RB 695

RESEARCH FOR INDUSTRY

THE AUSTRALIAN MINERAL DEVELOPMENT LABORATORIES

CONYNGHAM STREET · PARKSIDE · SOUTH AUSTRALIA
TELEPHONE 79 1662 · TELEGRAMS 'AMDEL' ADELAIDE

Please quote this reference in your reply:

1/1/10

20th June, 1963

The Director,
Department of Mines,
Rundle Street,
ADELAIDE.

Dear Sir,

We are transmitting to you ten copies of AMDL Report 149 entitled "Port Pirie Residues - Barren Liquor - Laboratory Investigations", dated June, 1963.

This report is the first in a series of final reports covering investigations connected with possible recovery of by-products from the Port Pirie Uranium Treatment Plant, and includes work commenced in the Research and Development Branch of your Department prior to the formation of AMDL.

Although the closure of the Radium Hill Project has reduced the immediate practical value of the results of this work, we believe the scientific value of these investigations to be high. This work led up to the production at Port Pirie during 1962 of relatively large quantities of high grade scandium oxide. This must be classed as a considerable technical achievement, since scandium was formerly considered to be a very rare element and was normally available only in gram quantities.

Part of the work here reported was described in a paper presented to a Symposium on Hydrometallurgy conducted by the South Australian Branch of the Australasian Institute of Mining and Metallurgy in February, 1960. The publication of this paper in AIMM Proceedings, No. 198 (1961) aroused considerable scientific interest.

Yours faithfully,

MICROFILMED

L. Wallace Coffer

L. Wallace Coffer
Director.

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AMDL Report 149
June, 1963

PORT PIRIE RESIDUES
Barren Liquor - Laboratory Investigations

by

R.G. Canning

to

SOUTH AUSTRALIAN GOVERNMENT
DEPARTMENT OF MINES

Investigated by: Industrial Chemistry Section
Officer in Charge: F.R. Hartley

THE AUSTRALIAN MINERAL DEVELOPMENT LABORATORIES
Adelaide South Australia

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1. INTRODUCTION

During the period of operation of the Port Pirie Uranium Treatment Plant, large volumes of "barren liquor", free from uranium, were run into the tailings dams. Barren liquor contained low concentrations of potentially valuable components, namely vanadium, chromium, thorium, yttrium, scandium, and lanthanides. These were derived, with uranium, from the mineral davidite, and were dissolved with uranium in the sulphuric acid leaching process. After separation of uranium from the liquor by ion exchange, these components remained almost completely in the resultant barren liquor.

The investigations described in this report began as a general examination of possible methods for the recovery of some or all of the above components from barren liquor. Previously, Moyle[1] had shown that more than half of the total lanthanides present could be recovered from barren liquor as a sodium lanthanide sulphate precipitate. This procedure recovered some of the thorium but none of the scandium, and also tended to concentrate the more abundant lighter lanthanides, with only a low recovery of the less common heavy lanthanides. As increased interest has been shown recently in the heavy lanthanide group and in yttrium and scandium, it was considered that some effort should be directed towards recovery of these elements rather than the lighter lanthanides which are more abundant generally.

Preliminary investigations were made in these Laboratories into the possible concentration of desired components by fractional precipitation at controlled acidities, and by the use of selective precipitants and selective leaching techniques. This portion of the work is described in Part I of this report.

The possibility of solvent extraction from barren liquor was also considered but, at the time of commencement of investigations, very little information was available regarding solvent reagents which could be used for extraction from sulphate solutions. However, as information about suitable solvent reagents became available, this line of investigation became the major one. Laboratory-scale solvent extraction investigations are described in Part II of this report, while pilot-scale tests and scandium production operations are to be described separately[2].

This report summarises the results of work dating back to August, 1957, and for the purpose of clarity, only the most significant portions of the experimental work are reported in detail.

2. SUMMARY

Examination of the composition of Port Pirie barren liquor showed that scandium, yttrium, thorium, the lanthanide elements, vanadium, and chromium were possible valuable components. Of these, scandium, yttrium and a separated heavy lanthanide group were probably of the most worth.

Part I of this report outlines investigations into the recovery of such components from barren liquor by precipitation and leaching techniques. Separation of valuable components from the major unwanted component, iron, could be achieved by precipitation at controlled pH levels, but separations from aluminium, the next largest unwanted component, were not so readily obtained. Products obtained by direct precipitation were low-grade, the maximum concentration of scandium and thorium oxides being 0.5 per cent, and chromium and vanadium oxides approximately 7 per cent. Precipitation from barren liquor with selective reagents, such as phosphate, oxalate, and fluoride, yielded products of no higher grade than those obtained by neutralization.

Further treatment of an alumina product containing scandium, thorium, and vanadium oxides (as obtained by neutralization of reduced liquor to pH 5) was possible, using several different procedures. The highest grade products were obtained by leaching hydroxide precipitates with sodium or ammonium carbonate solutions, then precipitating from the resultant carbonate filtrates with caustic soda. Products contained up to 25 per cent each of scandium and thorium oxides. Although overall recoveries of 70 per cent for each of these two components were recorded in bench-scale tests, a larger pilot-scale test gave disappointingly low recoveries of approximately 10 per cent. None of the procedures examined yielded products of sufficient grade in any one component to be marketable as such. Also, it was considered that precipitation and leaching procedures would prove uneconomic as plant-scale processes.

Part II of this report outlines solvent extraction investigations, including a preliminary examination of possible solvent systems. A kerosene solution of di(2-ethylhexyl) phosphoric acid (EHPA) was chosen as the most promising extractant, and systematic investigations established the extraction behaviour of barren liquor components under various conditions. Distribution curves, both extraction and stripping, for individual components were derived from batch tests and were confirmed by small-scale continuous operations.

Variables affecting extraction and stripping distributions were studied. These were pH of liquor, concentration of ferric ions in liquor, concentration of solvent reagent, time of contact, and phase volume ratio. Stripping behaviour of components with sulphuric acid, hydrochloric acid, and hydrofluoric acid strip solutions at different strengths was determined. Many other possible stripping reagents, acid, neutral, and alkaline, were tested. The possibilities of extraction with EHPA in diluents other than kerosene, and of extraction with other reagents of the same type as EHPA, were examined. It was shown that the EHPA/kerosene extractant was the most suitable, and extraction conditions could be chosen to achieve complete recovery of scandium alone, or to recover scandium, thorium, yttrium and the heavy lanthanide group of elements. Fractional stripping tests showed the possibility of obtaining several products, each rich in a particular group of components.

The following process was proposed for scandium recovery, with possible modifications to recover additionally thorium, yttrium, and heavy lanthanides:

i Partial or complete reduction of ferric ions in barren liquor

ii Extraction with 0.1M EHPA

iii Dilution of the extract with additional fresh solvent solution

iv Purification of the extract by stripping with $9\underline{N}$ H_2SO_4 containing 1 per cent NaCl, removing Th, Y, Ln, Fe, Ti etc. Alternatively, several products could be obtained by fractional stripping with successive strip solutions of increasing acid strength.

v Stripping of scandium from purified extract with NaOH solution, and recovery of scandium hydroxide from the separated aqueous phase by filtration or centrifugation. The sodium-form stripped solvent could be re-cycled after acidification.

3. RAW MATERIAL

The concentrations of thorium, scandium, yttrium, and lanthanide elements in Port Pirie barren liquor decreased during the period of operation of the uranium plant, corresponding approximately to a lowering of the grade of uranium concentrate being treated. Table 1 shows a typical analysis of barren liquor derived from average results during the early part of these investigations. At a later stage, scandium oxide was normally 0.02 gram per litre and other valuable components were also in lower concentrations. The average distribution of individual lanthanides within the group, including scandium and yttrium, is shown in Table 2. A distribution of lanthanides for Radium Hill davidite, reported by Dixon and Wylie[3], is included for comparison.

Table 3 shows the calculated annual throughput of possible valuable components at Port Pirie, based on average liquor assays from Table 1 and assuming an average barren liquor production of 75,000 gallons per day. The approximate annual values shown in Table 3 refer to information available at the commencement of this investigation. No figure was available for scandium as this element had been available only in gram quantities up to that time. It was considered that scandium, yttrium, and a separated heavy lanthanide group were the most valuable components in barren liquor. Individual lanthanide prices indicated that a separated heavy lanthanide group (containing erbium, ytterbium and lutecium) would be of much greater value than a total lanthanide mixed product composed mainly of the more abundant lanthanum and cerium group.

