{Mg^{++}}} \right)$$

and

$$\frac{{x_R^{Na^+}}^2}{x_R^{Mg^{++}}} = 0.592 \left(\frac{\left(x_S^{Na^+}\right)^2}{x_S^{Mg^{++}}} \right)^{1.05}$$

The equivalent fractions of sodium in the resin corresponding to each aqueous concentration were calculated from the formulae and are shown with the experimental results in Table 13.

TABLE 13.
SEPARATION OF SODIUM FROM MAGNESIUM.

Total Cations = 1.2 g.eq./l. Cl = 10 g.eq./l.
SO_4 = 0.20 g.eq./l.

	AQUEOUS		RESIN				
TEST	EQ. FRACTION		M. EQ. PER G. DRY H^+ FORM RESIN	EQ. FRACTION			
	Na	Mg	Total Cations	Na	Mg	Calculated Na	Diffce.
1	0.223	0.777	5.49	0.166	0.834	0.166	0
D.12	0.505	0.495	5.44	0.408	0.592	0.414	- 0.006
2	0.611	0.389	5.48	0.522	0.478	0.521	+ 0.001
3	0.707	0.293	5.51	0.630	0.370	0.625	+ 0.005
4	0.902	0.098	5.40	0.863	0.137	0.864	- 0.001

7. DISCUSSION.

7.1 Preliminary Investigations

The resin loadings shown in Table 1 indicate that the affinities of the three cations for the resin decrease in the order potassium, magnesium and sodium. It should be possible, therefore, to separate potassium from both sodium and magnesium in a single exchange unit.

For potassium - sodium solutions the equivalent fraction of potassium on the resin did not depend on the nature of the anion present, i.e. chloride or sulphate, but in potassium - magnesium solutions the potassium resin loadings were higher in sulphate than in chloride solutions. Since the composition of the bitterns if fixed and both chloride and sulphate are present it is not possible to take advantage of the increased adsorption of the potassium in sulphate solution.

The total anion loadings were higher than were expected and varied from 0.26 to 0.51 milliequivalents per gram of dry hydrogen form resin. Both the sulphate and chloride - sulphate solutions gave higher anion loadings than those obtained from solutions containing chloride only.

7.2 Separation of Potassium from Sodium

The empirical equations representing the equilibrium curves at both concentrations were very similar but the separation of the potassium was slightly better at the lower concentration. This is in agreement with theoretical considerations because it can be shown that mono-monovalent exchanges are basically unaffected by concentration changes (Appendix). However, some alteration of the distribution was to be expected because of the changes in the activities of the ions and the increased adsorption of neutral salts at the higher concentration. With a reflux of 98 per cent. of the product about 24 theoretical stages would be required to separate the potassium, at both concentration levels.

7.3 Separation of Potassium from Magnesium

The equilibrium curve representing the exchange at a concentration of 1.2 gram equivalents total cations per litre crossed the x = y line at 0.757 equivalent fraction of potassium. Hence, it would not be possible to obtain a product containing more than this concentration of potassium.

When the total cation concentration was increased to 2.1 gram equivalents per litre the separation was improved considerably and the equilibrium curve intersected to x = y line at 0.978 equivalent fraction of potassium. Theoretical considerations (Appendix) indicate that such an increase in the adsorption of the potassium was to be expected as mono-divalent exchanges are concentration dependent. At the higher concentration, and with a reflux of 98 per cent. of the product about 20 theoretical stages would be required to separate the potassium. This is a smaller number of stages than were required for the corresponding separation from sodium.

7.4 Separation of Potassium from Sodium and Magnesium

The results of the tests carried out at 1.2 gram equivalents of total cations per litre were slightly in error because the sodium to magnesium ratio was not constant. Although the errors were greater than experimental errors, the results were sufficiently accurate for comparison with the other tests. The equilibrium curves intersected the x = y line at 0.939 and 0.985 equivalent fractions of potassium respectively. The increased separation of the potassium was due to the decreased adsorption of the magnesium as shown in Figure 8. At 2.1 gram equivalents of total cations per litre and a reflux of 98 per cent. of the product about 22 theoretical stages would be required to separate the potassium, assuming a constant ratio of sodium to magnesium in the aqueous phase.

7.5 Separation of Potassium from Bitterns

The behaviour of all three cations in the column could not be determined graphically from equilibrium curves. The operating conditions determined for the separation of potassium from sodium and from magnesium, assumed feed solutions similar in composition to that of the bittern but with the magnesium or sodium replaced by an equivalent amount of the other cation. These operating conditions were equivalent to the maximum and minimum requirements for the separation of potassium from bitterns. At a concentration of 2.1 gram equivalents of total cations per litre, the conditions necessary to recover 90 per cent. of the potassium in a product containing 0.91 equivalent fraction of potassium would lie between the following limits.

Minimum Reflux (Enriching Section)	95.3 - 96.8%
" " (Stripping Section)	47.5 - 57.1%
Minimum no. theoretical stages	16.4 - 17.3
No. of stages at 98% reflux (Enriching Section)	19.2 - 23.8

These conditions are very similar to those obtained for the separation of potassium from sodium and magnesium where the sodium to magnesium ratio in solution was kept constant.

7.6 Separation of Sodium from Magnesium

Magnesium was adsorbed more strongly than sodium in these tests which were carried out at 1.2 gram equivalents of total cations per litre. No simple relationship could be found between the empirical equations representing this exchange and those obtained at a similar aqueous concentration for the potassium - sodium and potassium - magnesium tests. No tests were made at higher aqueous concentrations but the magnesium would be almost certainly adsorbed less strongly. This is indicated also by the graphs shown in Figure 8.

7.7 Neutral Salt Adsorption

The anion loadings found at each concentration level were not significantly altered by changes in the combinations of the cations in solution. Increased loadings were obtained in the more concentrated solutions. The following results were obtained by averaging the loadings for all the tests carried out at each of the two aqueous concentrations. Extreme values are included.

Aqueous Concentration g.eq./l.		1.2	2.1
Resin loadings m. eq. per dry H^+ form resin			
Chloride,	Cl	0.21(0.20 to 0.24)	0.43(0.40 to 0.45)
Sulphate,	SO_4	0.11(0.08 to 0.13)	0.17(0.15 to 0.22)
Total Anions		0.33(0.29 to 0.35)	0.60(0.55 to 0.64)
Total Cations		5.49(5.33 to 5.91)*	5.67(5.54 to 5.80)
Exchange Cations		5.17(5.01 to 5.42)	5.07(4.93 to 5.21)

* next highest value 5.74

It is probable that not all of the supernatant liquor was removed from the resin beads by filtration, hence the total anion and cation loadings were almost certainly high. The relative concentration of the sulphate in the resin was greater at both aqueous concentrations than that of the original solution.

7.8 Equilibrium Curves

The equilibrium curves drawn from the empirical equations represented the experimental data very closely. The greatest deviation between the experimental resin loadings and the loadings calculated from the empirical equations was 0.024 equivalent fraction of potassium. The Root Mean Square deviations for each series were less than ± 0.010 equivalent fraction. Any variations of the experimental data from the empirical equations were considered to be due to experimental errors.

8. CONCLUSIONS.

The investigations showed that potassium should be recoverable from salt bitterns by a single continuous counter-current ion exchange system with reflux of both the aqueous product and waste cations adsorbed on recycled resin.

Equilibrium tests at 1.2 and 2.1 gram equivalents of total cations per litre showed that a better separation of the potassium would be obtained at the latter concentration. Higher concentrations were not practicable because of the possibility of potassium salts crystallizing in the exchange columns from the product reflux solutions.

The bitterns would have to be diluted with water to about one third of the original concentration before entering the exchange column.

The operating conditions necessary to recover 90 per cent. of the potassium in a product containing 0.91 equivalent fraction of potassium were estimated from the conditions necessary for the separations of potassium from sodium and from magnesium. The estimated conditions were :-

Minimum Reflux of Enriching Section	96 - 97%
Minimum No. Theoretical stages	17 - 18
No. of stages at 98% Enriching Section reflux	20 - 24

Since the aqueous product would be nearly saturated with respect to potassium, a mixture of potassium chloride and sulphate crystals could be recovered by evaporation.

Further investigations would be required before the process could be evaluated. This would involve the operation of a small continuous countercurrent exchange column in order to determine the actual heights of the theoretical stages, to investigate the mechanics of resin transfer and to determine the life of the resin under the operating conditions. In view of the low market price of potassium salts and the high reflux required it is considered likely that such a process would not be economic. However, a similar process might be used for the separation and recovery of more valuable cations from solution.

APPENDIX

THE EFFECT OF CONCENTRATION ON RESIN SELECTIVITY.

The exchange of ions between resin and aqueous solution may be expressed by an equation similar to the normal mass action equation. Since the chemists' equilibrium constant is not strictly applicable to resin systems it is customary to substitute a selectivity coefficient. For a resin containing ion B^+ placed in a solution of ion A^+ the selectivity coefficient $(K_c)^{A^+}_{B^+}$ is defined as

$$(K_c)^{A^+}_{B^+} = \frac{\left[A^+_R\right] \left[B^+_S\right]}{\left[B^+_R\right] \left[A^+_S\right]}$$

This expression ignores activity coefficients of the ions in the two phases and cannot be used other than in extremely dilute solutions. The activity of the ions in solution may be corrected for in slightly more concentrated solutions but the activities of the ions in the resin phase cannot be accurately determined. For ions of different valency the equation becomes more complex e.g. for the exchange of ion B^+ with A^{++} the equation becomes

$$(K_c)^{A^{++}}_{B^+} = \frac{\left[A^{++}_R\right] \left[B^+_S\right]^2}{\left[B^+_R\right]^2 \left[A^{++}_S\right]}$$

The effect of concentration can be best seen by observing the change in the form of the selectivity coefficient in such exchanges.

Mono-Monovalent Exchanges

For the reaction

$$NaCl + RSO_3 \rightleftharpoons KCl + RSO_3Na$$

in very dilute solutions

$$(K_c)^{Na^+}_{K^+} = \frac{\left[Na^+_R\right] \left[K^+_S\right]}{\left[K^+_R\right] \left[Na^+_S\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots (a)$$

By substituting the values

$$X_R^{Na^+} = \text{Equivalent fraction } Na^+ \text{ in the resin} = \frac{[Na_R^+]}{CR}$$

$$1- X_R^{Na^+} = \text{Equivalent fraction } K^+ \text{ in the resin } \frac{[K_R^+]}{CR}$$

$$X_S^{Na^+} = \text{Equivalent fraction } Na^+ \text{ in solution} = \frac{[Na_S^+]}{C}$$

$$1- X_S^{Na^+} = \text{Equivalent fraction } K^+ \text{ in solution } = \frac{[K_S^+]}{C}$$

in which

CR = total normality of the exchange sites in the resin.

C = total normality of the solution.

Equation (a) becomes

$$\frac{X_R^{Na^+}}{1- X_R^{Na^{++}}} = (K_c)_{K^+}^{Na^+} \cdot \frac{X_S^{Na^+}}{1- X_S^{Na^+}}$$

The terms C and CR are not present in the final equation hence the selectivity coefficient is independent of the solution strength.

Mono-Divalent Exchanges

For the reaction

$$MgCl_2 + 2RSO_3K \rightleftharpoons (RSO_3)_2Mg + 2KCl$$

$$(K_c)_{K^+}^{Mg^{++}} = \frac{[Mg_R^{++}]\quad[K_S^+]^2}{[Mg_S^{++}]\quad[K_R^+]^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \text{(b)}$$

By substituting the values for the equivalent fractions of Mg^{++} and K^+ as in the previous example, equation (b) becomes

$$\frac{X_R^{Mg^{++}}}{\left(1- X_R^{Mg^{++}}\right)^2} = (K_c)_{K^+}^{Mg^{++}} \cdot \frac{CR}{C} \cdot \frac{X_S^{Mg^{++}}}{\left(1- X_S^{Mg^{++}}\right)^2} .$$

The apparent selectivity coefficient is therefore

$$(K_c)_{K^+}^{Mg^{++}} \cdot \frac{CR}{C} .$$

Since CR is fixed for any resin, the apparent selectivity coefficient is inversely proportional to the solution concentration.