TABLE 1: ANALYSIS OF PORT PIRIE BARREN LIQUOR

Components			g/l
	Thorium oxide	ThO_2	0.05
	Scandium oxide	Sc_2O_3	0.04
	Yttrium oxide	Y_2O_3	0.22
Lanthanide group	Lanthanum oxide	La_2O_3	0.5
	Cerium oxide	Ce_2O_3	0.3
	Praseodymium oxide	Pr_2O_3	0.01
	Neodymium oxide	Nd_2O_3	0.025
	Samarium oxide	Sm_2O_3	0.003
	Europium oxide	Eu_2O_3	0.001
	Gadolinium oxide	Gd_2O_3	0.006
	Terbium oxide	Tb_2O_3	0.007
	Dysprosium oxide	Dy_2O_3	0.05
	Holmium oxide	Ho_2O_3	0.01
	Erbium oxide	Er_2O_3	0.05
	Thulium oxide	Tm_2O_3	0.01
	Ytterbium oxide	Yb_2O_3	0.09
	Lutecium oxide	Lu_2O_3	0.008
	Titanium dioxide	TiO_2	0.2
	Aluminium oxide	Al_2O_3	8.0
	Ferric oxide	Fe_2O_3	5.0
	Ferrous oxide	FeO	15.0
	Vanadium oxide	V_2O_5	0.4
	Chromium oxide	Cr_2O_3	0.25
	Calcium oxide	CaO	0.7
	Magnesium oxide	MgO	2.5
	Silica	SiO_2	0.1

TABLE 2: DISTRIBUTION OF SCANDIUM, YTTRIUM, AND LANTHANIDES
Expressed as per cent of total oxides in group

Oxide	Liquor Produced from Radium Hill Concentrate 1959	Radium Hill Davidite (Dixon and Wylie, 1951)
Scandium	3.0	nd(a)
Yttrium	16.0	14.0
Lanthanum	38.0	41.0
Cerium	23.0	25.0
Praseodymium	0.7	1.1
Neodymium	1.9	1.5
Samarium	0.2	1.9
Europium	0.1	0.8(b)
Gadolinium	0.4	1.0
Terbium	0.5	0.5
Dysprosium	3.8	0.8(b)
Holmium	0.7	0.8(b)
Erbium	3.8	5.6
Thulium	0.7	0.5(b)
Ytterbium	6.6	5.2
Lutecium	0.6	0.5

(a) nd - not determined.
(b) Maximum figures.

TABLE 3: ANNUAL THROUGHPUT OF COMPONENTS
Barren Liquor production assumed to be
75,000 gallons per day

Component	Annual Throughput tons	Approx Annual Value £A
Vanadium oxide	45	70,000 (as pure V_2O_5)
Chromium oxide	28	10,000
Lanthanide oxides (mainly lanthanum and cerium)	100	15,000 (as mixed oxides)
Thorium oxide	5	20,000
Yttrium oxide	24	200,000
Scandium oxide	4	-(a)

(a) No quoted price available for large quantities.

PART I

PRECIPITATION AND LEACHING

4. EQUIPMENT AND REAGENTS

No special equipment was required. Measurements of pH were made with a Beckman Model H2[a] direct reading instrument.

Reagents were AR grade or the highest purity available. Iron nails, used for reduction of ferric ions in barren liquor, were cleaned immediately prior to use by immersion in 5M hydrochloric acid for 1 minute, followed by thorough washing with water.

5. EXPERIMENTAL PROCEDURE AND RESULTS

5.1 Analytical Methods

All components except iron were determined spectroscopically in samples of ignited oxides. Results quoted are averages of two or more similar tests, thus increasing the significance of analytical data.

Assays for iron were made colorimetrically, using the ortho-phenanthroline method. Concentration of ferric ions in barren liquor was determined by titration iodimetrically.

The distribution of components in precipitation and leaching tests was calculated from analyses of both solid residues and filtrates. Total recoveries of components were compared with the analysis of the head material in each test and, unless recoveries checked within the usual variation of spectroscopic assays (± 15%), the test was considered to be not significant and was disregarded.

5.2 Precipitation at Controlled pH

Neutralizing or precipitating reagents were added at room temperature in small portions, the solutions being stirred mechanically and the pH monitored continuously. Precipitates were allowed to stand several hours before filtration to ensure reaching equilibrium composition at the particular pH. For basicity separations, NaOH and Na_2CO_3 were added as solutions, and MgO, $MgCO_3$, and $CaCO_3$ as thin slurries in water.

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[a] Reference to specific equipment in this report is made to facilitate understanding and does not imply endorsement of such equipment by The Australian Mineral Development Laboratories.

For tests with liquor containing low concentrations of ferric ions, the necessary reduction was achieved by agitating the liquor over a bed of clean iron nails. At room temperature (20°C), in barren liquor at pH 1.7 to 1.9, the concentration of ferric ions could be reduced from 4.0 grams per litre to zero at a rate equivalent to the treatment of 0.3 gallon of liquor per hour per pound of nails. Consumption of metallic iron was very little more than theoretical for the equation:

$$Fe + Fe^{3+} = 3Fe^{2+}$$

indicating only a small dissolution of iron by acid attack with liberation of hydrogen.

Results of precipitation tests at controlled pH are summarised graphically in Figure 1, while Table 4 lists the compositions of typical precipitates, together with the proportions of components recovered in the precipitates. As expected, precipitation curves for the lanthanide elements (Figure 1) formed a series distributed between the two end members, lanthanum and lutecium. For clarity, only the curves for lanthanum and ytterbium (adjacent to lutecium) are shown. Thorium and titanium, not shown due to insufficient analytical data, were known to be completely precipitated at low pH, their behaviour being similar to oxidized(ferric) iron.

Tests made with liquor in which all ferric ions had been reduced to ferrous, showed that valuable components plus aluminium could be separated from most of the iron present by precipitation at pH 4.6 to 5.0, the ferrous ions remaining in solution. Since scandium and aluminium behaved similarly, no useful separation of these two components was obtained at any pH value.

Several series of fractional precipitation tests were made using barren liquor as received, and also after reduction of ferric ions. In barren liquor as received, precipitation of the chromium, vanadium, thorium and oxidized iron group at pH 3.5 usually co-precipitated some scandium, the extent of co-precipitation depending on the concentration of ferric ions. A second precipitate at pH 5.0 recovered the remaining scandium, together with all of the aluminium, and 25 to 50 per cent of the yttrium, ytterbium (heavy lanthanides) group. The second approach, involving preliminary reduction of the liquor, enabled a single precipitate at pH 4.6 to 5.0 to collect the main group of valuable components together with most of the aluminium, and portion of the heavy lanthanides group. A second precipitate containing the remainder of heavy lanthanides could be obtained at pH 6. Alternatively a second precipitate containing all the remaining lanthanides could be made using phosphate, fluoride, or oxalate as precipitant.

No significant differences in compositions of precipitates resulted from the use of the various neutralizing agents mentioned earlier, except that precipitates produced with calcium carbonate were contaminated with gypsum resulting from neutralization of sulphuric acid.

TABLE 4: PRECIPITATION AS HYDROXIDES
Port Pirie Barren Liquor

	Liquor as Received - Precipitation in Two Steps					Fe^{3+} Reduced Single Precipitation	
	pH 3.6		pH 5.0			pH 4.65	
	Anal %	Recovery of Component %	Anal %	Recovery of Component %	Cum Recovery of Component %	Anal %	Recovery of Component %
Fe_2O_3(a)	50.0	20	9.0	6	26	10.0	8
V_2O_5	5.0	80	0.7	20	100	7.0	100
Cr_2O_3	5.0	85	0.6	15	100	6.0	100
Sc_2O_3	0.15	15	0.45	85	100	0.45	95
Al_2O_3	15.0	12	70.0	88	100	60.0	94
ThO_2	0.6	80	0.10	20	100	0.3	100
Y_2O_3	nil	nil	0.13	5	5	0.4	20
Yb_2O_3	nil	nil	0.08	10	10	0.2	25

(a) Total iron.

Selective precipitation tests on original barren liquor were made with phosphate, oxalate, and fluoride, these reagents being added as solutions of their respective free acids. Sufficient reagent was added to be chemically equivalent to the total of metallic cations present in barren liquor. Further fractional precipitates were then obtained by adjustment of the pH with additions of NaOH solution. Tables 5, 6 and 7 show summaries of the results of these tests. Other tests (not reported in detail) were made using selective precipitants on filtrates from neutralization precipitations at pH 5. Mixed lanthanide products, heavily contaminated with iron, normally resulted.

TABLE 5: PRECIPITATION AS PHOSPHATES
Port Pirie Barren Liquor
At the initial pH (0.6) no precipitate formed
Fractional precipitates were obtained by pH adjustment

	pH 2.25		pH 3.8		
	Analysis of Precipitate %	Recovery %	Analysis of Precipitate %	Recovery %	Total Recovery %
Fe_2O_3(a)	3.0	4	3.1	3	7
V_2O_5	0.9	25	3.6	75	100
Cr_2O_3	0.15	10	0.75	40	50
Sc_2O_3	0.23	87	0.05	13	100
Al_2O_3	34.0	58	32.0	41	99
Y_2O_3	0.25	20	1.3	80	100
Yb_2O_3	0.4	68	0.25	32	100
La_2O_3	2.0	73	1.0	27	100

(a) Total iron.

TABLE 6: PRECIPITATION AS OXALATES
Port Pirie Barren Liquor

	Initial Precipitate		Fractional Precipitates by pH Adjustment				
	pH 0.6		pH 5.4		pH 6.5		
	Analysis of Precipitate %	Recovery %	Analysis of Precipitate %	Recovery %	Analysis of Precipitate %	Recovery %	Total Recovery %
Fe_2O_3(a)	84.0	46	66.0	20	32.0	31	97
V_2O_5	0.5	13	3.2	42	1.1	43	98
Cr_2O_3	0.03	2	0.6	20	0.2	18	40
Sc_2O_3	0.09	13	0.12	10	0.22	57	80
Al_2O_3	2.6	3	28.0	17	38.0	71	91
Y_2O_3	1.5	77	0.2	6	0.13	11	94
Yb_2O_3	0.5	71	0.07	6	0.06	16	93
La_2O_3	1.8	66	0.9	10	0.25	16	92

(a) Total iron.