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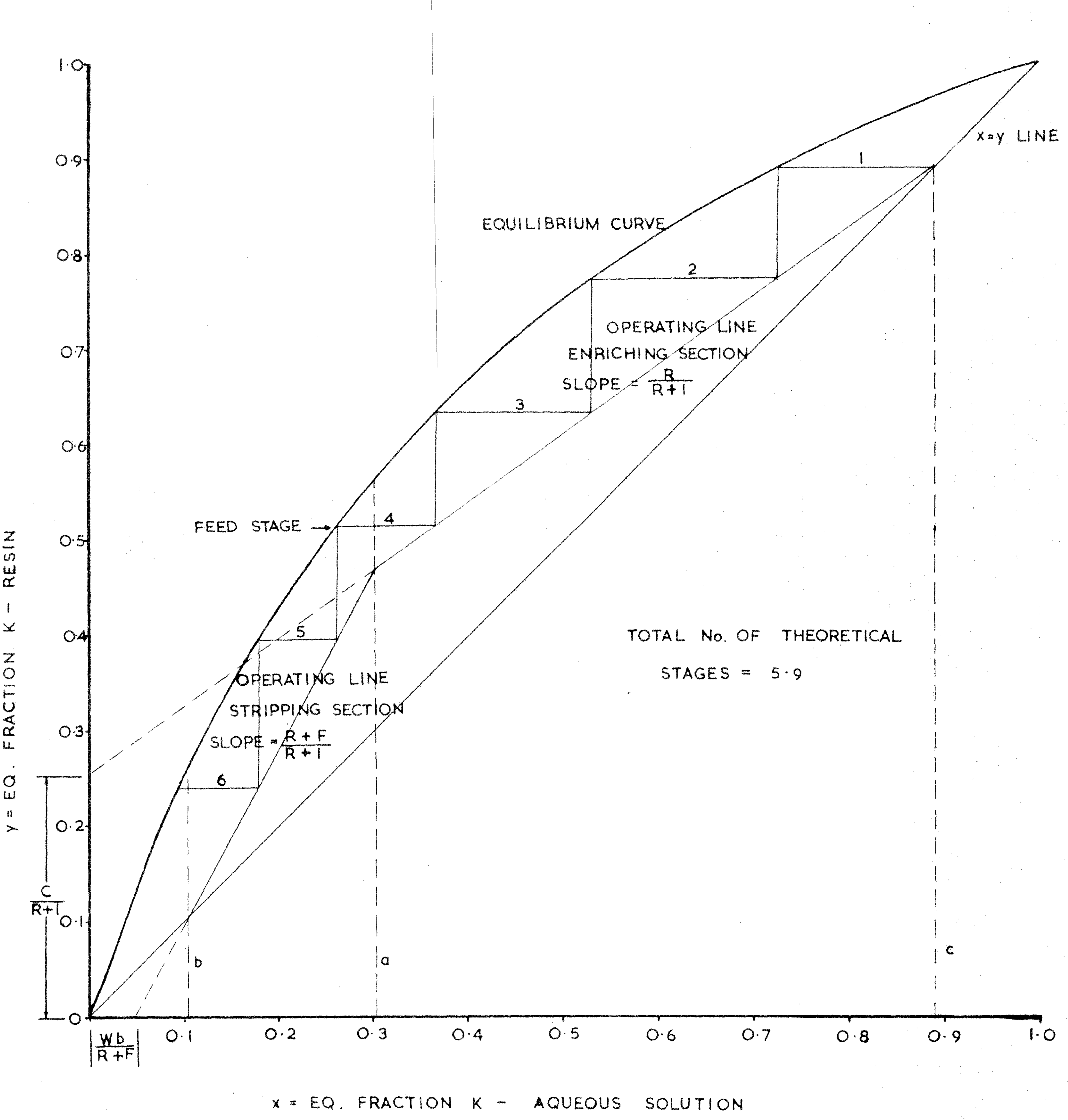
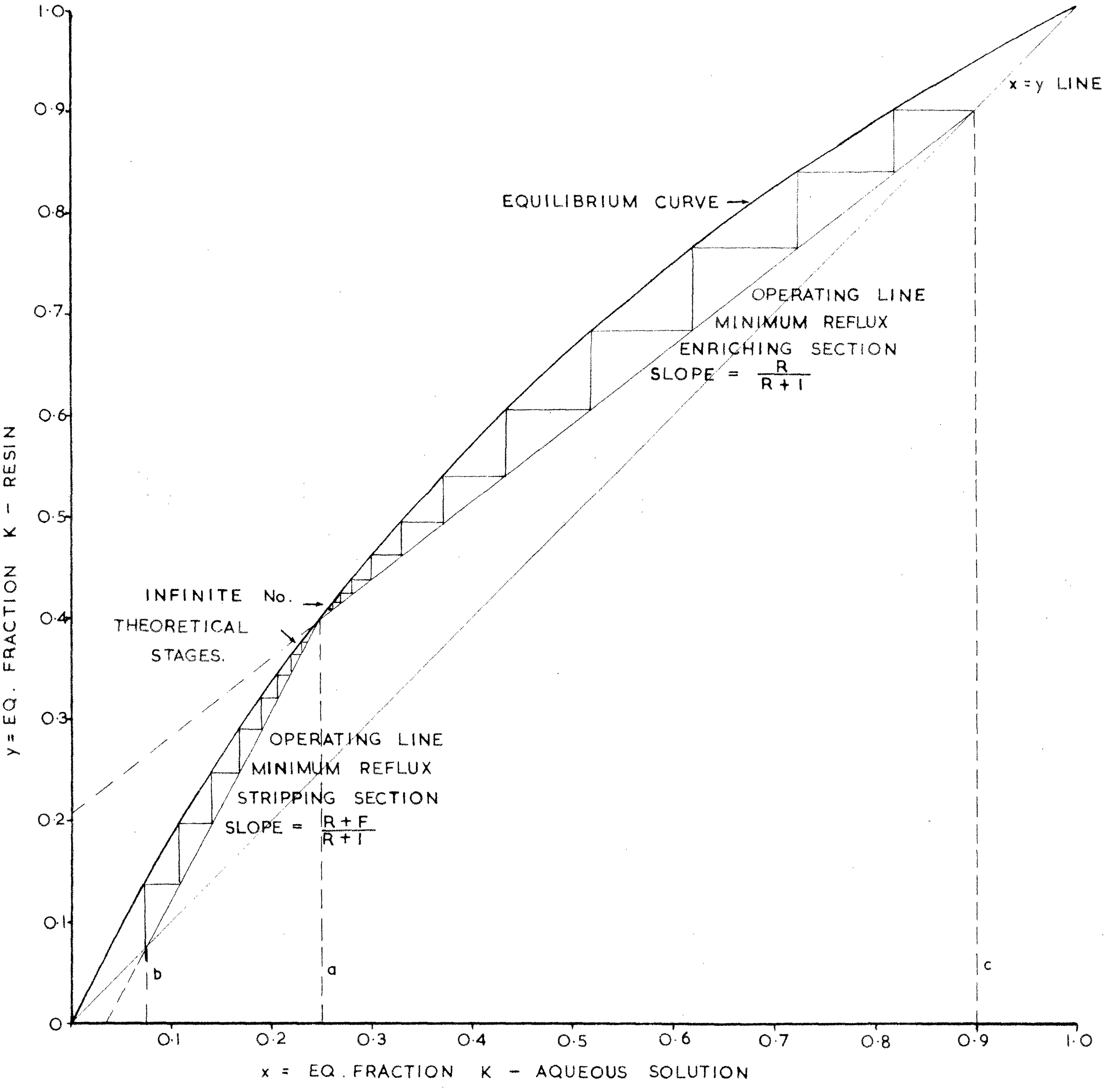
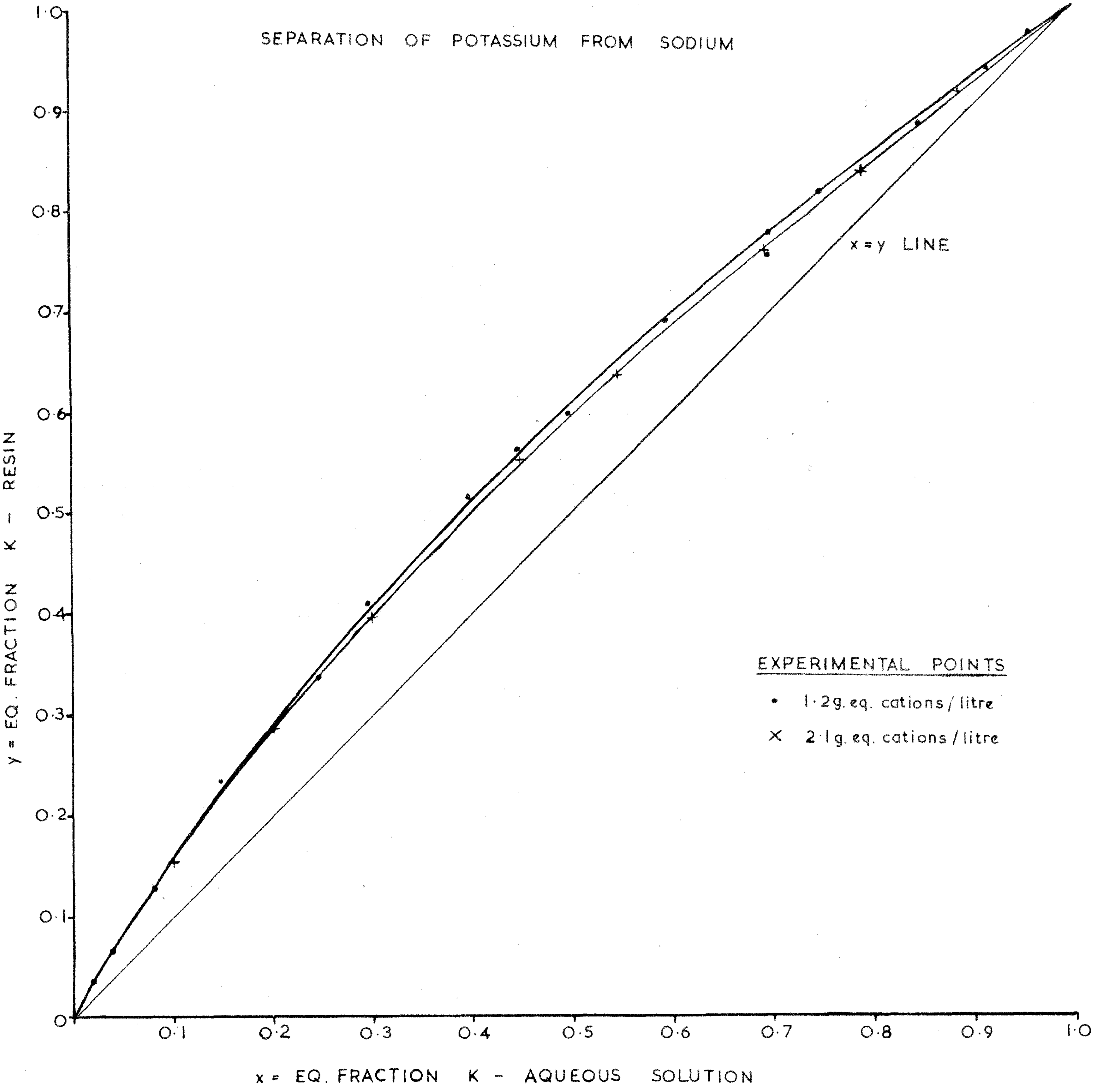
DETERMINATION OF THEORETICAL STAGES. FIG. 3.



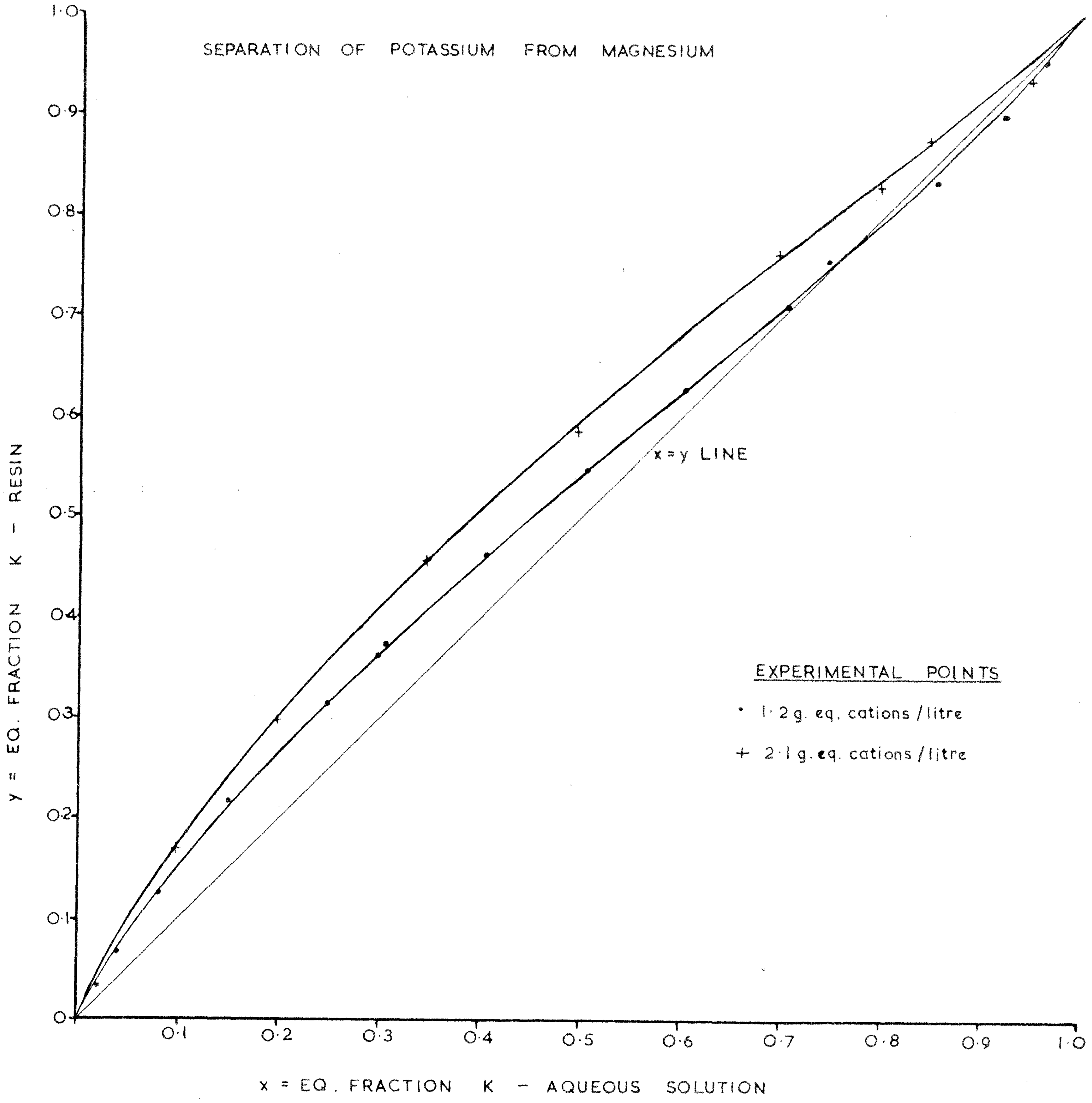
DETERMINATION OF MINIMUM REFLUX. FIG.4.



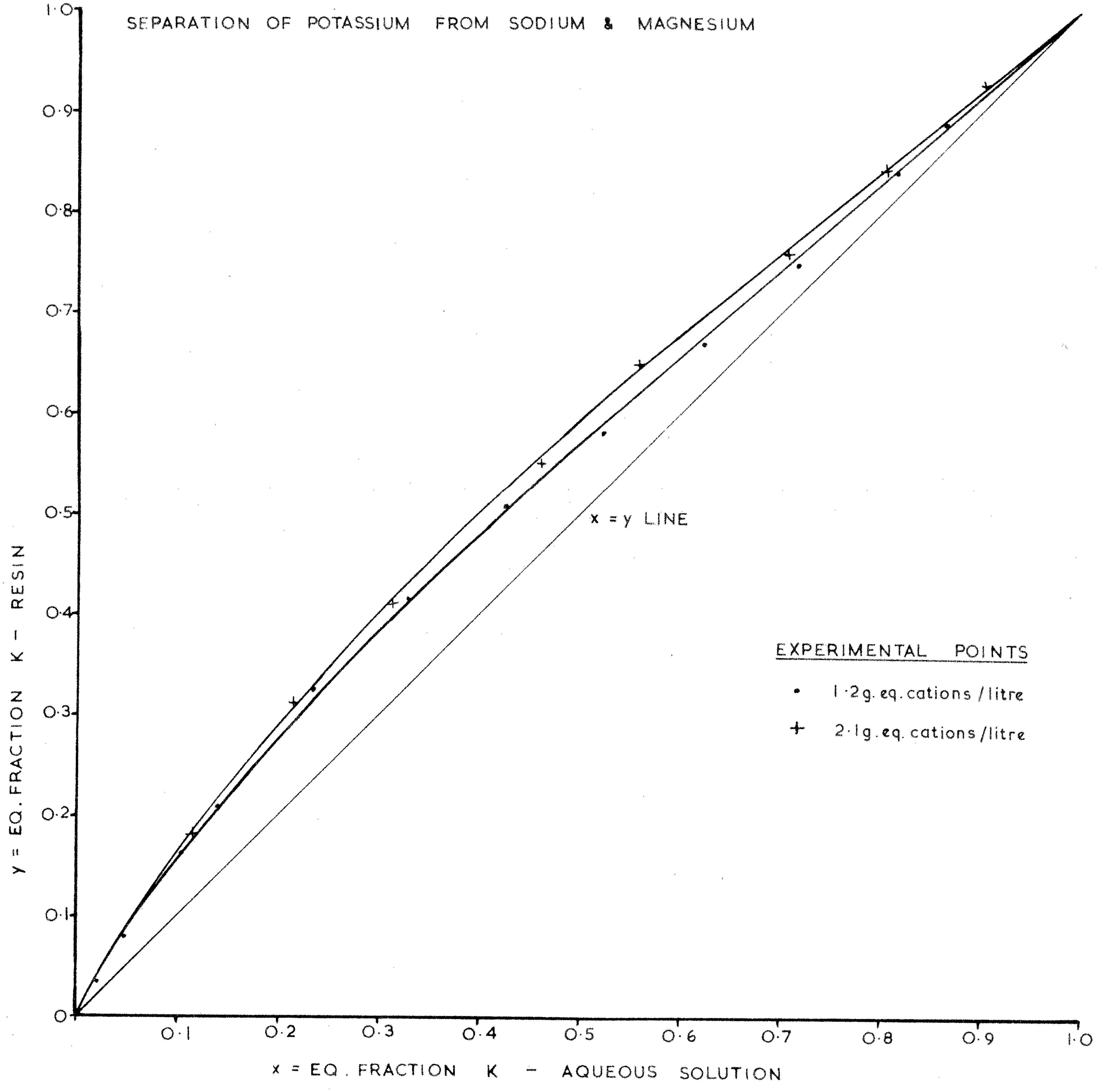
EQUILIBRIUM CURVES FIG. 5.