TABLE 7: PRECIPITATION AS FLUORIDES
Port Pirie Barren Liquor

	Initial Precipitate		Fractional Precipitates by pH Adjustment				
	pH 0.6		pH 4.0		pH 4.75		
	Analysis of Precipitate %	Recovery %	Analysis of[a] Precipitate %	Recovery %	Analysis of[a] Precipitate %	Recovery %	Total Recovery %
Fe[b]	4.0	5	8.0	6	24.0	34	45
V	nil	nil	0.4	20	1.0	80	100
Cr	nil	nil	0.5	27	0.8	73	100
Sc	0.2	77	0.05	14	0.02	9	100
Al	25.0	67	15.0	29	1.2	4	100
Y	1.0	94	0.09	6	nil	nil	100
Yb	0.6	94	0.05	6	nil	nil	100
La	2.5	99	0.04	1	nil	nil	100

(a) Analytical figures refer to components as elements.

(b) Total iron.

5.3 Alkali Leaching of Precipitates

Two approaches to the upgrading of hydroxide precipitates were investigated. These were:

i. Leaching with boiling caustic soda solution to remove the major unwanted component, aluminium, leaving a residue upgraded in valuable components.

ii. Leaching with alkali carbonate solutions at room temperature to dissolve scandium and thorium as soluble double carbonates, leaving other components with aluminium in the residue.

Leaching with caustic soda solution (10% NaOH) was carried out in stainless steel beakers with mechanical agitation and heating to near boiling for 1 hour. Quantities were adjusted to give slurries containing approximately 5 per cent solids on an ignited weight basis. To avoid possible passivation on drying, precipitates used for these tests were not dried before use. Leached slurries, after cooling, were filtered and the residues washed, dried and ignited for analysis. The dissolved components were recovered by acidification of the filtrates, then precipitation with a slight excess of ammonia and the addition of tannin solution as a scavenger.

Results for a typical hydroxide precipitate are summarised in Table 8.

TABLE 8: CAUSTIC SODA LEACHING OF PRECIPITATE
Hydroxide precipitate produced from barren liquor at pH 4.65
Precipitate (not dried) boiled for 1 hour with 10% NaOH solution

	Analysis		
	Original Precipitate from Barren Liquor pH 4.65 %	Residue after NaOH Leaching %	Extraction of Components %
Fe_2O_3 (total)	10.0	31.0	nil
Cr_2O_3	6.0	15.0	nil
V_2O_5	7.0	2.0	90
Al_2O_3	60.0	8.0	95
Sc_2O_3	0.4	1.0	$10^{(a)}$
ThO_2	0.3	1.0	$10^{(a)}$

(a) Maximum figure.

Leaching at room temperature with sodium or ammonium carbonate solution was made with slurries containing 5 per cent solids by shaking for 3 to 4 hours in stoppered Erlenmeyer flasks on a mechanical shaker. Dissolved components were recovered from carbonate filtrates by addition of caustic soda solution to precipitate hydroxides. As this precipitation was not always complete, the overall distribution of valuable components was determined by scavenging the final filtrate in a similar manner to the caustic soda solutions above, making certain that all carbon dioxide was removed by boiling the acidified filtrate before final precipitation with ammonia and tannin. Results of carbonate leaching tests are shown in Table 9.

TABLE 9: CARBONATE LEACHING OF PRECIPITATE
Hydroxide precipitate produced from barren liquor at pH 4.65 (as in Table 8)
Precipitate (not dried) leached for 4 hours at $20^{\circ}C$ with solutions as shown

	Extraction of Components, %		
	10% Na_2CO_3	10% $NaHCO_3$	20% Ammonium Carbonate
Fe (total)	nil	nil	nil
V	25.0	5.0	7.0
Cr	0.5	0.5	0.3
Sc	25.0	10.0(a)	42.0
Th	50.0	40.0	38.0
Al	2.0	0.5	0.7

(a) Maximum figure.

The best product obtained from the initial series of tests contained 10 per cent Sc_2O_3 and 15 per cent ThO_2. Although recoveries were less than 50 per cent, this represented a considerable upgrading from the original precipitate (analysis in Table 8). Further investigation of carbonate leaching showed that the pH was quite critical. For successful leaching, free caustic soda had to be absent and excess bicarbonate was also undesirable. Best results were obtained by using sodium carbonate as the neutralizing agent for precipitation from barren liquor. The filtered precipitate, in the form of wet filter cake (not dried), was then leached with 10 per cent Na_2CO_3 solution. By this means recoveries up to 70 per cent were obtained for scandium and thorium, the products containing up to 25 per cent each of scandium and thorium oxides.

5.4 Carbonate Leaching - Pilot Scale Test

Based on the results of bench-scale tests a larger scale carbonate precipitation and leaching test was conducted at the Thebarton laboratories. Approximately 150 gallons of barren liquor, obtained from Port Pirie in January, 1958, was treated according to the following steps:

i. Neutralization and precipitation with Na_2CO_3 solution to pH 4.5, at room temperature

ii. Leaching of the separated precipitate with 10 per cent Na_2CO_3 solution by agitating for 4 hours as a slurry containing an estimated 5 per cent solids (ignited weight)

iii. Further leaching of the separated residue, using a smaller volume of 7.5 per cent Na_2CO_3 solution

iv. Precipitation from the combined, clarified Na_2CO_3 solutions by addition of NaOH solution, and the recovery of this precipitate as a scandium and thorium product.

Samples of residues and filtrates at each stage were analysed to determine the distribution of components. Table 10 shows a summary of the results for the components of interest. The product precipitate, after ignition, weighed 0.02 lb, and contained 25 per cent Sc_2O_3.

The low recoveries obtained were not in accord with indications from bench-scale tests. One possible contributing factor was insufficient allowance for the NaOH content of commercial Na_2CO_3, resulting in too high a pH for the effective formation of soluble double carbonates of scandium and thorium.

Further bench-scale tests on a sample of the first precipitate showed that much of the scandium and thorium remaining in this precipitate could be leached with Na_2CO_3 solution by careful control of the pH of the mixture.

TABLE 10: CARBONATE LEACHING - PILOT-SCALE TEST

Process	Step	Efficiency of each Step			
		Sc %	Th %	Y %	Yb %
Precipitation from liquor	1	90	100	14.0	46.0
Carbonate leaching of precipitate	2 and 3	9	12	0.5	0.5
Product precipitation with NaOH	4	50	25	50.0	50.0

5.5 Passivation and Leaching of Precipitates

Selective leaching of desired components was considered to be possible if other components of barren liquor precipitates could be rendered passive by ignition at suitable temperatures.

A bulk sample was prepared from selected barren liquor precipitates by re-slurrying, filtering, and storing as undried filter cake. Portions of this sample were dried and ignited in silica dishes for periods of 2 hours at temperatures ranging from 100° to 1200°C. The ignited samples were further divided and the fractions leached separately with several different acids at different strengths, both at room temperature and at boiling point.

Room temperature tests were made by shaking a slurry containing approximately 5 per cent solids in stoppered Erlenmeyer flasks on a mechanical shaker for 1 hour. Boiling point leaching tests were made with similar slurries boiled for 1 hour.

Results for hydrochloric acid leaching tests are shown graphically in Figures 2 and 3. Sulphuric, sulphurous, and acetic acids gave results which were not significantly different. Table 11 shows a partial analysis of the bulk precipitate used for these tests, together with analyses of some of the precipitates obtained from acid filtrates resulting from leaching ignited portions of the original bulk precipitate. Ignition temperatures used for passivation are shown with each product analysis.

TABLE 11: PASSIVATION AND LEACHING TESTS
Analyses of Precipitates

	Bulk Precipitate [(a)]	Products from [(b)] 0.05M HCl		Products from [(c)] 1M HCl	
Passivation temp, °C	-	800 %	1000 %	800 %	1000 %
Fe_2O_3	16.0	0.5	0.9	9.0	11.0
V_2O_5	6.0	9.0	40.0	10.0	30.0
Cr_2O_3	4.0	0.01	0.1	0.5	1.5
Sc_2O_3	0.4	0.7	0.9	0.9	0.7
ThO_2	0.3	0.5	0.2	0.8	0.3
Al_2O_3	50.0	13.0	20.0	20.0	13.0

(a) Used for passivation tests.
(b) Leaching, 20°C
(c) Leaching at boiling temperature.

5.6 Cation Exchange Tests

Portion of a precipitate produced from reduced barren liquor at pH 5.0 was dissolved in sulphuric acid and adjusted to pH 1.0. Equilibrium loading tests were made with this solution on Zeocarb 225 cation exchange resin. The separated resin was eluted with 8M HCl and the eluate evaporated nearly to dryness, then diluted and precipitated with ammonia. Analyses of eluate solids and liquor solids were compared to show any separations achieved by loading on the resin. Similar tests were made with reduced barren liquor.

Results showed only very small separations of valuable components from the major components aluminium and iron. No useful concentrations of components appeared likely by cation exchange procedures.

6. DISCUSSION OF PRECIPITATION AND LEACHING RESULTS

Although scandium could not be separated to any extent from aluminium by precipitation techniques, separation from iron, the major unwanted liquor component, was possible. Two systems of precipitation by neutralization to controlled pH showed some possibilities (Table 4). These were:

i. Fractional precipitation of liquor in two steps at pH 3.6 and at pH 5.0

ii. Complete reduction of ferric ions in barren liquor, followed by a single precipitation at pH 4.6 to 5.0.