EQUILIBRIUM
CURVES
FIG.6.

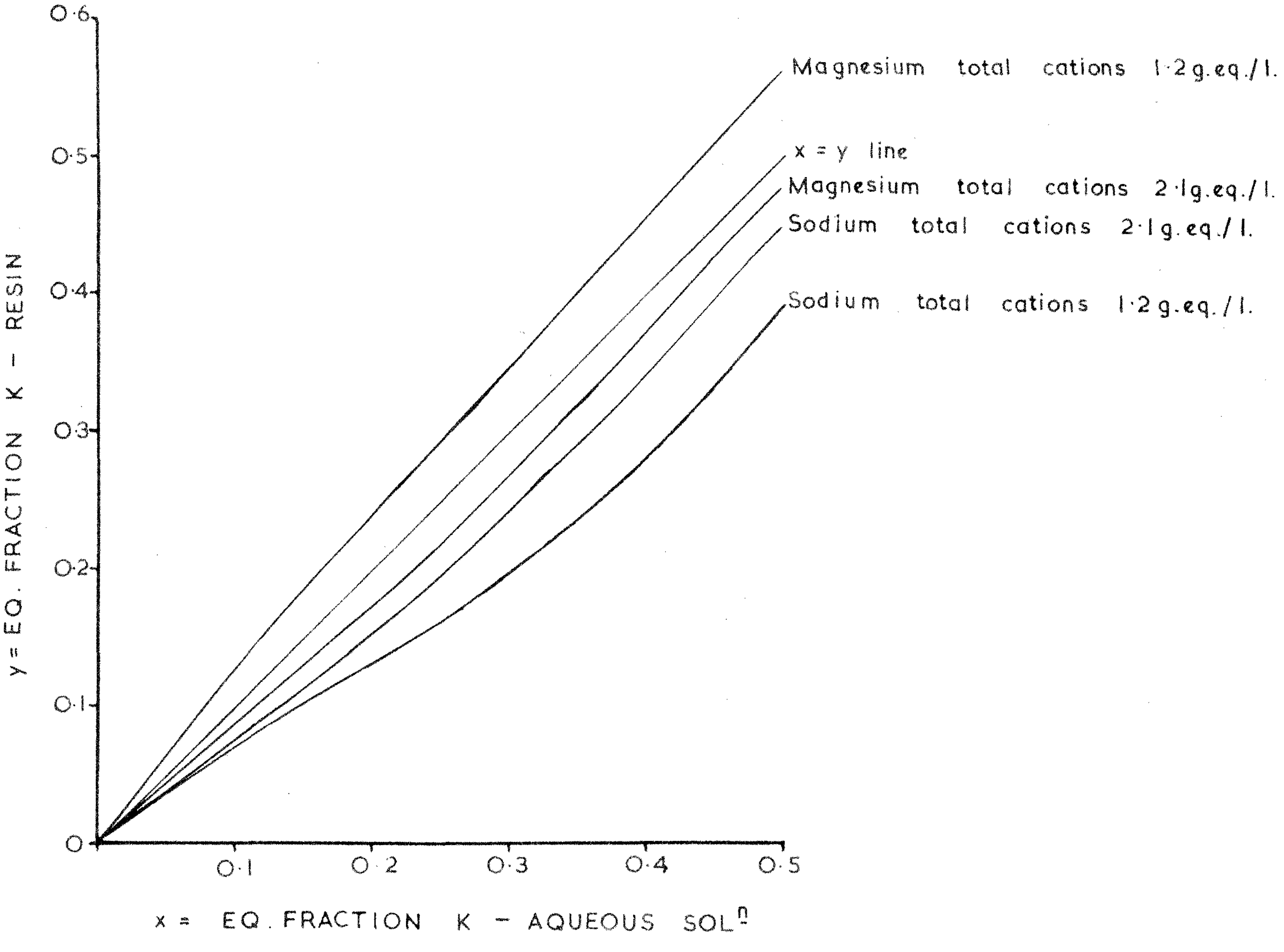


EQUILIBRIUM
CURVES
FIG.7.



EQUILIBRIUM
CURVES.
FIG.8.

SEPARATION OF POTASSIUM FROM SODIUM & MAGNESIUM



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RESEARCH AND DEVELOPMENT BRANCH

R.D. 69

"SALT INVESTIGATIONS .. RECOVERY OF POTASSIUM FROM SALT BITTERNS"

PART THREE

by

F. J. Moyle.

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This document consists of 6 pages. April, 1958.

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CONTENTS

ABSTRACT

The use of ion retardation as a separation procedure for the recovery of potassium from salt bitterns was investigated. The separation of potassium salts was not sufficiently great to be of practical use. It is unlikely that any variation of the procedure adopted would give an economic recovery of the potassium.

1. INTRODUCTION.

It was suggested that potassium might be recovered from bitterns by an ion retardation procedure (1).

This process involves the use of a unique type of ion exchange resin containing equivalent amounts of both an anion and a cation exchanger incorporated in each resin bead. The aqueous solution to be treated is passed through the exchanger and both cations and anions are adsorbed. When the adsorbing capacity of the resin is utilized as completely as possible the ions are eluted with water. Since the least strongly adsorbed ions are recovered in the first fractions of the effluent, it is possible to obtain a separation of certain ions. In practice a cyclic procedure involving the successive additions of feed and water rinse is used.

A sample of Retardion 11A-8 resin, which is made by polymerizing acrylic acid inside Dowex 1 resin, was obtained from the Dow Chemical Co., U.S.A. This resin was used in the following investigations which were carried out to determine the possibility of recovering potassium from salt bitterns.

2. MATERIAL EXAMINED.

A sample of salt bitterns was obtained from Solar Salt Ltd., in January, 1957. A chemical analysis of the sample, which was designated B.1, gave the following results.

Chemical Composition of Bittern B.1

Constituents		g/l.
Sodium,	Na	71.0
Potassium,	K	10.25
Magnesium,	Mg	36.5
Calcium,	Ca	nil
Chloride,	Cl	186.2
Sulphate,	SO_4	50.4
Carbonate,	CO_3	0.5
Bromine,	Br	1.76
Specific Gravity at 29°C		1.248

3. ANCILLARY MATERIALS.

3.1 "Retardion" Resin

Approximately 3 ounces of Retardion 11A-8 experimental resin was received from the Dow Chemical Company, U.S.A. This resin was used in all of the tests.

3.2 Chemical Reagents

The synthetic solutions used in the tests were prepared by dissolving "AnalaR" grade reagents in distilled water. All solutions contained both chloride and sulphate ions in a similar proportion to that of the bittern sample. The composition of each synthetic solution was determined by analysis.

4. EXPERIMENTAL PROCEDURE.

4.1 Resin Column

The resin column was prepared by suspending 70 grams of moist Retardion 11A-8 (50 to 100 mesh) resin in distilled water in a glass column 1.55 centimetres in diameter. The volume of the wet settled resin was 96.5 millilitres and the height of the resin in the column was 52 centimetres. The moisture content of a small sample of the resin was determined and the weight of resin in the column was calculated to be equivalent to 44 grams of dry "as received" resin. The total volume of water in the column was found to be 36.5 millilitres. Two burettes of 50 and 250 millilitres capacity respectively were suspended above the column and were connected to two pieces of glass tubing which passed through the rubber stopper at the top of the column. This enabled the cyclic introduction of water and feed solution without interruption to the flow of liquid through the column. The flowrate of 2 millilitres per minute was obtained by adjusting a screw clamp attached to the outlet tube at the bottom of the column.

4.2 Separation Tests

The feed solution to be tested was added to the column from the 50 millilitre burette, while at the same time water was displaced from the bottom of the column at the desired flowrate. When the required volume of feed had been added, the water rinse was run into the column from the 250 millilitre burette. All additions were made so as to minimise mixing. The addition of water was continued until the concentration of salts in the effluent was sufficiently low.

The resin was allowed to reach equilibrium prior to each test by repeating the successive additions of feed and water rinse for 4 or 5 cycles. Then the addition of feed and rinse was repeated, and small samples of the effluent were collected throughout the cycle. The fractions were analysed to determine the efficiency of the separation and to obtain a material balance. The resin was assumed to be in equilibrium when a material balance could be obtained on the feed and effluent solutions. The experimental data were plotted graphically to enable the separations obtained in each test to be observed easily. Since the composition of the effluent was not determined continuously but in separate samples, it was necessary to idealise the curves and to estimate the heights of some of the peaks.

5. RESULTS.

5.1 Separation of Potassium from Sodium

Two tests were carried out. In the first test the concentration of both sodium and potassium in the feed solution was 1.0 normal and in the second the composition of the feed approximated to that of salt bitterns with all of the magnesium replaced by an equivalent amount of sodium. Both solutions contained chloride and sulphate ions in a similar proportion to that of the bittern. Effluent samples of 15 millilitres volume were taken throughout both tests. These were analysed for sodium, potassium, chloride and sulphate and a material balance on feed and effluent samples showed that the resin behaviour was in equilibrium for both tests. The separations obtained in the first 200 millilitres of effluent are shown graphically in Figures 1 and 2. The water rinse was continued and in both instances the chloride concentration had decreased to 0.06 grams per litre when the total effluent volume was 400 millilitres.

5.2 Separation of Potassium from Magnesium

The composition of the feed solution was similar to that of salt bitterns but with all of the sodium replaced by an equivalent amount of magnesium. The operating conditions were similar to those of the previous tests with the exception that the effluent samples were 20 millilitres in volume. The separations obtained are shown graphically in Figure 3. The elution with water was continued beyond the stage shown in the graphs and the chloride concentration decreased to 0.6 grams per litre when the total effluent volume was 500 millilitres.

5.3 Separation of Potassium from Bitterns

The feed solution for this test was a sample of bittern, B.1, which had been diluted slightly to prevent the crystallizing of salts in the resin column. The operating conditions were similar to those of the previous tests. Effluent samples 20 millilitres in volume, were collected and analysed for sodium, potassium, magnesium, chloride and sulphate. The results are shown graphically in Figure 4. Further elution with water gave an effluent containing 0.6 grams chloride per litre when the total volume of effluent was equal to 500 millilitres.

6. DISCUSSION.

In all four tests there was a reasonable separation of the sulphate and chloride ions as shown by the spacing of the effluent peaks. This introduced a complication in that two separate peaks, one in the chloride-rich and one in the sulphate-rich portions of the effluent, were obtained for each of the cations.

Magnesium was the most difficult cation to elute from the resin with water. Only about one half of the magnesium ions were removed by 200 millilitres of water in the separation of potassium from bitterns (Fig. 4). There was a slight separation of potassium from both sodium and magnesium as shown by the slight differences in the positions of the effluent peaks. The separations would not be of practical use because it would be possible to obtain only a slightly enriched solution containing a relatively small proportion of the original potassium.

Since the potassium concentration of the bittern was relatively low it would be necessary to continue the washing until the effluent contained very little salts in order that the potassium enriched fraction of the next cycle would not be excessively contaminated. For the separation of potassium from sodium a volume of 200 millilitres rinse water would be sufficient but in the other two separations where magnesium was present a much larger volume would be required. Since only 10 millilitres feed solution were used, the major part of each cycle would consist of the elution with water.

It is probable that the separations could be improved by heating the solutions and by reducing the flow rate. Neither of these possibilities should be considered from a practical point of view because of the costs involved in heating large volumes of solution and the inefficient use of the resin at low flow rates.

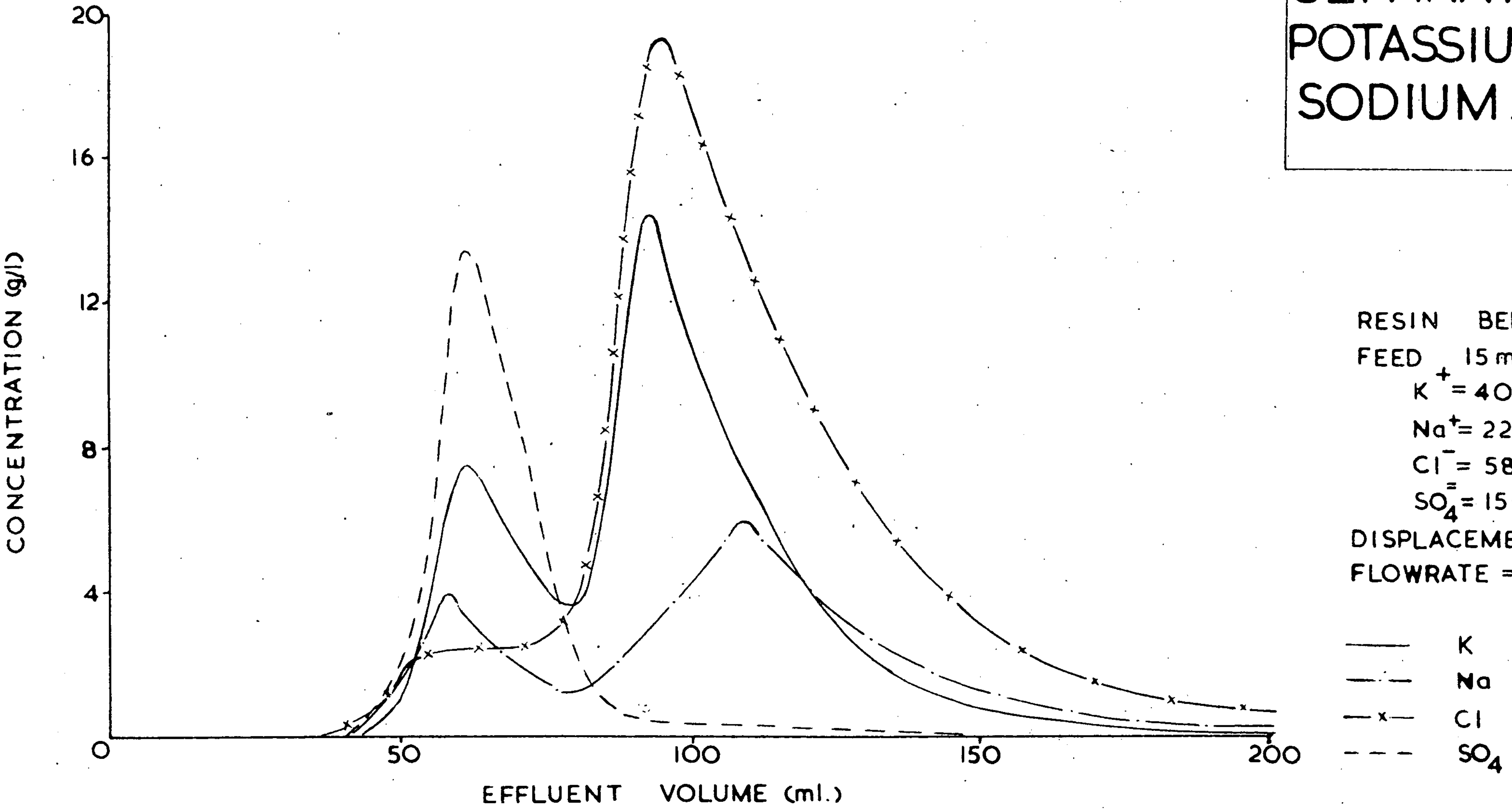
Precipitation of the sulphate with calcium chloride prior to ion exchange would eliminate the difficulties due to double elution peaks which were obtained for each of the cations. The separations obtained in the chloride rich fractions of the eluate were not very great, and the costs involved would be excessive. Large volumes of rinse water would still be required to ensure complete removal of the magnesium.

7. CONCLUSION.

The investigations have shown that effluent fractions slightly enriched in potassium can be obtained by passing feed solutions containing potassium, sodium and/or magnesium through Retardion 11A-8 ion exchange resin and rinsing with water. The separations were not sufficiently great to be of practical use in the recovery of potassium from salt bitterns. It is unlikely that any variation of the procedure would result in the economic recovery of potassium salts.

8. LITERATURE REFERENCE.

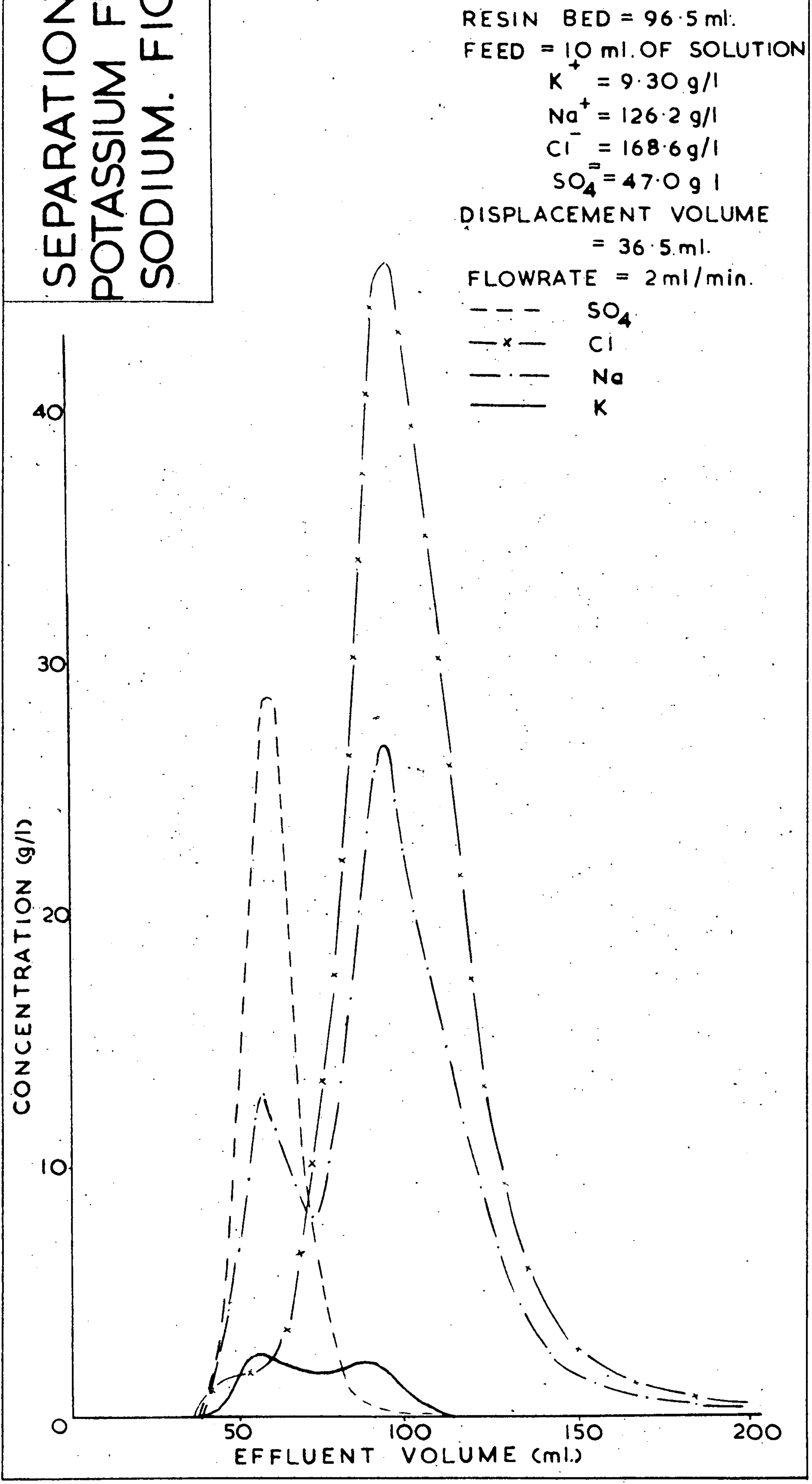
(1) "Ion Retardation" .. Dow Chemical Co.
April, 1957.



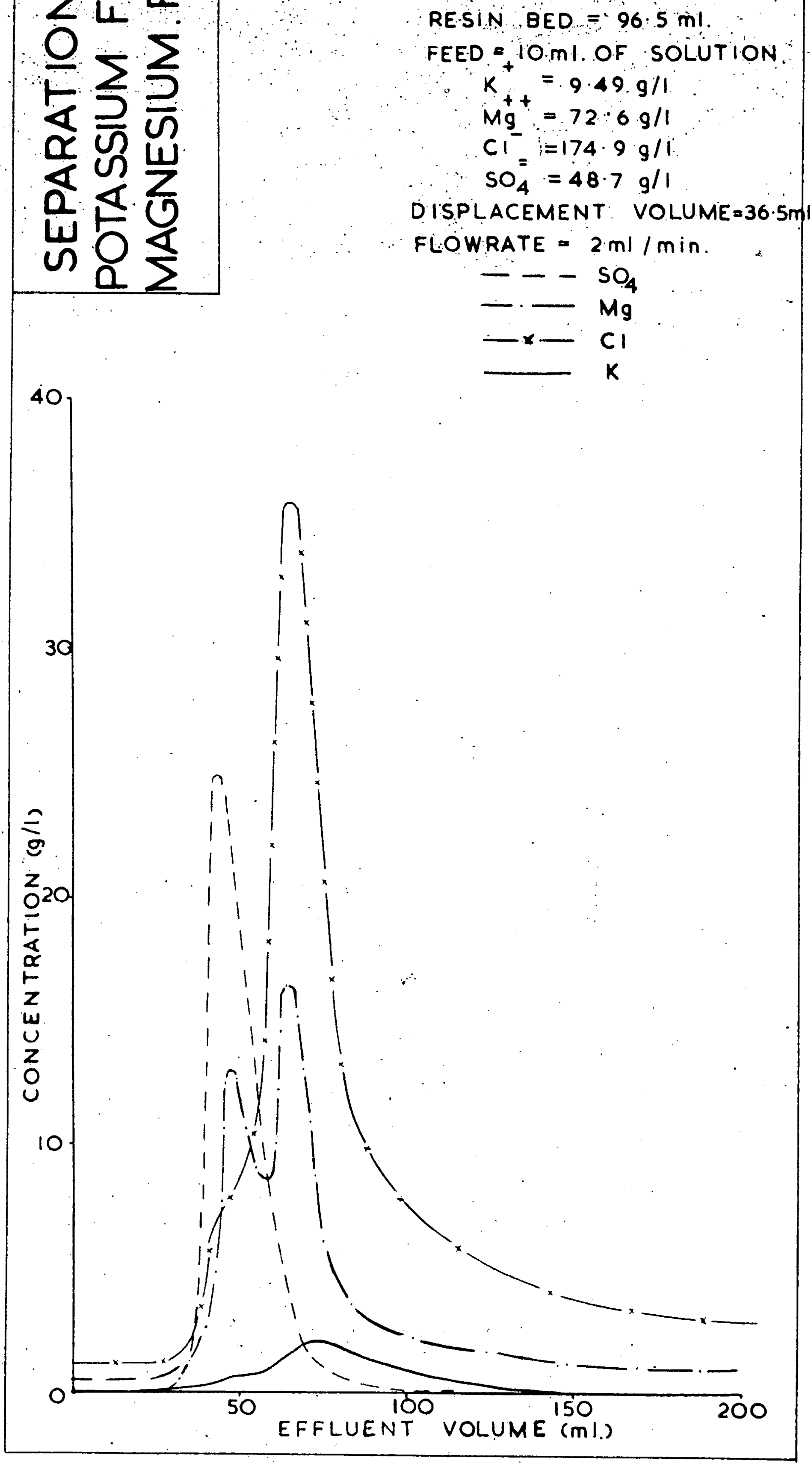
SEPARATION OF POTASSIUM FROM SODIUM. FIG. I.

RESIN BED = 96·5 ml.
FEED 15 ml. OF SOLUTION
K^+ = 40·1 g/l
Na^+ = 22·3 g/l
Cl^- = 58·7 g/l
$SO_4^=$ = 15·9 g/l
DISPLACEMENT VOL = 36·5 ml.
FLOWRATE = 2 ml / min.

SEPARATION OF POTASSIUM FROM SODIUM. FIG. 2.



SEPARATION OF POTASSIUM FROM MAGNESIUM. FIG.3.



RESIN BED = 96·5 ml.

FEED = 10 ml. OF SOLUTION

K^+ = 9·49 g/l

Mg^{++} = 72·6 g/l

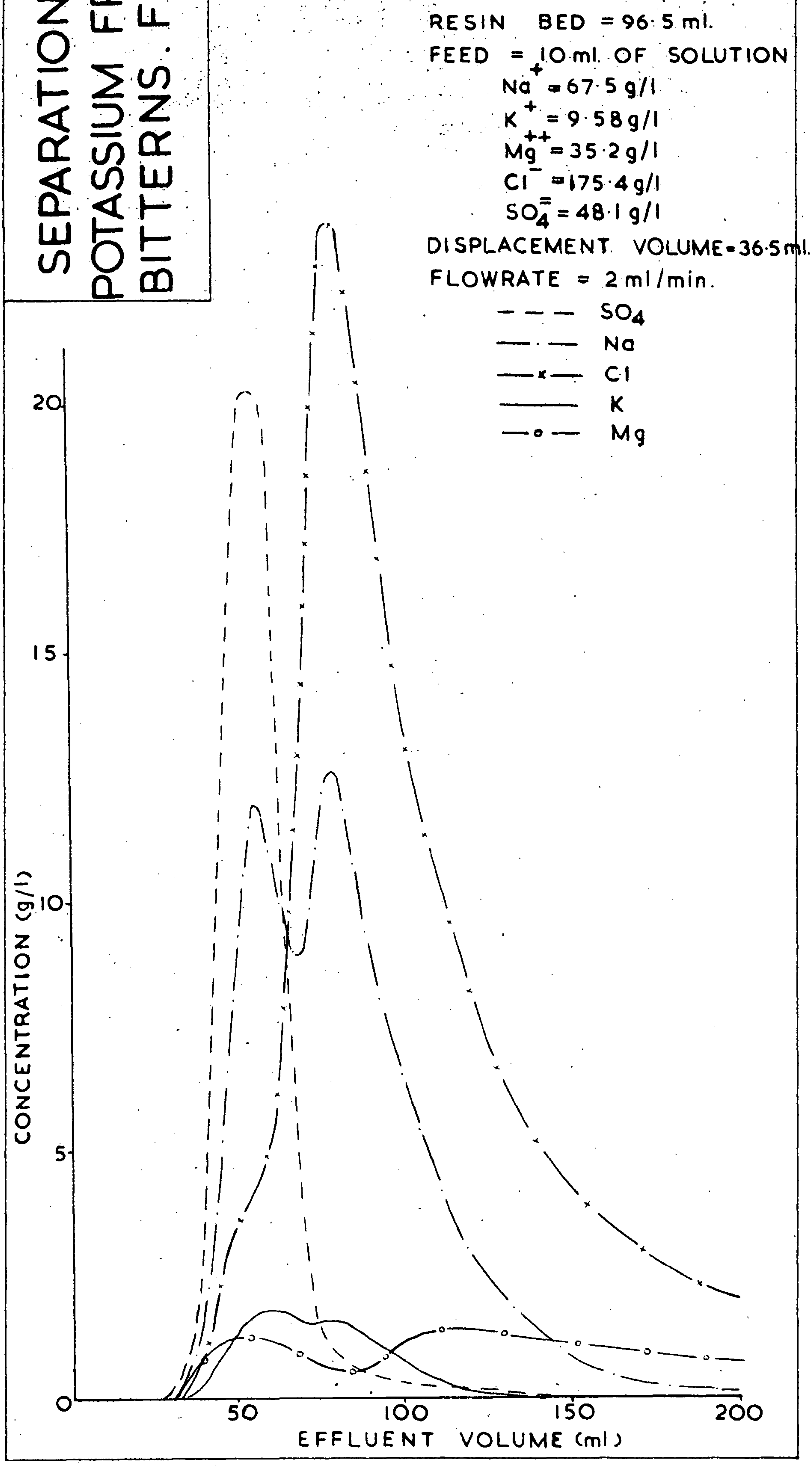
Cl^- = 174·9 g/l

$SO_4^=$ = 48·7 g/l

DISPLACEMENT VOLUME = 36·5 ml

FLOWRATE = 2 ml/min.

SEPARATION OF POTASSIUM FROM BITTERNS. FIG. 4.



RESIN BED = 96·5 ml.

FEED = 10 ml. OF SOLUTION

Na^+ = 67·5 g/l

K^+ = 9·58 g/l

Mg^{++} = 35·2 g/l

Cl^- = 175·4 g/l

$SO_4^=$ = 48·1 g/l

DISPLACEMENT VOLUME = 36·5 ml.

FLOWRATE = 2 ml/min.

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RESEARCH AND DEVELOPMENT BRANCH

R.D. 69

SALT INVESTIGATIONS .. "Recovery of Potassium from Salt Bitterns"

PART FOUR

by

F.J. Moyle.

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This document consists of 34 pages. DATE : July, 1959.

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PAGE.

ABSTRACT

The recovery of a saleable potassium product from potassium enriched salts obtained by evaporation of salt bitterns was investigated. Four methods of treatment, namely, flotation, leaching, ion exchange and hydrolysis of the magnesium salts were attempted. It is most unlikely that any of these methods could be used to produce potassium salts at a price to compete with that of imported material.

A review of the results obtained during the salt investigations indicates that further work is not warranted at present.