System i. yielded a first product at pH 3.6 containing most of the thorium, vanadium and chromium in a matrix of ferric oxide. The product recovered at pH 5.0 was mainly alumina, and contained most of the scandium, and part of the yttrium and heavy lanthanide group. Under some circumstances, scandium divided into each precipitate, hence this system was not adopted for further work.

System ii. yielded an alumina product in which most of the scandium, thorium, chromium, and vanadium were concentrated, together with part of the yttrium and heavy lanthanide group of elements.

In both systems, the scandium oxide content of the alumina products could not exceed 0.5 per cent, this figure being controlled by the ratio of alumina to scandia (200:1) in barren liquor. Further products containing the remainder of the yttrium and heavy lanthanide group could be obtained from the final filtrates in each system by neutralization to pH 6.0. Alternatively the complete lanthanide group, light elements as well as the heavy group, could be precipitated from the pH 5.0 filtrates as phosphates or fluorides. Such mixed lanthanide products were not considered to be of any great value.

Precipitation from barren liquor using the selective reagents, phosphate, oxalate, and fluoride, did not achieve significant separations of valuable components from the major unwanted components, iron and aluminium. Since part neutralization was necessary to obtain these products, and since the product grades were no higher than those obtained with direct precipitation by neutralization, selective precipitants offered no real advantage. No further work was done with these systems.

Further treatment of an alumina product containing scandium, thorium and vanadium, (as obtained by neutralization of reduced barren liquor to pH 4.65) was shown to be possible by three different procedures. Firstly, leaching with hot caustic soda solution dissolved most of the alumina and vanadium oxide leaving a residue upgraded in other valuable components, but still relatively low-grade (Sc_2O_3 1.0 per cent). This procedure would be uneconomic, since the reagent was consumed by the major unwanted component. Secondly, leaching with cold carbonate solution dissolved scandium and thorium, yielding a product rich in these two components, up to 25 per cent of each oxide. However, good recoveries were difficult to achieve, and one large-scale test of this procedure was unsuccessful in this respect. Thirdly, passivation of the alumina product by ignition at 800°C, followed by leaching with 1N acid at boiling point, yielded a product containing a large proportion of the scandium, thorium, and vanadium. Alternatively, vanadium could be recovered separately by passivation at 1000°C, and then leaching with cold dilute acid.

None of the above procedures yielded products of sufficient grade in any one or more components to be marketable as such. Further separation and concentration treatments would be required. Because of this, and because of the multiplicity and involved nature of the operations in the above procedures, it was considered that these would prove to be uneconomic when examined as plant-scale processes.

7. CONCLUSIONS ON PRECIPITATION AND LEACHING

Various low-grade products containing one or more valuable components could be produced from barren liquor by precipitation and leaching processes. Because of the multiple operations involved, and the nature of these operations, such processes would be uneconomic except under unusual circumstances.

At this stage of the investigation, preliminary work had demonstrated the possibility of recovering some valuable components from barren liquor by means of solvent extraction. As this type of process showed promise of technical feasibility and of economic operation, all further work was directed to this aspect of barren liquor treatment.

PART II

SOLVENT EXTRACTION

8. POSSIBLE SOLVENT SYSTEMS

Before commencing detailed investigations, various solvent extraction systems were considered for recovery of components from low grade sulphate solutions. Scandium and thorium nitrates could be extracted into ethyl ether,[4] or into a kerosene solution of tri-butyl-phosphate[5]. Such systems showed possibilities for purification of impure scandium and thorium products but were not applicable to the recovery of these components from barren liquor. Scandium could be extracted as the thiocyanate from hydrochloric acid solution into ethyl ether,[6] but a high concentration of thiocyanate was required and sulphate ions interfered. Recently developed amine solvents, as used for uranium recovery, could be used for extraction of thorium from sulphate solutions[7] and this process possibly could be applied to barren liquor for recovery of thorium.

The most promising solvent reagents were long chain alkyl esters of phosphoric acid. These were developed initially for the recovery of uranium and vanadium from sulphate leach liquors[8]. Kerosene solutions of such reagents will extract many metal ions successfully from solutions of chlorides, nitrates or sulphates[9]. Extractants of this type behave as liquid cation exchange media, and the extracted cations may normally be stripped in a similar manner to that used for cation exchange resins. Madigan[10,11] used this type of solvent for the recovery of thorium from Crocker Well leach liquors.

Among the reagents of this type available commercially, the one chosen for the present work was di-(2-ethyhexyl)-phosphoric acid, designated EHPA in this report. Other esters, namely mono-dodecyl-phosphoric acid and mono-heptadecyl phosphoric acid were tested, but showed no advantage in the separation or recovery of components. The mono-esters possessed the disadvantage that they could not be used in alkaline stripping circuits because of the behaviour of their sodium salts.[10,11]

9. THEORY OF EXTRACTION BY DI-(2-ETHYLHEXYL)-PHOSPHORIC ACID (EHPA)

The extracting species for lanthanides with EHPA has been postulated[12] as a chelate (Figure 4). The extraction may be expressed, as a close approximation, by the following equations:

$$(M^{+3})\ Aq + 3(EHPA)\ Org \rightleftharpoons (M\,(EHPA)_3)\ Org + (\ 3(H^+)\ )\ Aq \ldots \qquad (1)$$

$$\frac{[M\ (EHPA)_3]\ Org}{[M^{+3}]\ Aq} = K.\ \frac{[EHPA]^3\ Org}{[H^+]^3\ Aq} \quad \ldots\ldots\ldots\ldots \qquad (2)$$

$$D = K\ \frac{[EHPA]^3\ Org}{[H^+]^3\ Aq} \quad \ldots\ldots\ldots\ldots \qquad (3)$$

where the subscripts Aq and Org refer to equilibrium aqueous and organic phases respectively and the square-bracketed quantities refer to molar concentrations. Unit activities are assumed in the absence of other data. D is the distribution coefficient for the tri-valent metal M, and K is the pertinent constant. Equation (3) may be more generally expressed as:

$$D = K \left(\frac{[HR]_{Org}}{[H^+]_{Aq}} \right)^n \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where n is the valence of the species being extracted and R is any weakly acidic chelating extractant.[13]

10. PRELIMINARY INVESTIGATIONS

Published work[9-12] indicated that EHPA would extract thorium, yttrium, and the heavy lanthanides, but no information was available about the behaviour of scandium. Preliminary laboratory tests were therefore made, using a very small quantity of spectrographically pure scandium oxide. These tests indicated that scandium was definitely extracted from sulphate solutions at pH 0.5 or higher by a 0.1<u>M</u> solution of EHPA in kerosene. Results were confused by difficulty in stripping the extracts. Confirmation of the extraction of scandium, thorium, and heavy lanthanides was obtained from tests using a sulphate solution, adjusted to pH 2, of a concentrate of scandium and thorium. The concentrate had been prepared by selective precipitation from barren liquor and by carbonate leaching. Scandium was extracted more strongly than thorium. Successful preliminary extractions with EHPA were also made directly from Port Pirie barren liquor.

Initial stripping tests showed that scandium was difficult to recover from EHPA extracts, the most promising strip reagent being caustic soda solution. Emulsions were readily formed with dilute solutions of this reagent (0.1<u>N</u>). Increasing the ionic concentration of the aqueous solution by the addition of a neutral salt such as sodium sulphate, or the use of stronger caustic soda solutions (1<u>N</u> to 2<u>N</u>) prevented emulsion formation. Blake, Brown and Coleman[8] showed, when extracting uranium with EHPA, that a third phase was formed containing the sodium salt of the ester when NaOH or Na_2CO_3 solution was used for stripping. The addition of a small proportion of ethyl-hexyl alcohol to the solvent solution overcame this difficulty, the sodium salt of EHPA being soluble in the modified organic phase. It was shown experimentally in the present investigation that nonanol, which was more readily available, was also effective for this purpose.

No reliable quantitative figures were obtained from these preliminary investigations, but the results were sufficiently encouraging to justify a systematic examination of possible extraction and stripping conditions. Early work showed that ferrous iron and aluminium were not extracted to any extent, thus good separations could be obtained from the two major unwanted components in barren liquor. However, ferric ions were strongly extracted from barren liquor to the exclusion of a large proportion of the desired components. Reduction of ferric ions to ferrous before solvent extraction was therefore desirable. This introduced some further complications due to the rapid hydrolysis of titanium in the barren liquor after reduction of ferric ions. Hydrolysed titanium was separated from the liquor for some extraction tests before it was realised that some scandium and thorium were co-precipitating with the hydrolysate and were therefore being lost. Controlled reduction, to a point where the concentration of ferric ions was just sufficient to prevent hydrolysis, was then adopted, and was used successfully for most of the systematic investigations.

11. SYSTEMATIC INVESTIGATIONS

11.1 Equipment

Extraction and stripping tests were normally made in stoppered glass separatory funnels, mixing being obtained by manual shaking. For long contact times, the solutions were stirred mechanically in beakers, then the mixture transferred to separatory funnels to allow the phases to disengage and the lower phase to be separated.

Stripping tests with fluoride solutions were made in polythene beakers, the phases being mixed with propeller-type agitators shaped from perspex. Phase separations were achieved in improvised separatory funnels made from polythene funnels with clamped nylex tubing attached.

Continuous tests were conducted in perspex mixer-settler units described later (Section 13.2). No other equipment was required apart from the usual laboratory apparatus.

11.2 Reagents

11.2.1 Solvents

Samples of di-(2-ethylhexyl)-phosphoric acid were obtained from two sources. These were estimated by potentiometric titration to be 98 and 96 per cent pure respectively, with less than 1 per cent of mono-ester present in each.