1. INTRODUCTION.

The following methods of recovering potassium salts from salt bitterns have been investigated and reported in parts one, two and three of this report :-

(a) Direct precipitation of the potassium with dipicrylamine
(b) Solvent extraction of the potassium
(c) Normal ion exchange
(d) Ion retardation
(e) Continuous ion exchange
(f) Evaporation

Only (e) and (f) showed promise. Although direct recovery of high grade potassium salts by continuous ion exchange treatment of salt bitterns was shown to be possible it is unlikely to be economic because of the high reflux necessitated by the relatively low concentration of the potassium in the bitterns. Salts enriched in potassium were produced by both the direct evaporation of the bitterns and evaporation after the removal of the sulphate ions by precipitation. Experimental work carried out at Price by Ocean Salt Limited has shown that the specific gravity of bitterns can be increased to 1.355 by solar evaporation. Since all of the potassium salts have crystallized before this specific gravity is reached evaporations could be carried out using solar energy. However, the potassium-enriched salts produced in this way contain too high a proportion of undesirable salts to be marketable without further treatment.

This report is concerned with methods of treating the enriched salts to recover a saleable product. Four methods, namely, flotation, continuous ion exchange, leaching, and hydrolysis of the magnesium salts were investigated. A fifth method, namely, electrolysis of aqueous or molten salt solutions of the enriched salts was considered but the power cost was thought to be prohibitive

2. FLOTATION.

These investigations can be divided into two sections; the preparation of suitable quantities of the potassium enriched salts and the actual flotation tests. The preparation of the salts is described below and the flotation tests which were carried out in the Metallurgical Section of this Branch are reported in Appendix 1.

The procedures used in the preparation of the salts and the results obtained are reported fully for comparison with the smaller scale tests which have been reported previously (Moyle, 1957). Direct comparison is not possible since in the earlier work the crystallized salt was separated from the supernatent liquor by filtration, whereas in these investigations the salts were allowed to drain in order to simulate conditions in salt fields. The salts were not washed.

Samples of salt were prepared by each of three methods, namely,

(a) Direct evaporation of the bitterns

(b) Evaporation of the bitterns after the removal of sulphate ions by precipitation with calcium chloride

(c) Evaporation of the bitterns after the removal of sulphate ions by precipitation with lime.

2.1. Material Examined

Bitterns B.6 and B.9 were obtained from Solar Salt Limited, Port Patterson in 44-gallon drums and B.14 was a synthetic bittern prepared by adding appropriate amounts of sodium and potassium salts to a magnesium chloride brine. The bitterns B.6 and B.9 both contained smaller quantities of total salts than bittern B.1 which was obtained previously from the same source. The chemical compositions of the bitterns including B.1 are shown in Table 1.

TABLE 1.
CHEMICAL COMPOSITION OF BITTERNS

Sample	B.1	B.6	B.9	B.14
Contents, g/l.				
Na	71.0	91.5	87.4	88.0
K	10.25	5.75	6.3	6.55
Mg	36.5	20.7	21.6	22.6
Ca	nil	nil	1.1	nil
Cl	186.2	185.0	182.5	172.5
SO_4	50.4	28.35	30.2	33.55
Br	1.76	1.10	1.10	1.55
Specific Gravity	1.248	1.222	1.228	n.d.

n.d. = not determined

2.2 Experimental Procedure

2.2.1 : Precipitation -

The calculated amount of precipitating agent was slurried with water and added slowly to the agitated bittern. The pulp was stirred for an hour after addition of the reagent, then allowed to stand overnight and the clear supernatent liquor siphoned off.

2.2.2 : Evaporation -

The evaporations were made in two stages. The first stage was carried out in a steel tank 3 feet by 2 feet 6 inches and 10 inches deep. Solar evaporation conditions were simulated by suspending four 1,000 watt radiators over the tank to supply the necessary heat. An electric fan was used to produce a draught. Surface ripples were generated with the aid of several laboratory stirrers. The heaters were switched on daily from 9 a.m. to 5 p.m. and the bitterns were allowed to cool overnight. The liquid was kept at a temperature not exceeding 35°C by controlling with a "Variac" transformer the voltage applied to two of the radiators. Evaporation was continued until the liquor was just saturated with respect to potassium salts. The supernatent liquor was siphoned off and the crystallized salts were drained for several hours to remove surplus brine. The salts were dried under the heaters for several days before being collected, weighed and sampled.

The second stage of evaporation was carried out in a smaller steel tray, 2 feet 6 inches by 3 feet by 5 inches deep. When it was considered that all of the potassium salts had crystallized the liquor was siphoned off as before and the dried salt was collected and weighed.

The weights of the salts and the volumes of the liquors were recorded and used together with chemical analyses of the products in calculating material balances.

2.3 Results

2.3.1 : Direct Evaporation of Bitterns -

A sample of bittern B.6 (160 litres) was evaporated for 99 hours heating time in the larger steel tank.

The chemical analyses of the products and a material balance are shown in Table 2.

TABLE 2.
DIRECT EVAPORATION OF BITTERN B.6
First Stage

Heating Time 99 hours. Total Evaporation Time - 336 hours

Sample	Bittern Feed B.6	Product liquor B.7	Product salt B.7 Salt
Specific Gravity	1.222	1.288	-
Volume, l.	160	43.0	-
Weight, kg.	-	-	40.82

Contents	g/l	Total Wt. g.	g/l	Total Wt. g.	%	Total Wt. g.
Na	91.5	14,640	38.05	1,636	31.9	13,020
K	5.75	920	18.0	774	0.47	192
Mg	20.65	3,304	63.0	2,709	1.43	584
Cl	185.0	29,600	192.0	8,256	52.4	21,390
SO_4	28.35	4,536	88.0	3,784	2.25	918
Br	1.10	176	3.10	133	0.11	45

The results of the second stage evaporation are presented in Table 3.

TABLE 3.
DIRECT EVAPORATION OF BITTERNS.
Second Stage

Heating Time - 52 hours. Total Evaporation Time - 240 hours

Sample	Feed B.7	Product Liquor B.8	Product Salt B.8 Salt
Specific Gravity	1.288	1.343	-
Volume, l.	43	7.41	-
Weight, kg.	-	-	20.87

Contents	g/l	Total Wt. g.	g/l	Total Wt. g.	%	Total Wt. g.
Na	38.05	1,636	3.55	26	7.38	1,540
K	18.0	774	1.80	13	3.44	718
Mg	63.0	2,709	115.0	852	8.56	1,786
Cl	192.0	8,256	309.55	2,293	27.76	5,793
SO_4	88.0	3,784	39.40	292	16.10	3,360
Br	3.10	133	8.50	63	0.32	67

2.3.2 : Evaporation of Bitterns after the Removal of Sulphate with Calcium Chloride -

Bittern B.9 (120 litres) was treated with 4.4 kilograms of calcium chloride (equivalent to 96 per cent. of the sulphate present in the bittern) dissolved in 11 litres of water. The precipitate was allowed to settle overnight before the supernatent liquor (B.10) was decanted. The chemical analyses of the liquors and the precipitate are shown in Table 4.

TABLE 4.
PRECIPITATION WITH CALCIUM CHLORIDE.

Sample	Bittern Feed B.9		Precipitant $CaCl_2$	Product Liquor B.10		Ppt.	
Specific Gravity	1.228		-	1.207		-	
Volume, l.	120		11	122.2		-	
Weight, kg.	-		-	-		6.77	
Contents	g/l	Total Wt., g.	Total Wt., g.	g/l	Total Wt., g.	%	Total Wt., g.
Na	87.4	10,490	-	84.6	10,340	9.76	660
K	6.3	756	-	6.0	733	0.36	24
Mg	21.6	2,592	-	19.65	2,401	1.64	111
Ca	1.1	132	1,443	1.90	232	18.72	1,266
Cl	182.5	21,900	2,610	193.2	23,600	17.48	1,183
SO_4	30.2	3,624	-	4.05	495	46.32	3,134
Br	1.1	132	-	0.80	98	0.16	11

The bittern B.10 from the precipitation was used in the first stage of the evaporation. The results are given in Table 5.

TABLE 5.
EVAPORATION OF BITTERN AFTER REMOVAL OF SULPHATE WITH CALCIUM CHLORIDE
First Stage

Heating Time - 89 hours. Total Evaporation Time - 384 hours

Sample	Feed B.10		Product Liquor B.11		Product Salt B.11 Salt	
Specific Gravity	1.207		1.261		-	
Volume, l.	122.2		28.1		-	
Weight, kg.	-		-		31.30	
Contents	g/l	Total Wt. g.	g/l	Total Wt. g.	%	Total Wt. g.
Na	84.6	10,340	16.15	454	31.86	9,972
K	6.0	733	21.00	590	0.48	150
Mg	19.65	2,401	69.50	1,953	1.64	513
Ca	1.90	232	2.30	65	0.52	163
Cl	193.2	23,600	247.5	6,952	54.34	17,010
SO_4	4.05	495	2.25	63	1.24	388
Br	0.80	98	3.55	100	nil	nil

The bittern B.11 was transferred to the second pond and the evaporation was continued for a further 37 hours. Results are shown in Table 6.

A further quantity of liquor was drained from the salts over a period of several weeks. The salt which remained was designated B.12A. The chemical analysis of a sample of this salt is given in Table 7.

TABLE 6.
EVAPORATION OF BITTERNS AFTER REMOVAL OF SULPHATE WITH CALCIUM CHLORIDE.
Second Stage

Heating Time - 37 hours. Total Evaporation Time - 216 hours.

Sample	Feed B.11		Product Liquor B.12		Product Salt B.12 Salt	
Specific Gravity	1.261		1.334		-	
Volume, l.	28.1		9.7		-	
Weight, kg.	-		-		9.07	
Contents	g/l	Total Wt. g.	g /l	Total Wt. g.	%	Total Wt. g.
Na	16.15	454	1.60	16	5.70	517
K	21.00	590	0.75	7	5.31	482
Mg	69.50	1,953	114.0	1,106	8.00	726
Ca	2.30	65	4.10	40	0.53	48
Cl	247.5	6,952	339.3	3,291	37.31	3,384
SO_4	2.25	63	0.80	8	0.56	51
Br	3.55	100	6.65	65	0.35	32

TABLE 7.
CHEMICAL COMPOSITION - Salt B.12A

Contents	%
Na	5.70
K	6.08
Mg	8.17
Ca	0.28
Cl	37.7
SO_4	0.56
Br	0.31

2.3.3 : Evaporation of Bitterns after Removal of Sulphate with Lime -

The precipitating agent used in this experiment was "Limil" which contained free lime equivalent to 46.2 per cent. calcium. "Limil" equivalent to the sulphate was slurried with 10 litres of water and added to the bittern B.14 (120 litres). The precipitate which formed was bulky and difficulty was experienced in separating a clear liquor. The results are presented in Table 8.

TABLE 8.
PRECIPITATION WITH "LIMIL"

Sample	Bittern Feed B.14		Precipitant "Limil"	Ppt.		Product Liquor B.15	
Specific Gravity	n.d.		-	-		1.182	
Volume, l.	120		-	-		85	
Weight, kg.	-		3,500	62.4		-	
Contents	g/l	Total Wt., g.	Total Wt., g.	%	Total Wt., g.	g/l	Total Wt., g.
Na	88.0	10,560	-	5.68	3,544	83.6	7,106
K	6.55	786	-	0.44	274	6.4	544
Mg	22.60	2,712	-	3.06	1,909	12.7	1,080
Ca	nil	nil	1,782 (a)	2.84	1,772	2.5	212
Cl	172.5	20,700	-	11.86	7,400	165.0	14,030
SO_4	33.55	4,026	-	6.66	4,156	4.5	382
Br	1.55	186	-	0.10	62	1.5	127

n.d. = not determined
(a) = Total calcium

The liquor (B.15) was evaporated for a total heating time of 85 hours when the specific gravity increased to 1.265. The compositions of liquors and salts are given in Table 9.

TABLE 9.
EVAPORATION OF BITTERN AFTER REMOVAL SULPHATE WITH LIME
First Stage

Heating Time - 85 hours. Total Evaporation Time - 360 hours.

Sample	Feed B.15		Product Liquor B.16		Product Salt B.16 Salt	
Specific Gravity	1.182		1.265		-	
Volume, l.	85		8.5		-	
Weight, kg.	-		-		22.7	
Contents	g/l	Total Wt. g.	g/l	Total Wt. g.	%	Total Wt. g.
Na	83.6	7,106	18.2	155	29.3	6,650
K	6.4	544	25.1	213	1.29	293
Mg	12.7	1,080	69.5	591	2.15	488
Ca	2.5	212	4.3	37	0.71	161
Cl	165.0	14,030	251.0	2,134	51.81	11,760
SO_4	4.5	382	1.5	13	1.54	350
Br	1.5	127	7.6	65	0.26	59

The bittern from the first stage was evaporated for a total heating time of 48 hours when the specific gravity increased to a value of 1.324. The results are shown in Table 10.

TABLE 10.
EVAPORATION OF BITTERN AFTER REMOVAL OF SULPHATE WITH LIME
Second Stage

Heating Time - 48 hours. Total Evaporation Time - 216 hours

Sample	Feed B.16		Product Liquor B.17		Product Salt B.17 Salt	
Specific Gravity	1.265		1.324		-	
Volume, l.	8.5		3.8		-	
Weight, kg.	-		-		2.18	
Contents	g/l	Total Wt. g.	g/l	Total Wt. g.	%	Total Wt. g.
Na	18.2	155	2.6	10	6.44	140
K	25.1	213	1.5	6	9.20	201
Mg	69.5	591	106.3	404	7.72	168
Ca	4.3	37	6.9	26	0.38	8
Cl	251.0	2,134	293.3	1,114	38.9	848
SO_4	1.5	13	0.8	2	0.58	13
Br	7.6	65	13.7	52	0.58	13

2.4 Discussion

2.4.1 : Preparation of Enriched Salts -

2.4.1.1 - Precipitation :

The sulphate concentration of bittern B.9 was slightly greater than that of bittern B.6 although both were received at the same time. In consequence the calcium chloride added was equivalent to only 96 per cent. of the sulphate. About 86 per cent. of the sulphate was removed in the precipitate. Since the precipitate was not washed, 4 to 6 per cent. of the original salts were lost. The precipitate settled rapidly and retained only 7 per cent. of the liquid volume even though the supernatant liquor was removed by decantation.

The theoretical amount of lime was added to the second precipitation and 92 per cent. of the sulphate was removed. Owing to the gelatinous nature of the magnesium hydroxide which precipitated with the gypsum, one third of the total soluble salts were retained in the precipitate. By washing the precipitate a further quantity of salts should be recoverable but this would be difficult because of the slimy nature of the precipitate. Although lime is cheaper than calcium chloride the greater hold up of liquor in the precipitate and the fact that the gypsum would not be saleable because of the presence of magnesia, would discourage its use as a precipitant.

Owing to the low overall recovery of the potassium, the cost of either precipitating agent per unit of recovered potassium salts would be high. In fact, it is unlikely that either precipitant could be used economically even if all of the potassium salts could be recovered as a saleable product from the liquor remaining after the removal of the sulphate.

2.4.1.2 - Evaporation :

The bitterns used in these experiments had a lower salt concentration than in bittern B.1, used previously, hence longer evaporation times were required to reach the desired specific gravity.

The salts were not washed as in the earlier work because it was expected that the flotation tests would be carried out using the final bittern as the aqueous medium. When due allowance is made for this difference the results are in general agreement with those of the previous smaller scale investigations. The crude sodium chloride produced by the first stage of evaporation could be redissolved in fresh sea water prior to the normal solar evaporation for the recovery of common salt. This would reduce the loss of potassium and would increase the normal yield of solar salt.

Attempts were made by officers of the Mineralogical Section to determine the nature of the individual salts present in the products. The lack of published data and the complex nature of the salts have so far prevented any definite identification of the salts.