Other solvents tested were monododecyl- and monoheptadecyl-phosphoric acid esters.

11.2.2 Diluents

Lighting grade household kerosene was used for most of the tests. To allow alkaline stripping of the extract, the kerosene diluent was modified by the addition of up to 4 per cent by volume of nonanol. Other diluents tested were benzene, toluene, xylene, carbon tetrachloride, and nonanol.

11.2.3 Inorganic Reagents

AR grade reagents were used throughout.

11.3 Experimental Procedure

Laboratory batch tests were conducted, either by shaking manually in separatory funnels or by mechanical stirring in beakers, followed by transfer to separatory funnels for phase separation. Initially all contacting was carried out at organic to aqueous phase ratios of two or more. Large overall aqueous to organic ratios were achieved by successive contacts of fresh aqueous with the same organic solution. Later tests were made successfully with large reversed phase ratios in single contacts, up to 40 aqueous to 1 organic. This achieved a given equilibrium between aqueous and organic, with cleaner phase separation than that which occurred after a large number of successive contacts, as in the earlier system. The method of a single contact with reversed phase ratio was adopted for the bench scale development of extraction distribution curves. For most of these tests, barren liquor was pre-treated to reduce ferric ions to ferrous. Stirring the solution in contact with iron nails achieved the required reduction very simply. Hydrolysis of titanium occurred in the fully reduced liquor and, in early tests, the precipitate was separated before solvent extraction. In later tests, complete reduction was avoided and a sufficient concentration of ferric ions was maintained to stabilize the solution and prevent hydrolysis of titanium.

As supplies of pure scandium, yttrium, and individual heavy lanthanides were not readily available, all experimental work was based on extraction from barren liquor obtained from Port Pirie. Distributions of individual components were calculated from analytical results.

To enable systematic stripping tests to be made, a quantity of extract was prepared by treating approximately 40 litres of barren liquor (ferric ions reduced to ferrous), using a 2-stage mixer-settler continuous system, shown in Figure 20. A description is given in Section 13.

At a later stage in the investigations, further continuous extraction and stripping tests were made in multistage systems, using the same type of mixer-settler units. Radioactive scandium was used as a tracer in some of these tests.

11.4 Analytical Methods

Results were derived mainly from spectroscopic assays, as this was the only method available for determination of individual lanthanides and certain other components, particularly at the low concentrations in barren liquor. A greater degree of significance was obtained by averaging results from several tests. Each series was repeated several times and all spectroscopic results quoted in this report are averages from two or more similar tests. Solid samples for spectroscopy were prepared from aqueous phases by precipitation with ammonia followed by ignition to oxides, and from organic phases by burning off the kerosene with the aid of a filter paper wick, then ignition of the residues to inorganic phosphates. Iron was determined chemically by the ortho-phenanthroline colorimetric method. Phosphate determinations were made on ignited samples by fusion with sodium carbonate followed by leaching with water, then colorimetric assay of the filtered sodium carbonate solutions for phosphate.

The concentration of EHPA in organic solutions was determined by potentiometric titration with alcoholic potassium hydroxide. The use of phenolphthalein indicator was satisfactory for the end point but the potentiometric method distinguished between mono- and di-esters if both were present. Determinations of nonanol were made directly in kerosene solutions by gas chromatography or by a titration procedure involving esterification before determination. Nonanol losses to aqueous phases were determined by extraction from large aqueous volumes with carbon tetrachloride, then gas chromatographic determination of nonanol in the extract.

When radioactive scandium (Sc^{46}, half-life 8 5 days) was used for control of small-scale continuous tests, sufficient activity was added to the feed liquor to enable 1 per cent of this level to be detected in the raffinate. Ample activity was then present in the extracts for control of stripping tests. Assays were made directly on samples of aqueous and organic solutions, using a gamma-scintillometer.

12. RESULTS

12.1 Pre-Treatment of Liquor

By contacting the liquor with iron nails, ferric ions could be completely reduced to ferrous, after which vanadium reduction (V^{IV}) to (V^{III}) commenced. In batch tests at 20°C, the concentration of ferric ions was reduced from 4 grams per litre to zero at a rate equivalent to the complete reduction of 1.4 litres (0.3 gallon) of liquor per hour per pound of nails. A small rise in pH indicated some dissolution of iron with evolution of hydrogen, but a check of the weight of iron dissolved against the quantity of ferric ions reduced indicated that the consumption of acid and the corresponding loss of iron were relatively insignificant.

Complete reduction of ferric ions normally caused immediate hydrolysis of titanium. Table 12 shows a comparison of the proportions of liquor components precipitated in hydrolysates produced at various pH values. Reasonable concentrations of scandium and thorium (up to 8 per cent of each oxide) were found in the ignited solids prepared from hydrolysates at pH 2 and pH 3, but when considered as products, these did not represent sufficiently high recoveries of the desired components.

TABLE 12: HYDROLYSIS IN REDUCED BARREN LIQUOR Fe^{3+} Nil

pH	Proportions of Components Precipitated		
	Ti %	Sc %	Th %
1.5	50	30	20
2.0	80	40	30
3.0	80	40	30
3.5[(a)]	100	50	100

(a) Precipitate at pH 3.5 from liquor containing Fe^{3+} 4 g/l.

Complete reduction and hydrolysis thus divided the desired components into two fractions, both of which would require further treatment to recover valuable components. Attempts were therefore made to reduce the concentration of ferric ions to as low a level as possible without causing hydrolysis of titanium. The concentration of ferric ions required to stabilize the liquor and prevent hydrolysis of titanium was variable. One sample of liquor was stable at 0.1 gram Fe^{3+} per litre, while another hydrolysed within 2 hours at 0.5 gram Fe^{3+} per litre. Variation in the concentration of titanium appeared to be the main factor controlling the difference in liquor stability, in agreement with the work of Hayton[14].

12.2 Extraction with EHPA in Kerosene

12.2.1 Effect of Ferric Ions

A comparison of extract analyses in Table 13 shows the large effect of ferric ion concentration on extract composition and on the total load in the solvent. From a liquor containing 5 gram Fe^{3+} per litre a fully loaded extract was obtained with the iron representing 40 per cent of the total load. From a liquor containing 0.2 gram Fe^{3+} per litre, the extract was approximately half-loaded, with iron representing only 3 per cent of the actual load. Increased recovery of valuable components was obtained in this half-loaded solvent. Extraction of iron could not be eliminated completely, even from liquors in which all ferric ions had been reduced to ferrous. This was considered to be due partly to some re-oxidation during agitation of the mixed phases, and partly to a small extraction of ferrous ions.

TABLE 13: EXTRACT ANALYSES: EFFECT OF FERRIC IONS

Conditions: Liquor pH: 1.7
EHPA: 0.1$\underline{M}$
Contact time: 1 min.
Phase ratio: 5 aqueous: 1 organic

Fe^{3+} in liquor - g/l	0.2	5
Extract Analysis g/l		
Fe	0.03	0.7
Ti	0.07	0.3
Sc	0.21	0.18
Th	0.19	0.15
Y	0.6	0.5
Yb	0.4	0.3
V	0.01	0.004
Al	0.02	0.03
Total load in extract (as milli-equivalents/litre):	54	104

12.2.2 Effect of Time

Table 14 shows a summary of the distributions obtained for several components from comparable extraction tests, made with contact times ranging from 15 seconds to 10 minutes. Scandium, yttrium, and ytterbium (representing the heavy lanthanides) reached equilibrium very rapidly in 30 seconds or less, whereas ferric ions were still being extracted after 10 minutes. Other tests indicated that more than 30 minutes contact was required to reach equilibrium for ferric ions.

The recorded fall in distribution coefficients for yttrium, ytterbium, and vanadium after 1 minute was due to increased loading of ferric ions, thus decreasing the free EHPA concentration on which the distributions depend (Section 9).

Results showed that a very short contact time of 15 seconds or less could be employed to limit the extraction of ferric ions without affecting recoveries of scandium, yttrium, and heavy lanthanides.

TABLE 14: EXTRACTION DISTRIBUTION COEFFICIENTS
Effect of Time
Conditions: Liquor pH: 1.7
EHPA: 0.1$\underline{M}$
Phase ratio: 1:1

Contact Time		D_E(a)				
		Sc	Y	Yb	V	Fe^{3+}
15	seconds	$30^{m(b)}$	15	40	0.6	1.8
30	"	30^{m}	30	50	0.8	2.4
1	minute	30^{m}	20	50	0.8	3
2	"	30^{m}	10	40	0.7	4
10	"	30^{m}	5	40	0.5	5

(a) D_E - $\frac{\text{concentration in organic phase}}{\text{concentration in aqueous phase.}}$

(b) m - Minimum figure.

12.2.3 Effect of EHPA Concentration

In Figure 5, extraction distribution coefficients for several components are plotted against the concentration of free EHPA in the equilibrium organic phase. The extraction distribution coefficient (D_E) is defined as the ratio of the concentrations of any component in the equilibrated phases ($\frac{\text{organic}}{\text{aqueous}}$). For this series of tests, extractions were made from partly reduced barren liquor at pH 1.9, with 1 minute contact time.