2.4.2 : Flotation -

The results of the flotation investigations are reported fully in the Appendix. Difficulty was experienced in technique and the results were not promising. The work was also hampered by the lack of information regarding the nature of the salts present in products. It seems unlikely that a flotation process could be used on such a complex material.

3. CONTINUOUS ION EXCHANGE.

Previous investigations (Moyle, 1958) have shown that in theory, potassium can be recovered from salt bitterns in a continuous ion exchange column. However, high reflux ratios would be required because of the relatively low concentration of potassium in the bitterns. It was suggested that by using the enriched salts obtained by evaporation of the bittern, a higher grade feed solution would be used and more favourable operating conditions would result.

Two types of enriched salt were produced in the experiments described in Section 2. The composition of these was as follows :-

	Enriched Salts	
Sample	B.8	B.12A
Chemical Composition	%	%
Na	7.38	5.70
K	3.44	6.08
Mg	8.56	8.17
Ca	nil	0.28
Cl	27.76	37.7
SO_4	16.10	0.56
Br	0.32	0.31

Hence two different types of feed solution could be used, namely one containing both chloride and sulphate anions and one containing essentially only chloride anions. The following experiments were concerned with the separation of potassium from solutions containing only chloride anions. Equilibrium curves have been obtained and operating conditions calculated for the separation of potassium from sodium and from magnesium.

A major difficulty with the prediction of the operating conditions in the main exchanger for any combination of cations is that the graphical method cannot be used when more than two cations are involved. The operating conditions could be obtained by calculation if the equilibrium resin loadings could be predicted from the aqueous concentrations. An attempt has been made to give a method for determining resin loadings when three cations are involved. The results are given in Appendix 2.

3.1 Experimental Procedure

3.1.1 : Feed Concentration -

In the absence of sulphate anions the maximum allowable concentration of total cations was higher than for mixed chloride sulphate solutions. A concentration of 3.5 gram equivalents of total cations per litre was used.

3.1.2 : Equilibrium Experiments -

Two series of experiments were carried out; the first in which only sodium and potassium were present and the second in which only magnesium and potassium were present. The experimental procedure was identical with that of previous equilibrium experiments (Moyle, 1958).

Potassium form Dowex 50 resin was used in all experiments.

3.1.3 : Product Feed and Waste Concentrations -

Product Concentration

The product concentration was set at 0.90 equivalent fraction potassium as in previous experiments.

Feed Concentration

For Salt B.12A the feed composition would be as follows :-

Na = 0.228 equivalent fraction
K = 0.143 " "
Mg = 0.629 " "
(calcium calculated as magnesium)

A feed flowrate of 6.99 gram equivalents per unit time would be required for a recovery of 90 per cent. of the potassium and production of one gram equivalent of product per unit time.

Waste Concentration

Assuming a 90 per cent. recovery of the potassium, the waste concentration would be 0.017 equivalent fraction of potassium and the waste flowrate would equal 5.99 gram equivalents of total cations per unit time.

3.2 Results

3.2.1 : Separation of Potassium from Sodium -

Solutions containing 3.5 gram equivalents of sodium and potassium chlorides were used in the experiments. The results which are shown in Table 11 gave a straight line logarithmic plot which corresponded to the following relationship :-

$$\frac{X_R^{K^+}}{X_R^{Na^+}} = 1.403 \left(\frac{X_S^{K^+}}{X_S^{Na^+}} \right)^{0.940}$$

where R and S refer to resin and solution phases respectively and X^{K^+} and X^{Na^+} represent equivalent fractions of K^+ and Na^+.

The above equation was used to calculate the concentration of potassium in the resin corresponding to each of the aqueous concentrations. The calculated values together with the differences between calculated and determined concentrations are shown in Table 11.

TABLE 11.
SEPARATION OF POTASSIUM FROM SODIUM

Total Cations = 3.5 g-equiv/l. Chloride = 3.5 g-equiv/l.

TEST	- AQUEOUS Eq. Fraction Na	K	m. eq. per g. Dry H^+ Resin Total Cations	- RESIN - Eq. Fraction Na	K	Calculated K	Diffce.
28	0.893	0.107	6.52	0.848	0.152	0.160	- 0.008
29	0.792	0.208	6.58	0.717	0.283	0.285	- 0.002
30	0.693	0.307	6.42	0.606	0.394	0.395	- 0.001
31	0.544	0.456	6.12	0.453	0.547	0.543	+ 0.004
32	0.444	0.556	6.17	0.371	0.629	0.643	- 0.005
33	0.296	0.704	6.26	0.241	0.759	0.760	- 0.001
34	0.197	0.803	6.16	0.153	0.847	0.840	+ 0.007
35	0.098	0.902	6.30	0.083	0.917	0.919	- 0.002
			AVGE. :6.32			R.M.S.	± 0.005

The operating conditions necessary to give the required separation of potassium from sodium were obtained graphically from the equilibrium curve (Figure 1) which was determined by the above equation. The results are presented in Table 12.

TABLE 12.
OPERATING CONDITIONS
SEPARATION OF POTASSIUM FROM SODIUM.

3.5 g-equiv. total Cations/litre.

Reflux, %	ENRICHING SECTION		STRIPPING SECTION		Total No. Theoretical Stages
	R	Theoretical Stages below Feed Stage	Reflux, %	Theoretical Stages above Feed Stage	
91.7 (a)	11.05	infinite	61.2	infinite	infinite
95	19	15	77.0	7.5	23.5
97	32.33	14	84.8	4.8	19.8
100 (b)	infinite	12	100	3.8	16.8

(a) minimum reflux
(b) minimum no. of stages.

3.2.2 : Separation of Potassium from Magnesium -

The solutions of potassium and magnesium chlorides used in these experiments contained 3.5 gram equivalents of total cations per litre. The straight line through the points of the logarithmic plot is represented by the following equation :-

$$\frac{X_R^{K^+}}{X_R^{Mg^{++}}} = 1.64\left(\frac{X_S^{K^+}}{X_S^{Mg^{++}}}\right)^{0.890}$$

The experimental results together with the potassium resin loadings calculated from the above equation are shown in Table 13.

TABLE 13.

SEPARATION OF POTASSIUM FROM MAGNESIUM

Total Cations = 3.5 g-equiv/l.   Chloride = 3.5 g-equiv/l.

TEST	AQUEOUS Eq. Fraction Mg	AQUEOUS Eq. Fraction K	m. eq. per g. Dry H+ resin Total Cation	RESIN Eq. Fraction Mg	RESIN Eq. Fraction K	RESIN Eq. Fraction Calculated K	Diffce.
25	0.892	0.108	6.53	0.802	0.198	0.200	- 0.002
26	0.792	0.208	6.27	0.671	0.329	0.332	- 0.003
27	0.693	0.307	6.15	0.561	0.439	0.442	- 0.003
28	0.543	0.457	6.19	0.422	0.578	0.584	- 0.006
29	0.444	0.556	6.31	0.334	0.666	0.666	0
30	0.295	0.705	6.30	0.219	0.781	0.780	+ 0.001
31	0.197	0.803	6.13	0.148	0.852	0.851	+ 0.001
32	0.098	0.902	6.20	0.079	0.921	0.922	- 0.001
		AVGE. :	6.26			R.M.S.	± 0.003

The operating conditions for the required separation of potassium from magnesium were determined graphically from the equilibrium curve (Figure 2) and are shown in Table 14.

TABLE 14.
SEPARATION OF POTASSIUM FROM MAGNESIUM

Total Cations 3.5 g-equiv/l.

Reflux, %	ENRICHING SECTION		STRIPPING SECTION		Total No. Theoretical Stages
	R	Theoretical Stages below Feed Stage	Reflux, %	Theoretical Stages above Feed Stage	
86.0	6.14	infinite	54.4	infinite	infinite
90.0	9	12	62.5	5.1	18.1
94.0	15.67	10	73.6	3.4	14.4
97.0	32.33	9	84.8	2.5	12.5
100.0	infinite	8	100.0	2.4	11.4

(a) minimum reflux
(b) minimum no. of theoretical stages

3.3 Discussion

3.3.1 : Separation of Potassium from Sodium -

The equilibrium curve was very similar to all previous curves obtained for this separation. It is apparent that the concentration of total cations has little effect on the shape of the curve and that similar results are obtained for both chloride and sulphate solutions. The smaller minimum reflux of 92 per cent. was due to the increased concentration of potassium in the feed liquor.

3.3.2 : Separation of Potassium from Magnesium -

An even greater improvement was found for this separation. A minimum reflux of only 86 per cent. was sufficient. This was due in part to the increased separation at the higher concentration of 3.5 gram equivalents of total cations per litre and in part to the greater relative concentration of potassium in the feed solution.

3.3.3 : Separation of Potassium from Enriched Salts -

It is not possible to predict the operating conditions necessary to separate potassium from a solution of enriched salts obtained by the evaporation of bitterns after the removal of sulphate. However it is certain that less severe conditions would be required than were found necessary for the recovery of potassium directly from bitterns. It should be noted also that the salt B.12A could be washed to remove entrained liquor before entering the ion exchange process. This would remove mainly magnesium chloride and would increase the concentration of potassium in the feed solution. Hence better separations would be obtained than are apparent from the results given above.

No investigations were carried out on the separation of potassium from enriched salts produced by the direct evaporation of the bitterns. Lower feed concentrations than were used in the above investigations would have to be employed because of the presence of sulphate in the enriched salts. An improvement on previous operating conditions should result since the potassium concentration in the feed would still be higher. It was considered that the determination of equilibrium curves for this separation were not warranted at this stage.

4. LEACHING.

The investigations were confined to salt B.12A which contained essentially only chloride anions. Three types of leaching were investigated, namely, water leaching at room temperature, water leaching at elevated temperatures and magnesium chloride leaching at elevated temperatures.

4.1 Experimental Procedure and Results

4.1.1 : Room Temperature Water Leaching -

A weighed sample of the salt was stirred with a measured volume of water until the pulp had reached equilibrium. The undissolved salt was filtered without washing and sucked as dry as possible on a Büchner funnel. Both the salt and the final liquor were analysed to give the distribution of the various constituents. The results are presented in Tables 15 and 16.

TABLE 15.
ROOM TEMPERATURE WATER LEACHING.

160 g. B.12A with 110 ml. H_2O

Sample	Undissolved Salt		Liquor
Wt., g.	26 (wet)		–
Volume, ml.	–		192
Contents	**Wt., g.**	**% of Total**	**Wt., g.**
Na	4.89	54	4.25
K	4.20	43	5.52
Mg	0.28	2	12.70
Ca	0.10	21	0.38
Cl	11.8	20	48.4
SO_4	0.25	28	0.64
Br	0.03	6	0.46

TABLE 16.
ROOM TEMPERATURE WATER LEACHING.

149 g. B.12A with 55 ml. H_2O

Sample	Undissolved Salt		Liquor
Wt., g.	57 (wet)		–
Volume, ml.	–		114
Contents	**Wt., g.**	**% of Total**	**Wt., g.**
Na	7.29	86	1.17
K	6.8	75	2.28
Mg	2.8	23	9.46
Ca	0.23	59	0.16
Cl	25.3	45	31.0
SO_4	0.59	70	0.25
Br	0.10	22	0.36

4.1.2 : Elevated Temperature Water Leaching -

A weighed sample of B.12A was stirred with a measured volume of water at 95°C until no more salt dissolved. The solution was filtered rapidly through a preheated Büchner funnel and the salt sucked dry. The undissolved salt was designated "First Salt". The filtrate was allowed to cool overnight and the salt which crystallized was filtered and sucked dry. This was designated "Second Salt". The two salts and the final filtrate were assayed to determine the distribution of the various components. The results are presented in Tables 17 and 18.

TABLE 17.
ELEVATED TEMPERATURE WATER LEACHING

150 g. B.12A with 80 ml. H_2O

Sample	"First Salt"		"Second Salt"		Filtrate	
Wt., g. (Wet)	12		14		–	
Volume, ml.	–		–		N.D.	
Contents	Wt., g	%	Wt., g	%	Wt., g	%
Na	4.34	54	1.68	21	2.07	25
K	0.29	3	5.05	58	3.41	39
Mg	0.46	4	0.23	2	11.81	94
Ca	0.11	24	0.04	9	0.30	67
Total halides	8.08	14	7.92	14	40.06	72
SO_4	0.26	29	0.07	8	0.57	63

N.D. = not determined

TABLE 18.
ELEVATED TEMPERATURE WATER LEACHING

150 g. B.12A with 65 ml. H_2O

Sample	"First Salt"		"Second Salt"		Filtrate	
Wt., g. (Wet)	20		37		–	
Volume, ml.	–		–		112	
Contents	Wt., g	%	Wt., g	%	Wt., g	%
Na	5.7	69	1.44	17	1.10	14
K	0.57	7	5.9	69	2.08	24
Mg	0.68	5	2.68	22	9.05	73
Ca	0.15	42	0.10	28	0.11	30
Total halides	10.95	20	15.05	27	29.6	53
SO_4	0.34	42	0.23	28	0.24	30

4.1.3 : Elevated Temperature Magnesium Chloride Leaching –

The experimental procedure was similar to that used in 4.1.2 with the exception that a 20 per cent. w/v solution of magnesium chloride was used instead of water. The results are given in Table 19.

TABLE 19.
ELEVATED TEMPERATURE MAGNESIUM CHLORIDE LEACHING

150 g. B.12A with 100 ml. 20% $MgCl_2$ solution

Sample	"First Salt"		"Second Salt"		Filtrate	
Wt., g. (Wet)	18		55		–	
Volume, ml.	–		–		122	
Contents	Wt., g.	%	Wt., g.	%	Wt., g.	%
Na	5.45	71	1.41	19	0.77	10
K	0.37	4	7.09	85	0.89	11
Mg (a)	0.65	4	4.86	28	11.64	68
Ca	0.10	20	0.16	32	0.24	48
Total Halides (a)	10.56	15	22.42	33	35.65	52
SO_4	0.27	30	0.35	39	0.28	31

(a) including magnesium and chloride from original solution

4.2 Discussion

4.2.1 : Room Temperature Leaching -

Under favourable conditions the magnesium could be removed, but only at the expense of over 50 per cent. of the potassium. This loss of potassium is probably sufficient to eliminate this method of treatment for magnesium removal prior to potassium-sodium separation.

4.2.2 : Elevated Temperature Leaching -

The procedure employed was similar in principle to that used in the recovery of potassium chloride from mixtures containing sodium chloride and carnallite. The magnesium content of salt B.12A was higher than that of the usual mixtures for which the process was designed. Hence two experiments were carried out using water instead of magnesium chloride solution.

Most of the magnesium was recovered in the filtrate. The procedure was not so successful in separating the sodium and even under the more favourable conditions the product contained a considerable proportion of sodium chloride. Only one half of the potassium would be recovered in a magnesium free product. Most of the remaining potassium was present in the filtrate. Further amounts of potassium could be recovered by evaporating the filtrate and combining the salt which crystallized with the feed for the next leach.

In view of the presence of the sodium salts in the product and the need for several treatments to recover a major proportion of the potassium, it is unlikely that any successful process could be based on this type of leaching.