From the theory expressed by equation (4) in Section 9, the slope of the line for each component on a log/log plot should equal n, the valence, for that component. In most of the tests from which Figure 5 was drawn, the extract was loaded to at least 50 per cent of theoretical capacity, and the free EHPA remaining was determined as a difference between total EHPA and that equivalent to the total cationic load of the extract, determined as individual components. This introduced some uncertainty into the results. However, it was clear that the lanthanides approached theoretical behaviour, while iron and titanium did not. Distribution coefficients for scandium were too high to be shown on the graph (Figure 5).

The effect of EHPA concentration on extract composition can be judged by comparing Figures 6 and 7. Figure 6 shows the results of a series of tests at different phase ratios using 0.1$\underline{M}$ EHPA, and Figure 7 a similar set of results with 0.01$\underline{M}$ EHPA. Partly reduced barren liquor, with Fe^{3+} at 0.5 gram per litre and pH 1.9, was used for this series of tests. Contact time was 1 minute. The figures are drawn to equivalent scales and so placed that a vertical line through both figures represents on each plot the same quantity of extracting EHPA reagent per unit volume of liquor.

12.2.4 Variation of Phase Volume Ratio

The variation of extract composition obtained with increasing aqueous to organic phase volume ratios is also shown in Figures 6 and 7. Scandium is extracted so strongly by EHPA that, in the presence of excess aqueous liquor, it will displace other components from the organic phase. A high degree of selectivity for scandium can therefore be achieved, together with a good concentration in the organic phase, by extracting at high aqueous to organic volume ratios.

Table 15 shows extraction coefficients determined from the above series of tests.

12.2.5 Effect of pH of Aqueous Phase

Table 16 shows extraction distribution coefficients obtained from reduced barren liquor at different pH levels. The tendency for some components to hydrolyse at higher pH values affected the results, particularly regarding titanium, while the emulsions formed at pH 3.0 and 3.5 made phase separation very difficult. It was apparent that a continuous process would be difficult to operate with feed liquor at a pH higher than 2.5. Distribution coefficients were favourable for good recoveries of scandium, yttrium, and heavy lanthanides at pH 1.5, but for appreciable recovery of vanadium, a higher pH was indicated.

TABLE 15: EXTRACTION DISTRIBUTION COEFFICIENTS
Effect of phase volume ratio and EHPA concentration
Conditions: Partially reduced liquor, Fe^{3+}: 0.5 g/l
pH: 1.9
Contact time: 1 minute

EHPA Concentration in Solvent	Phase Volume Ratio aq: org	Volume of Liquor per gram mol of EHPA litres	D_E(a)					
			Sc	Y	Yb	Er	Ti	Fe^{3+}
0.1M	1	10	$100^{m(b)}$	30^m	100	10^m	5^m	2
	4	40	100^m	5	25	3	2	-
	8	80	80^m	1	3	1	2	0.3
	16	160	30	1	2	1	2	-
	28	280	20	1	2	1	0.5^m	-
	40	400	10	0.9	2	1	0.5	0.4
0.01M	1	100	10^m	0.02	0.07	0.02	0.3	0.1
	2	200	10^m	0.01	0.02	0.01	0.15	0.05
	3	300	4	-	0.01	-	0.01	-
	4	400	4	0.009	-	0.008	0.05	0.05

(a) D_E - $\frac{\text{concentration in organic}}{\text{concentration in aqueous}}$

(b) m - Minimum figure.

TABLE 16: EXTRACTION DISTRIBUTION COEFFICIENTS
Effect of pH
Conditions: Reduced liquor, Fe^{3+}: nil
Phase volume ratio: 1:1
EHPA 0.1M
Contact time: 1 minute

pH	D_E						
	Sc	Ti	Y	Yb	Er	V	Al
1.5	$30^{m(a)}$	11	10	30	8	0.7	0.002
1.7	30^{m}	3	20	50	10	0.8	0.003
2.0	30^{m}	1	30	100	20	2.0	0.004
$3.0^{D(b)}$	30^{m}	-	50	100	25	2.1	0.02
3.5^{D}	30^{m}	0.2	70	60	40	2.8	0.03

(a) m - Minimum figure.
(b) D - Difficult phase separation due to emulsion.

12.2.6 Insoluble EHPA Compounds

Compounds of EHPA with scandium, yttrium, and lanthanides were shown to be insoluble in kerosene except in the presence of excess free EHPA. In extracts which were loaded to more than approximately 50 per cent of theoretical, gelatinous precipitates of these compounds tended to separate in the organic phase. The gel remained in the organic phase and did not settle very rapidly, hence it was considered possible to operate a mixer-settler unit continuously under conditions which would produce such gel precipitates. The outflowing loaded extract would carry the gel precipitate out of the unit as a uniform suspension.

Ignition of these gel precipitates, after filtration and washing with kerosene, resulted in inorganic phosphates containing 60 to 70 per cent P_2O_5.

Analyses were made spectroscopically for metallic components, and chemically for phosphate. In several carefully controlled tests, the quantity of phosphorus in the precipitate was shown to correspond to the loss of EHPA from the kerosene solution, determined by titration. Also the total gram-equivalents of cations in the precipitate approximately equalled the gram-moles of phosphorus involved, as is the case for compounds of EHPA.

Two analyses of ignited phosphates, obtained from gel precipitates are shown in Table 17.

TABLE 17: ANALYSIS OF EHPA GEL PRECIPITATES
Extracts made from reduced barren liquor at pH 1.7, Fe^{3+} nil, with 0.1M EHPA

		Extract A	Extract B
Phase ratio	$\frac{\text{aqueous}}{\text{organic}}$	5	20
Degree of loading of extract	% of theoretical	60	100
Weight of ignited gel precipitate	g/l of extract	1.2	11.6
Analysis of ignited gel precipitate,	% Sc_2O_3	1.5	9
	ThO_2	1	3
	Y_2O_3	17	14
	Er_2O_3	4	2.5
	Yb_2O_3	10	9
	Al_2O_3	0.2	0.2
	other Ln_2O_3	6	2
	P_2O_5	60	60
	Fe, Ti, Ca, Mg, V	neg(a)	neg

(a) neg - Negligible.

The solubility of EHPA gel compounds in solvents other than kerosene was investigated. An apparently clear solution could be obtained in xylene but the solid could be recovered on a filter paper showing that this was a dispersion rather than a true solution. A true solution could be obtained by prolonged agitation in kerosene containing a large excess of free EHPA.

The effect of various aqueous stripping solutions on a kerosene suspension of gel was determined. Preliminary tests showed no attack by 2N H_2SO_4 and only partial attack by 2N NaOH, but stronger acids, such as 9N H_2SO_4, appeared to attack the gel, stripping the cationic components into the aqueous phase, and re-constituting a clear kerosene solution of free EHPA.

Table 18 sets out the results of tests with aqueous strip solutions using a 0.1M EHPA extract in which a considerable proportion of the cationic load was present as suspended gel precipitate.

TABLE 18: ATTACK OF EHPA GEL PRECIPITATES

Aqueous Strip Solution		Visual Estimate of Rate of Attack of Gel	Degree of Attack[(a)] after 30 min Contact Time
1N	H_2SO_4	no attack	no attack
3N	H_2SO_4	no attack	no attack
10N	H_2SO_4	completely attacked after 5 minutes contact	complete
3N	HCl	partly attacked after 30 minutes contact	45 per cent
10N	HCl	complete within 1 minute	complete
1N	HF	attacked slowly, but complete after 30 minutes	complete
3N	HF	complete within 10 minutes	complete
10N	HF	complete within 1 minute	complete
2N	NaOH	partly attacked	not determined

(a) Calculated from ignited weights of recovered gel.

Later work showed that the strength of aqueous acid required to attack the gel depended on the composition of the gel. Where a high proportion of scandium was present, up to 18N H_2SO_4 was necessary for complete attack. Also the addition of 1 to 2 per cent NaCl to the sulphuric acid solution accelerated the attack.

The gel precipitate formed in 0.01M EHPA extract was found to have similar properties to that from 0.1M extract. For both types of precipitate, treatment with 9N to 18N sulphuric acid was required to produce clear solutions in both phases; i.e., the properties of the gel precipitate, once formed, were independent of the concentration of EHPA in the extract.

12.2.7 Extraction with Sodium-Form EHPA

A comparison of extracts produced from acid-form and sodium-form EHPA solutions respectively, under otherwise similar conditions, showed no significant differences. No alteration of pH of the aqueous phase occurred during extraction with sodium-form solvent, but a slightly lower pH resulted from extraction with acid-form solvent. This was not detectable where large aqueous to organic volume ratios were employed.

Sodium-form solvent, as obtained from caustic soda stripping of a scandium extract, could therefore be recycled directly to extraction of liquor. However, later continuous work showed the desirability of converting the stripped solvent to the acid form prior to extraction from liquor in order to avoid a tendency to form emulsion.

12.2.8 Extraction Distribution Curves

Figures 8 to 17 inclusive show distribution curves for various components drawn from the results of several series of extraction tests. Curves are shown for three different EHPA concentrations, 0.01M (scandium only), 0.1M and 0.2M. Barren liquor used for these tests, containing 0.03 grams per litre Sc_2O_3 (equivalent to 0.02 g/l Sc), was at the normal pH of 1.7 to 1.9. Except where otherwise indicated, ferric ions were partly reduced prior to extraction tests. These distribution curves are not true equilibrium curves because all extraction tests were made with short contact times of 15 to 30 seconds typical of process conditions. The abnormal shapes of the curves for titanium and ferric ions are believed to be due to the large time dependence of the extraction of these ions, and also to the susceptibility of titanium to hydrolysis.

By means of the McCabe-Thiele construction, as shown in some of the above diagrams, the recovery of each component was estimated for a given aqueous to organic flow ratio and a given number of counter-current stages in a continuous system. Information so obtained was used in the design of pilot plant flow sheets. Tables 19 and 20 summarise the information obtained from distribution curves by this means.

TABLE 19: EXTRACTION WITH 0.1M EHPA
Recovery of Components in 3 counter-current stages
Data derived from distribution curves, Figures 8 to 17

Component	Aqueous:Organic Flow Ratio		
	30:1 Recovery %	10:1 Recovery %	2:1 Recovery %
Sc	98	100	100
Th	40	98	100
Yb	25	70	99
Er	10	35	98
Ho	5	15	75
Y	10	30	97

TABLE 20: EXTRACTION WITH 0.1M EHPA
Maximum Aqueous to Organic Flow Ratio which Allows 95% Recovery in 3 Counter-Current Stages
Data derived from distribution curves, Fig. 8 to 17

Component	Maximum Aqueous: Organic Flow Ratio
Sc	30: 1
Th	10: 1
Yb	5: 1
Er	2: 1
Ho	1: 1
Y	2: 1

12.3 Extraction with EHPA in Other Diluents

Diluents other than kerosene were examined in an attempt to overcome the problem of gel formation caused by EHPA compounds precipitating from kerosene solution. Solutions of 0.1M EHPA in the diluents listed in Table 21 were tested as extractants under conditions which caused heavy gel formation in a kerosene solution of 0.1M EHPA. Results are summarised in Table 21.

TABLE 21: EHPA EXTRACTS IN DILUENTS OTHER THAN KEROSENE

Diluent	Extraction of Components	Gel Formation
Benzene	Less than in kerosene	Small
Toluene	Less than in kerosene	Small
Xylene	Comparable with kerosene	Gel separated slowly
Carbon tetrachloride	Comparable with kerosene	Negligible
Nonanol	Comparable with kerosene	Greater than in kerosene

The most promising diluents were xylene and carbon tetrachloride. The latter, being heavier than aqueous solutions, would require an entirely different arrangement of equipment for multi-stage continuous operation, in order to avoid air-lift pumping of the solvent phase. For this reason, and because of their higher cost, these diluents were not seriously considered for large-scale operations. However, laboratory stripping tests were made on extracts prepared in xylene and carbon tetrachloride (Section 12.6).

12.4 Extraction with Other Solvent Reagents

Other available reagents similar to EHPA were tested as extractants under comparable conditions. Mono-dodecyl-phosphoric acid and mono-heptadecyl-phosphoric acid gave extraction results similar to EHPA, but these reagents possessed the disability that alkaline stripping could not be applied, their sodium salts being soluble in aqueous alkaline solutions. Mono-octyl-phosphoric acid and di-n-butyl-phosphoric acid were found to form gel precipitates in excess of that produced by EHPA solutions.

12.5 Stripping of EHPA Extracts in Kerosene

12.5.1 Acid Stripping

Results of stripping tests with a variety of acid reagents are summarised in Table 22 in which equilibrium distribution coefficients are shown for the main components of interest. The majority of stripping tests were made with 0.1M EHPA extracts in kerosene, as this strength reagent appeared most suitable for extraction from barren liquor. Several series of tests were made with extracts obtained with 0.01M, and 0.2M EHPA solutions, but detailed results of these are not presented. Differences between stripping behaviour of these extracts and 0.1M extract were reasonably in accordance with theoretical expectations. Treatment of fully loaded 0.01M EHPA extract (containing gel) with 9N H_2SO_4, not only reconstituted a clear solvent phase, but also stripped a large proportion of the scandium in addition to all other components. With extracts of 0.05M EHPA and stronger, 9N H_2SO_4 did not strip significant proportions of the scandium.

Distribution curves obtained from stripping tests with 9N H_2SO_4 and 0.1M EHPA extracts are shown in Figures 18 and 19. As scandium was the most strongly held component in the extract, and titanium next, acid stripping could be used as a purification step, stripping essentially all components except scandium and part of the titanium. The use of 9N H_2SO_4 or stronger was required to ensure attack of EHPA gel. Such a purification step would provide a means of obtaining scandium free from yttrium and heavy lanthanides, and, vice versa, the yttrium group of components could be recovered free from scandium. This would not be possible with 0.01M EHPA extract where scandium was also stripped with 9N H_2SO_4.

The curves shown in Figures 18 and 19, and similar curves (not reported) resulting from tests with acid reagents of various concentrations, were used to determine operating conditions for continuous pilot-scale tests. Aluminium, although extracted only slightly from barren liquor, was still present in extracts in sufficient concentration to require consideration in stripping. The stripping behaviour of iron, titanium, and aluminium was therefore examined together with that of the more valuable components.

During investigations of the behaviour of EHPA gel precipitates (Section 12.2.6) the addition of sodium chloride to a sulphuric acid strip solution was observed to accelerate the attack on the gel. Following this lead, a detailed study was made of distributions from 0.1M EHPA extracts into a range of sulphuric acid solutions containing chloride.

In sulphuric acid solutions up to 3N, the addition of small quantities of NaCl (1 to 5 per cent weight per volume) increased the stripping coefficients for iron appreciably without affecting the behaviour of other components. With acid concentrations in the region 9N to 12N, greatly increased stripping of yttrium, aluminium, and heavy lanthanides, as well as iron, resulted from chloride additions. The distribution of scandium was not altered.

TABLE 22: ACID STRIPPING OF 0.1M EHPA EXTRACT
Extract initially loaded to 50% of theoretical capacity.
Contact time: 15 minutes

Stripping Reagent	Distribution Coefficient - D_S(a)						
	Sc	Th	Ti	Y	Yb	Fe^{3+}	Al
1N H_2SO_4	0.005	3	0.02	2	1	0.3	2
3N H_2SO_4	0.01	10	0.5	8	4	1.5	8
9N H_2SO_4	0.05	40	1.5	40	20	5.0	12
1N HF	2.0	100^{m}(b)	25.0	100	20	1.0	20
3N HF	30.0	100^{m}	100.0	500	200	7.0	100
3N HCl	0.005	3	0.3	6	5	-	15
10N HCl	0.002	1	0.2	100	50	-	2
2M oxalic acid	0.03	100^{m}	-	100	10	-	150

(a) D_S - $\frac{\text{Concentration in aqueous}}{\text{concentration in organic}}$.

(b) m - Minimum Figures.

12.5.2 Alkaline Stripping

During early experimental work stripping with dilute (0.2N) NaOH or Na_2CO_3 solutions was shown to result in emulsion formation. However, more concentrated NaOH solutions could be used, provided the solvent solution contained at least 2 per cent by volume of nonanol to prevent third phase formation. Some difficulty was experienced in obtaining a clear stripped solvent phase, with the hydroxide precipitate completely settled into the aqueous phase. At a later stage in the investigations, controlled studies of the effect of time of contact, and of alkali concentration, showed that satisfactory stripping of scandium from a purified extract could be achieved. The required concentration of NaOH was 2N to 3N and contact times of 30 minutes or longer were necessary. With shorter contact times, a tendency for EHPA gel precipitates to form in the solvent phase interfered with stripping. Under these conditions, phosphate contamination of the aqueous hydroxide precipitate was noted. However, provided correct conditions were used, a clear stripped solvent phase could be obtained, and the hydroxide precipitate settled completely in the aqueous phase.

Attempts to strip scandium with ammonia were unsuccessful, and with carbonate solutions only partly successful. Potassium hydroxide was more efficient than sodium hydroxide under comparable conditions, but was not considered for use in continuous pilot-scale operations due to its higher cost.

12.5.3 Stripping with Other Reagents

In addition to the acids listed in Table 22 and the alkaline reagents referred to above, various other possible stripping reagents were examined. Results of these tests are shown in Table 23.

TABLE 23: STRIPPING OF 0.1M EHPA EXTRACT WITH VARIOUS REAGENTS
Extract initially loaded to 50% of theoretical capacity.
Contact time: 15 minutes

Stripping Reagent	Distribution Coefficient - D_S[(a)]			
	Sc	Th	Y	Yb
1N NaF	0.2	0.3	0.04	0.04
5N NH_4F	2.0	2.0	2.0	1.0
Sodium oxalate (saturated)	0.03	$0.5^{m(b)}$	0.05	0.05
2M Sodium citrate	0.01^{m}	0.5^{m}	0.03	0.03
2M Citric acid	0.01^{m}	0.1	0.2	0.1
2M Tartaric acid	0.01^{m}	1.0	2.0	1.0
5% EDTA(c) at pH 8	1.0	-	30.0	2.0

(a) $D_S = \frac{\text{Concentration in aqueous}}{\text{concentration in organic}}$

(b) m Maximum figure.

(c) ethylene-diamine-tetra-acetic acid.

12.5.4 Fractional Stripping Tests

Several series of batch tests showed that fractional stripping in steps of increasing acid strength could be used to produce a series of products rich in different components. Typical results are those obtained from a small-scale continuous experiment, using 2 counter-current stripping stages for each of 3 sulphuric acid solutions in turn. Table 24 shows the distribution of components between the 3 strip solutions and the final organic phase. The first strip solution was rich in vanadium, yttrium, and the lanthanides, erbium and dysprosium (also holmium, not shown). The second solution contained most of the thorium and much of the heaviest lanthanides (ytterbium group), while the third acid strip removed the bulk of the remaining heavy lanthanides, leaving a final organic solution containing almost pure scandium, recoverable by alkaline stripping.