5. HYDROLYSIS OF MAGNESIUM CHLORIDE.

The hydrolysis of magnesium chloride with steam to yield hydrochloric acid and magnesia has been known for many years and patents have been taken out for processes utilizing this reaction$^{(1)}$. The following experiments were carried out to determine whether the magnesium salts could be removed by this means from the mixed salts.

5.1 Experimental Procedure

Samples of salt were hydrolysed in a 30 inch silica tube inside a horizontal electrically heated tube furnace. One end of the silica tube was packed with porcelain beads to preheat the steam. Suitable gas tight connections were made to allow the continuous passage of steam over the sample and the collection in water of the hydrogen chloride produced. The amount of acid produced was determined by titration of the water solution with standard sodium hydroxide solution. The temperature of the furnace was measured with a chromel-alumel thermocouple which was inserted between the furnace lining and the silica reaction tube.

5.2 Results

5.2.1 : Effect of Temperature -

Samples of B.12A and magnesium chloride hexahydrate were heated separately in the furnace with an excess of steam. The temperature of the furnace was increased in steps of 50°C allowing fixed periods of time at each temperature. The quantities of hydrochloric acid evolved at each temperature per gram of original salt are shown in Table 20.

TABLE 20.
EVOLUTION OF HYDROGEN CHLORIDE

Sample	B.12A	B.12A(a)	$MgCl_2 . 6H_2O$
Time at each Temperature, mins.	60	30	30
Hydrogen Chloride mg/g. of Salt Temperature, °C.			
200	12.8	4.0	8.0
250	30.3	8.4	48.9
300	27.4	41.2	102.9
350	28.1	27.4	19.3
400	19.3	18.2	21.5
450	93.1	51.1	65.0
500	5.1	55.5	45.3
550	nil	2.2	0.7
Total Hydrogen Chloride mg/g. Salt	216.1	208.0	311.6

(a) dried at 120°C for several hours.

5.2.2 : Product Composition -

Samples of Salts B.12A and B.8 (16 g. and 10 g. respectively) were hydrolysed at 500°C with an excess of steam until the evolution of hydrochloric acid was negligible. The cooled residues were extracted with water and filtered to remove the insoluble magnesium hydroxide precipitate. The clear solutions were analysed to give the results shown in Table 21.

TABLE 21.

Sample	B.12A	B.8
Weight, g.	16	10
Water Extract, g/l.		
Na	1.70	1.07
K	1.60	0.56
Mg	0.02	0.18
Ca	0.04	n.d.
Total halides	3.96	1.05
Sulphate	0.13	2.34

n.d. = not determined

5.3 Discussion

5.3.1 : Effect of Temperature -

No appreciable difference was found in the hydrolysis of the magnesium chloride in Salt B.12A and in the hexahydrate. The hydrochloric acid was evolved in two stages from both salts. Approximately one half of the acid was collected below 400°C and the remainder between 400 and about 500°C.

5.3.2 : Product Composition -

Approximately 99 per cent. of the magnesium chloride in Salt B.12A was hydrolysed and only a trace of magnesium remained in the water extract. Only 86 per cent. of the magnesium was removed from Salt B.8, indicating that at least 14 per cent. of the magnesium was present as sulphate. Although the major portion of the magnesium was hydrolysed, that remaining was equal to one third of the weight of the potassium. In both experiments all of the sodium was recovered with the potassium. The magnesium in Salt B.12A could be almost completely removed by hydrolysis as a preliminary step in the recovery of a saleable potassium salt. The economics of such a process are doubtful and would depend on suitable markets for dilute hydrochloric acid and magnesium oxide and on a suitable and cheap method of recovering the potassium from the sodium-potassium chloride water extract.

6. CONCLUSIONS.

It is unlikely that any of the methods which have been investigated could be economically applied to the separation and recovery of potassium from bitterns.

Previous investigations (Moyle, 1957, 1958), have shown that evaporation of the bitterns was the only means of separating the potassion which showed promise but only an enriched salt was produced. Further treatment would be necessary to obtain a satisfactory product. It is unlikely that any of the methods of treating the enriched salt which have been considered in this report would be economically feasible.

The complex nature of salt bitterns introduces many difficulties and methods which have been successfully applied to less complex starting materials are not suitable. Since most of the imported potassium salts are produced from deposits of carnallite and sylvite by simple and cheap processes any competing process based on bitterns must also be cheap. Although several of the methods investigated were capable of producing potassium salts it is unlikely that any of them could produce the required product at a sufficiently low market price to compete with the imported materials. It is considered that further investigation of this project is not warranted at present.

7. LITERATURE REFERENCES.

Moyle, F.J. R.D. 69 - Part One (1957)

Moyle, F.J. R.D. 69 - Part Two (1958)

(1) Australian Patent Application No. 21899 - 26th September, 1956.

APPENDIX 1 .. FLOTATION OF POTASSIUM SALTS

Flotation investigations were carried out in the Metallurgical Section, in an endeavour to concentrate the potassium from enriched salts produced by the treatment of salt bitterns.

1.1 Material Examined

The two samples labelled B.8 and B.12 each contained a mixture of salts. Chemical analyses of the salts and their corresponding mother liquors are shown in Table 22. Sample B.12 was almost sulphate free and hence should contain fewer complex salts than B.8 and be more amenable to flotation concentration. For this reason B.12 only was used in these investigations.

TABLE 22.
CHEMICAL ANALYSES OF SAMPLES B.8 and B.12

Sample	B.8		B.12	
Contents	Salt %	Liquor g/1.	Salt %	Liquor g/1.
Na	7.38	3.55	5.70	1.60
K	3.44	1.80	6.08	0.75
Mg	8.56	115.0	8.17	114.0
Ca	–	–	0.28	4.10
Cl	27.76	309.6	37.7	339.3
SO_4	16.10	39.4	0.56	0.80
Br	0.32	8.50	0.31	6.65

1.2 Equipment

A 50 gram Fagergren flotation cell was used for all experiments.

1.3 Experimental Procedure

The required amount of the enriched salts was mixed with mother liquor in the flotation cell. The flotation reagents, dissolved in water, were added and the pulp was thoroughly agitated. Air was then blown into the cell and the froth was removed continuously, until no more concentrate could be recovered.

1.4 Results

Two preliminary experiments were carried out using a cationic type collector (Armac H.T.D.) and a frother (Dow 250).

The first was carried out on the material as received but in the second the salts were ground with a pestle and mortar in contact with the mother liquor before flotation. The results are shown in Table 23.

TABLE 23.
PRELIMINARY FLOTATION INVESTIGATIONS

Test	Fraction	Weight, %	Potassium, %	Distribution
1	Conc.	29	12.1	27.6
	Tail	71	8.1	62.4
	Feed	100	9.3	100.0
2	Conc.	58	10.7	62.0
	Tail	42	9.1	38.0
	Feed	100	10.0	100.0

Differences between the amounts of salt placed in the cell at the beginning of the experiment and the sum weight of the fractions recovered were noted. All calculations were made on the weight of fractions recovered.

Three tests were carried out to determine the effectiveness of certain reagents which have been successfully used with other mixtures of soluble salts(2). The conditions under which the experiments were carried out are shown in Table 24.

TABLE 24.
CONDITIONS OF FLOTATION

Test	Reagents	Amounts of Reagents
3	Anionic collector (Sodium Lauryl Sulphate)	1 lb/ton
	Lead nitrate	1 lb/ton
	Pine oil	as required
	To float NaCl	
4	Cationic Collector (Armac 16 D)	0.8 lb/ton
	Fuel oil	1.5 lb/ton
	Pine oil	as required
	To float KCl and Carnallite	
5	Cationic Collector (Armac 16 D)	0.8 lb/ton
	Lead nitrate	1.0 lb/ton
	Pine oil	as required
	To float NaCl	

The results appear in Table 25.

TABLE 25.
FLOTATION RESULTS

Test No.	Fraction	Weight, %	Potassium, %	Distribution, %
3	Conc.	11.3	11.6	14.6
	Tail	88.7	8.6	85.4
	Feed	100.0	8.9	100.0
4	Conc.	10.7	10.3	12.0
	Tail	89.3	9.0	88.0
	Feed	100	9.2	100.0
5	Conc.	36.0	11.5	50.5
	Tail	64.0	6.3	49.5
	Feed	100.0	8.2	100.0

The results obtained in experiment 5 were unexpected and this test was repeated under the same conditions and also after light grinding of the feed with a pestle and mortar prior to flotation. The results are given in Table 26. In the latter test a much improved froth and a large increase in the amount of salts floating were found. This was repeated to see if accidental contamination during grinding had altered the flotation characteristics. However, the same effect was noted in the repeat experiment.

TABLE 26.
FLOTATION RESULTS

Test No.	Fraction	Weight, %	Potassium, %	Distribution, %
6 no grinding	Conc.	17.8	10.4	17.6
	Tail	82.2	10.5	82.4
	Feed	100.0	10.5	100.0
7 light grinding	Conc.	80.8	10.7	82.6
	Tail	19.2	9.5	17.4
	Feed	100.0	10.5	100.0

1.5 Discussion

Flotation did not produce any appreciable concentration of the potassium. Anionic and cationic reagents(2) similar to those which have been used elsewhere to float both potassium and sodium salts were tried. A slight increase in potassium grade was found in the concentrates from all experiments including those expected to float the sodium salts. Slight grinding resulted in the production of a voluminous froth which carried a large proportion of the material into the concentrate. This indicated the necessity of sizing the feed. However, sizing by conventional means would possibly result in contamination from screens etc. Hydraulic sizing would be more satisfactory but the small amount of mother liquor available made this method impracticable. The calculated feed grade in all experiments was higher than that reported for the original salt. This was probably due to the difficulties of weighing the hygroscopic salts accurately and the re-solution of some of the magnesium salts during flotation.

1.6 Conclusions

No appreciable concentration of the potassium salts was obtained in any of the experiments. Since the reagents tried were similar to those which have been used successfully elsewhere to float both potassium and sodium salts it would appear that the Salt B.12A is not amenable to concentration by flotation.

APPENDIX 2 .. CONTINUOUS ION EXCHANGE

Potassium resin loadings were presented in part two of this report for solutions containing sodium potassium and magnesium ions for the particular case in which the magnesium to sodium ratio in the solution was kept at unity. As was expected the loadings lay between those found for solutions containing potassium and sodium and potassium and magnesium respectively. It was noted that in all instances the loadings were almost exactly half way between the two values. It is suggested that for other magnesium to sodium ratios the potassium loading would also lie between the two values and would be linearly dependent on the ratio of the sodium to magnesium provided that the total cation concentration was kept constant. This assumes that the sodium and magnesium do not interact but compete for the resin sites in proportion to their concentrations.

The following investigations were undertaken to show whether the above assumption was valid. Resin loadings calculated from equilibrium curves obtained for solutions containing sodium and potassium, magnesium and potassium, and sodium and magnesium ions were compared with experimentally determined values. Also equilibrium aqueous concentrations were calculated from resin loadings and compared with experimental values.

2.1 Materials

2.1.1 : Resin -

Dowex 50 resin screened to -18, +25 mesh was used in all of the experiments.

2.1.2 : Aqueous Solutions -

Synthetic stock solutions were prepared from "Analar" grade salts and these were mixed in measured quantities to obtain the desired liquor compositions.

2.2 Experimental Procedure

The procedure used was similar to that of all previous work (Moyle, 1957, 1958).

2.3 Results

2.3.1 : Sodium-Magnesium Separation –

The equilibrium curve for the separation of sodium and magnesium at a concentration of 2.1 gram equivalents of total cations per litre had not been included in previous work. In order to calculate results it was necessary therefore to obtain this curve. The results are given in Table 27 and the equilibrium curve is shown in Figure 3. The equilibrium curve at 1.2 gram equivalents of total cations per litre is included for comparison. The logarithmic plot corresponded to the following equation :

$$\frac{X_R^{Mg^{++}}}{X_R^{Na^+}} = 1.064\left(\frac{X_S^{Mg^{++}}}{X_S^{Na^+}}\right)^{1.067}$$

where R and S represent resin and solution phases and X^{Na^+} and $X^{Mg^{++}}$ represent equivalent fractions of Na^+ and Mg^{++}.

TABLE 27.
SEPARATION OF SODIUM AND MAGNESIUM

Total Cations = 2.1 g-equiv. per litre
Cl to SO_4 ratio = 5

TEST	AQUEOUS		RESIN	
	Na	Mg	Na	Mg
5	0.115	0.885	0.108	0.892
6	0.214	0.786	0.192	0.808
7	0.312	0.688	0.281	0.719
8	0.459	0.541	0.438	0.562
9	0.557	0.443	0.559	0.441
10	0.705	0.295	0.693	0.307
11	0.803	0.197	0.806	0.194
12	0.901	0.099	0.914	0.086

2.3.2 : Calculation of Resin Loadings from Aqueous Concentrations –

The experiments were carried out at both 1.2 and 2.1 gram equivalents of total cations per litre. All three cations were present in varying amounts. The resin loadings were calculated from the previously determined equilibrium curves, as follows :-

Aqueous equilibrium concentration for 1.2 gram equivalents total cations per litre.

K = 0.121 equivalent fraction
Mg = 0.096 " "
Na = 0.783 " "

From the potassium magnesium curve the potassium resin loading for an aqueous concentration of 0.121 equivalent fraction potassium = 0.178

From the potassium sodium curve the potassium resin loading for an aqueous concentration of 0.121 equivalent fraction potassium = 0.184

Difference = 0.006

$$\text{Ratio } \frac{\text{magnesium (aqueous)}}{\text{magnesium} + \text{sodium (aqueous)}} = \frac{96}{879} = 0.109$$

Therefore calculated loading is

$$\begin{aligned} &= 0.184 - 0.109 \times 0.006 \\ &= 0.184 - 0.0006 \\ &= \underline{0.183} \end{aligned}$$

The magnesium and sodium values were calculated from the readings obtained from the appropriate equilibrium curves. The experimentally determined and calculated values for the resin loadings are shown in Tables 28 & 29.

TABLE 20.

CALCULATED vs. DETERMINED RESIN LOADINGS

Total Cations = 1.2 g-equiv. per litre.

TEST	SODIUM			MAGNESIUM			POTASSIUM			TOTAL LOADING
	Equivalent fraction			Equivalent fraction			Equivalent fraction			Equivalent fraction
	Calc.	Detd.	Diffce, %	Calc.	Detd.	Diffce, %	Calc.	Detd.	Diffce, %	Calc.
35	0.703	0.685	+ 3	0.129	0.128	+ 1	0.183	0.187	- 2	1.015
36	0.490	0.486	+ 1	0.354	0.331	+ 7	0.188	0.183	+ 3	1.032
4	0.365	0.342	+ 7	0.467	0.451	+ 4	0.204	0.207	- 1	1.036
37	0.071	0.073	- 3	0.764	0.748	+ 2	0.185	0.179	+ 3	1.020
38	0.485	0.475	+ 2	0.125	0.122	+ 2	0.413	0.403	+ 3	1.023
6	0.271	0.248	+ 9	0.350	0.341	+ 3	0.414	0.411	+ 1	1.035
39	0.144	0.141	+ 2	0.497	0.492	+ 1	0.391	0.367	+ 7	1.032
40	0.071	0.069	+ 3	0.564	0.562	+ 1	0.384	0.369	+ 4	1.019
41	0.190	0.206	- 8	0.053	0.053	0	0.768	0.741	+ 4	1.011
42	0.145	0.160	- 9	0.117	0.120	- 3	0.756	0.720	+ 5	1.018
10	0.115	0.106	+ 8	0.142	0.152	- 7	0.762	0.742	+ 3	1.019
43	0.029	0.032	- 9	0.257	0.275	- 7	0.723	0.693	+ 4	1.009
44	0.057	0.066	- 14	0.028	0.028	0	0.921	0.906	+ 2	1.006
13	0.040	0.038	+ 5	0.036	0.033	+ 9	0.930	0.929	+ 1	1.006
45	0.029	0.034	- 14	0.074	0.077	- 4	0.903	0.889	+ 2	1.006
46	0.014	0.018	- 22	0.093	0.099	- 6	0.896	0.883	+ 2	1.003

TABLE 29.

CALCULATED vs. DETERMINED RESIN LOADINGS

Total Cations = 2.1 g-equiv. per litre

TEST	SODIUM			MAGNESIUM			POTASSIUM			TOTAL LOADING
	Equivalent fraction			Equivalent fraction			Equivalent fraction			Equivalent fraction
	Calc.	Detd.	Diffce, %	Calc.	Detd.	Diffce, %	Calc.	Detd.	Diffce, %	Calc.
23	0.768	0.754	+ 2	0.090	0.098	- 8	0.150	0.148	+ 1	1.008
24	0.578	0.566	+ 2	0.287	0.281	+ 2	0.155	0.153	+ 1	1.020
15	0.410	0.400	+ 3	0.434	0.420	+ 3	0.183	0.180	+ 1	1.027
25	0.096	0.100	- 4	0.743	0.737	+ 1	0.165	0.163	+ 1	1.004
26	0.533	0.540	- 1	0.090	0.087	+ 3	0.389	0.373	+ 4	1.012
17	0.295	0.284	+ 4	0.314	0.308	+ 2	0.416	0.408	+ 2	1.025
27	0.180	0.165	+ 9	0.444	0.434	+ 2	0.397	0.401	- 1	1.021
28	0.095	0.098	- 3	0.521	0.510	+ 2	0.399	0.392	+ 2	1.015
29	0.216	0.210	+ 3	0.036	0.037	- 3	0.755	0.753	+ 1	1.007
30	0.170	0.171	- 1	0.087	0.086	+ 1	0.754	0.743	+ 2	1.011
20	0.117	0.111	+ 6	0.126	0.132	- 5	0.769	0.757	- 1	1.012
31	0.046	0.042	+ 10	0.210	0.214	- 2	0.752	0.744	+ 1	1.008
32	0.077	0.083	- 7	0.020	0.019	+ 5	0.908	0.898	+ 1	1.005
22	0.040	0.036	+ 11	0.044	0.041	+ 7	0.919	0.923	- 1	1.003
33	0.047	0.043	+ 9	0.053	0.055	- 4	0.905	0.902	+ 1	1.005
34	0.030	0.029	+ 3	0.069	0.070	- 2	0.905	0.901	+ 1	1.004

2.3.3 : Calculation of Aqueous Concentrations from Resin Loadings -

The measured resin loadings for each experiment were used to calculate the aqueous equilibrium concentrations by a similar method. The calculated results for both 1.2 and 2.1 gram equivalents of total cations per litre gave similar agreement to the results shown in Tables 28 & 29 in all respects.

2.3.4 : Calculation of Theoretical Stages -

As a further test of the assumption the equilibrium concentrations of sodium, potassium and magnesium in the main exchanger were calculated for the separation of potassium from bittern B.1. The following assumptions were made :-

(a) 90 per cent. of the potassium was recovered in the product

(b) the product contained 0.91 equivalent fraction potassium

(c) the reflux in the enriching section equalled 98 per cent.

Several ratios of sodium to magnesium in the product were tried until the calculated composition of the aqueous solution in the feed stage equalled that of bittern B.1. The composition of the waste solution was calculated from a material balance, and this value was used in calculating the stage compositions of the stripping section. The results are presented in Table 30. In each stage the calculated values were adjusted to give a total equivalent fraction of unity.

TABLE 30.

CALCULATED STAGE COMPOSITIONS

Expressed as Equivalent Fractions*

STAGE	ENRICHING						STRIPPING					
	AQUEOUS			RESIN			AQUEOUS			RESIN		
	Na	Mg	K	Na	Mg	K	Na	Mg	K	Na	Mg	K
1	0.034	0.070	0.896	0.028	0.062	0.910	0.510	0.486	0.004	0.495	0.496	0.009
2	0.042	0.080	0.878	0.034	0.070	0.896	0.500	0.493	0.007	0.481	0.503	0.016
3	0.051	0.089	0.860	0.042	0.080	0.878	0.490	0.498	0.012	0.470	0.505	0.025
4	0.063	0.104	0.833	0.051	0.088	0.861	0.483	0.499	0.018	0.460	0.504	0.036
5	0.079	0.121	0.800	0.062	0.103	0.835	0.476	0.498	0.026	0.451	0.500	0.049
6	0.100	0.144	0.756	0.078	0.120	0.802	0.470	0.495	0.035	0.441	0.495	0.064
7	0.127	0.171	0.702	0.099	0.142	0.759	0.463	0.492	0.045	0.435	0.485	0.080
8	0.159	0.205	0.636	0.125	0.169	0.706						
9	0.198	0.244	0.558	0.156	0.202	0.642						
10	0.243	0.289	0.468	0.195	0.240	0.565						
11	0.293	0.335	0.372	0.239	0.284	0.477						
12	0.344	0.374	0.282	0.288	0.329	0.383						
13	0.388	0.406	0.206	0.338	0.368	0.294						
14	0.434	0.426	0.140	0.381	0.399	0.220						
15	0.466	0.439	0.095	0.426	0.419	0.155						
16	0.491	0.445	0.064	0.457	0.432	0.111						
17	0.511	0.444	0.045	0.482	0.437	0.081						
18	0.526	0.440	0.034	0.501	0.437	0.062						

* Compositions of salts leaving the stages.

2.4 Discussion

2.4.1 : Sodium Magnesium Separation -

At 2.1 gram equivalents of total cations per litre the sodium and magnesium ions had similar affinities for the resin. The equilibrium curve which deviated only slightly from a straight line crossed the x = y line at 0.285 equivalent fraction of magnesium.

2.4.2 : Calculation of Resin Loadings from Aqueous Concentrations -

At both concentration levels the calculated resin loadings were in reasonable agreement with the determined values. The relatively high deviations at the lower concentrations of the various ions were due in some measure to analytical difficulties.

2.4.3 : Calculation of Aqueous Concentrations from Resin Loadings -

The results obtained were very similar to those obtained for the previous calculations of resin loadings. An average difference of approximately 5 per cent. was found for most experiments.

2.4.4 : Calculation of Stages -

The results showed that the method of calculation was not strictly accurate since the calculated aqueous feed stage concentrations for stripping and enriching sections did not agree. The error was of the order of 10 per cent. The calculations indicated that about 23 to 25 stages would be required for the desired separation which was in fair agreement with the previous estimate of 20 - 24 (R.D. 69 part two).

2.5 Conclusions

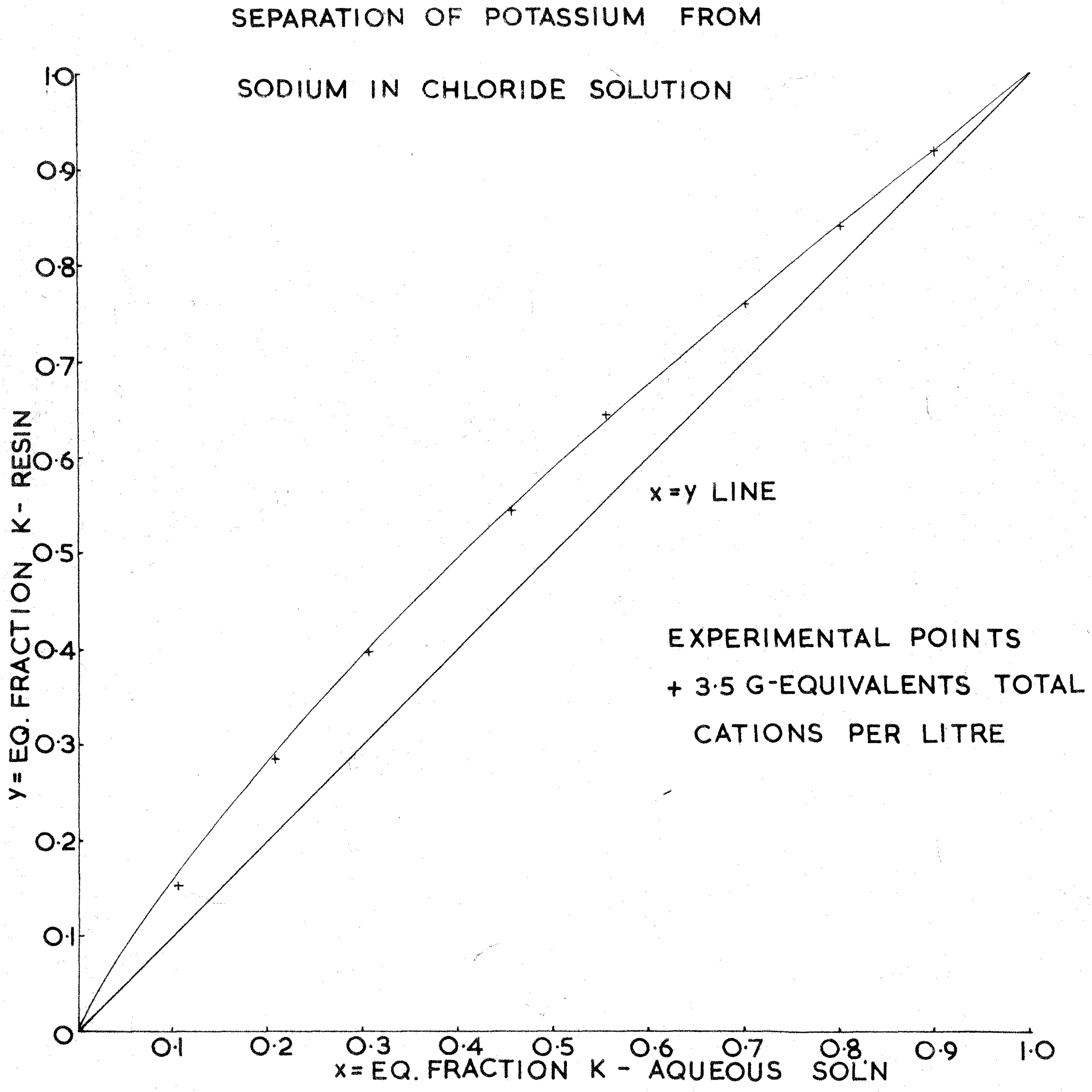
It is apparent that the assumptions made were not strictly correct.

However, the method could probably be used to give an approximate idea of the conditions existing in the main exchange column in the presence of three cations.

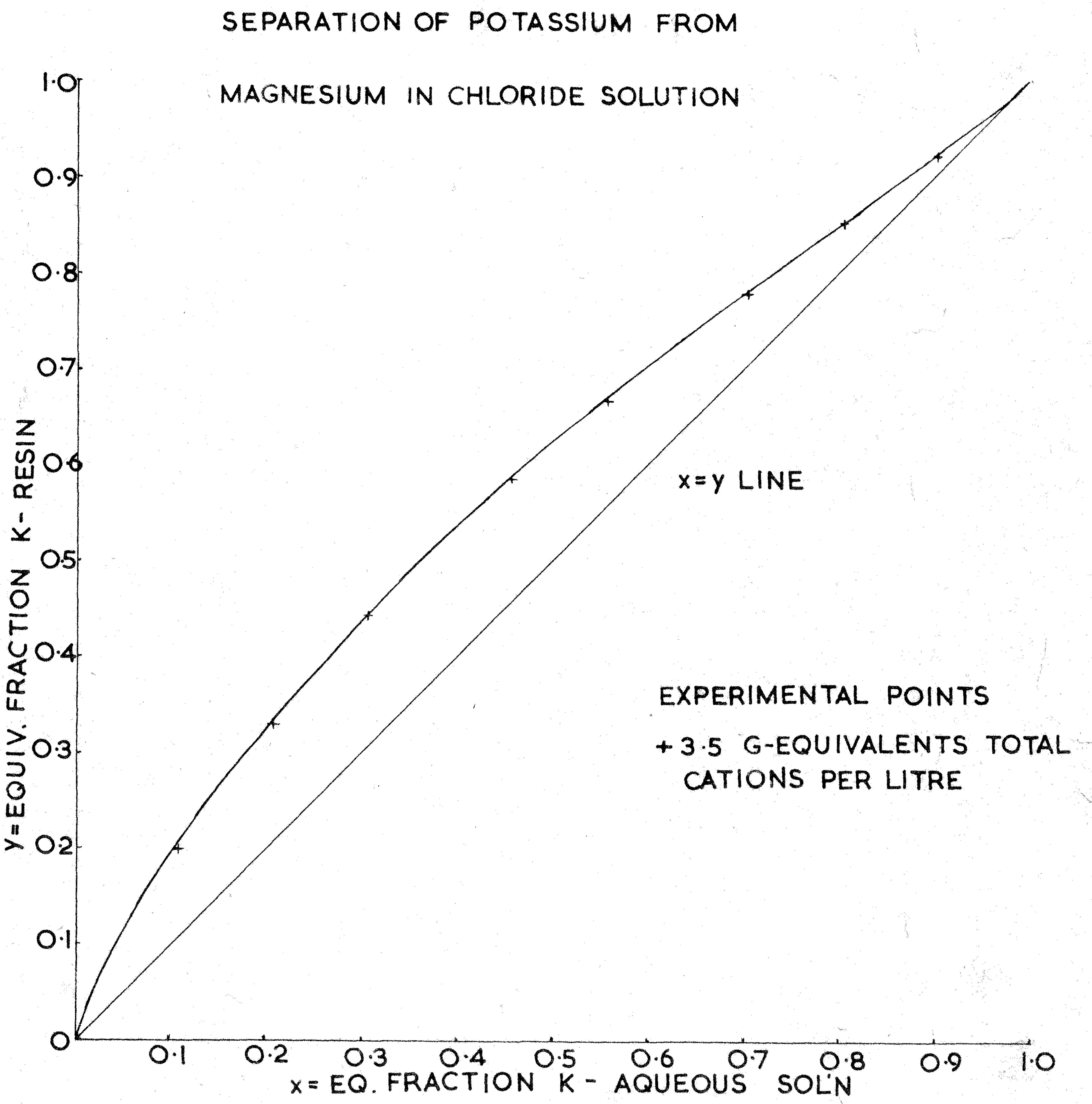
LITERATURE REFERENCES.

Moyle, F.J. R.D. 69 Part One (1957)
Moyle, F.J. R.D. 69 Part Two (1958)
(2) Denver Equipment Index - Denver Equipment Company, Colorado.

EQUILIBRIUM
CURVE
FIG. 1



EQUILIBRIUM
CURVE
FIG. 2.



SEPARATION OF POTASSIUM FROM
MAGNESIUM IN CHLORIDE SOLUTION

EQUILIBRIUM
CURVE
FIG. 3

SEPARATION OF MAGNESIUM FROM
SODIUM - CHLORIDE/SULPHATE SOLUTION