TABLE 24: FRACTIONAL STRIPPING TEST
Distribution of components between successive strip solutions and 0.1M EHPA extract

	Distribution - Per cent of Feed								
	Sc	Th	Y	Yb	Er	Dy	Ti	V	Al
1st Strip 0.5N H_2SO_4	$0.1^{m(a)}$	8	66.0	5	56	83.0	0.1^{m}	97.0	31
2nd Strip 2N H_2SO_4	0.1^{m}	84	29.0	50	37	15.0	2.0	2.0	41
3rd Strip 9N H_2SO_4	0.5	6	5.0	39	6	2.0	12.0	1.0	25
Final Organic Solution	99.3	3^{m}	0.1	6	1	0.1	86.0	0.01^{m}	3

(a) m - Maximum figure.

Other fractional stripping systems involving hydrofluroic acid strip solutions were also investigated but are not reported here. The use of a single sulphuric acid strip as a purification step, followed by alkaline stripping to recover a high-grade scandium hydroxide product, was considered the most useful system, and was studied in several series of batch experiments before application to continuous operations.

12.6 Stripping of EHPA Extracts in Other Diluents

Extracts produced with 0.1M solutions in xylene and carbon tetrachloride did not form gel precipitates as readily as kerosene extracts (Table 21). These extracts were investigated for stripping behaviour with 9N H_2SO_4 and 2.5N NaOH. In the xylene extract, all components were stripped with sulphuric acid more readily than from its kerosene counterpart, but NaOH stripping was unsuccessful, resulting in the formation of EHPA gel precipitate in the solvent phase. The carbon-tetrachloride extract behaved similarly to kerosene solutions without formation of gel precipitate.

13. SMALL-SCALE CONTINUOUS TESTS

13.1 General

Early in these investigations several litres of EHPA extract were required for systematic batch stripping tests. Although little was known at that time regarding the best operating conditions for continuous extraction from barren liquor, this quantity of extract could be produced most conveniently by continuous operation. Accordingly, the first continuous experiment in these investigations was set up as a 2-stage counter-current extraction system (Figure 20) producing 6 litres of bulk extract from approximately 40 litres of barren liquor.

Later, the results of batch experiments were confirmed by a series of continuous extraction and stripping tests, providing design information for pilot-scale tests.

13.2 Equipment and Procedures

Box type mixer-settler units with mixer capacity 300 ml and settler capacity 1,000 ml and constructed entirely of perspex were used. Each unit had provision for internal re-cycle of the solvent phase, allowing overall flow ratios up to 30 aqueous to 1 organic to be used, while still maintaining an excess of organic over aqueous in the mixer. For extraction tests, liquor feed-rates of 150 ml per minute were employed, corresponding to a nominal residence time of 40 seconds in each mixer. For stripping tests, the extract feed flow-rate was 25 ml per minute, equivalent to a residence time of approximately 10 minutes in each mixer. Interface levels in the settlers were controlled by adjustment of overflow legs. All connections were made with nylex tubing.

Samples were taken from the system when equilibrium was assumed to have been established after the total solvent inventory of the system had been replaced twice, with all feed solutions at the correct, steady flow-rates, and the mixers operating satisfactorily over the period. A second set of samples was taken after a period of equilibrium operation of sufficient duration to replace the solvent inventory once more. Results from the two sets of samples were averaged to simplify calculations and reporting. Operation of each mixer was checked periodically by determining the phase volume ratio in the mixed zone. This was normally 2 solvent to 1 aqueous. Radioactive scandium, used in some tests, enabled more accurate determination of scandium than was possible by spectroscopy.

13.3 Continuous Extraction Tests

Results of the preliminary continuous extraction test mentioned above are given in Table 25. Two mixer-settler units were connected for counter-current operation as in Figure 20. Barren liquor at pH 1.6, with ferric ions reduced to nil, was extracted with 0.1M EHPA solution in kerosene at a flow ratio of 5 aqueous to 1 organic. An aqueous flow of 100 ml per minute and a solvent flow of 20 ml per minute were maintained for this test. The hydrolysate which formed in the feed liquor after reduction of ferric ions was separated before extraction by allowing it to settle and then decanting the clear reduced liquor. It may be noted in Table 25 that a negative figure is recorded for the extraction of vanadium in the first stage. Vanadium, extracted in the second stage by fresh solvent, was displaced back to the aqueous phase in the first stage by more strongly extracted components entering that stage in the fresh liquor.

TABLE 25: PRELIMINARY CONTINUOUS EXTRACTION TEST
2-Stage Extraction with 0.1M EHPA
Flow-ratio: 5 aq:1 org
Liquor pH.: 1.6
Fe^{3+} nil

Component	Analysis of Extract g/l	Extraction in each Stage, as per cent of Feed		
		1st Stage[a]	2nd Stage	Total
Sc	0.2	95.0	5.0	100.0
Th	0.2	90 0	10.0	100.0
Y	0.95	26.0	67.0	93.0
Yb	0.35	81 0	18.0	99.0
V	0.06	minus 12.0	16.0	4.0
Fe(total)	0.05	0.02	0.03	0.05
Al	0.06	0.2	0.1	0.3

(a) 1st Stage refers to that cell into which fresh liquor is fed.

Further continuous extraction tests were made in a 3-stage counter-current system, using a range of flow ratios up to 30 aqueous to 1 organic. Tables 26 to 28 summarise results of tests at flow ratios up to 10. Higher ratio tests were made with added radioactive scandium, and results of these tests for scandium only, are given in Table 29. In these tables "first stage" refers to the point of liquor feed, and "third stage" is the fresh solvent stage.

Physically, the system operated satisfactorily at all flow ratios. In high ratio tests, EHPA gel formed in fully loaded solvent extract in the first stage. By modifying the solvent overflow tube to draw off the extract from below the surface of the solvent phase in the settler, any build-up of gel was controlled. Such cells were run continuously for more than 2 days without difficulty. However, if gel were allowed to build up in the solvent phase of a settler and eventually to re-cycle internally to the mixer, operation of the mixer was upset, with consequent inefficient extraction.

Extracts obtained at high flow-ratios were richer in scandium with lower recoveries of other components, as indicated by Figure 6. The more accurate distribution curves for scandium, drawn from radiometric assays, agreed reasonably well with curves drawn from earlier results obtained by averaging spectroscopic assays.

TABLE 26: CONTINUOUS EXTRACTION TEST 1
3-Stage Extraction with 0.1M EHPA
Flow-ratio: 5 aq:1 org
Liquor pH : 1.55
Fe^{3+} : 0.2 g/l

Component	Analysis of Extract[(a)] g/l	Extraction in each Stage, as per cent of Feed			
		1st Stage	2nd Stage	3rd Stage	Total
Sc	0.21	93.0	6.4	0.6	100.0
Th	0.19	53.0	43.0	4.0	100.0
Y	0.68	11.0	14.0	29.0	54.0
Yb	0.42	37.0	39.0	15.0	91.0
Er	0.08	2.0	10.0	28.0	40.0
V	0.01	- 1.4	0.1	2.8	1.5
Fe(ferric)	0.37	7.0	10.0	10.0	27.0
Al	0.02	0.03	0.03	0.04	0.10
Ti	0.07	23.0	15.0	15.0	53.0

(a) As elements.

TABLE 27: CONTINUOUS EXTRACTION TEST 2
3-Stage Extraction with 0.1$\underline{M}$ EHPA.
Flow-ratio: 7.5 aq: 1 org
Liquor pH : 1.55
Fe^{3+} : 0.1 g/l

Component	Analysis of Extract$^{(a)}$ g/l	Extraction in each Stage, as per cent of Feed			
		1st Stage	2nd Stage	3rd Stage	Total
Sc	0.30	89.0	10.3	0.7	100.0
Th	0.48	50.0	42.0	8.0	100.0
Y	0.78	20.0	7.0	25.0	52.0
Yb	0.60	29.0	38.0	20.0	87.0
Er	0.11	13.0	16.0	17.0	46.0
Fe(ferric)	0.49	12.0	26.0	18.0	56.0
V	0.02	-0.3	-0.5	2.8	2.0
Al	0.04	0.05	0.03	0.03	0.11
Ti	0.12	15.0	32.0	16.0	63.0

(a) As elements.

TABLE 28: CONTINUOUS EXTRACTION TEST 3
3-Stage Extraction with 0.1$\underline{M}$ EHPA
Flow-ratio: 10 aq: 1 org
Liquor pH : 1.55
Fe^{3+} : 0.1 g/l

Component	Analysis of Extract$^{(a)}$ g/l	Extraction in each Stage, as per cent of Feed			
		1st Stage	2nd Stage	3rd Stage	Total
Sc	0.39	90.0	9.5	0.5	100.0
Th	0.54	37.0	48.0	15.0	100.0
Y	0.67	11.0	3.0	22.0	36.0
Yb	0.91	39.0	25.0	25.0	89.0
Er	0.12	10.0	3.0	26.0	39.0
V	0.005	-0.7	-0.5	1.5	0.3
Fe (ferric)	0.52	6.0	13.0	8.0	27.0
Al	0.02	-0.01	0.02	0.03	0.04
Ti	0.10	9.0	9.0	12.0	30.0

(a) As elements.

TABLE 29: CONTINUOUS EXTRACTION TESTS 4, 5, AND 6
3-Stage Extraction with 0.1M EHPA
Radio-active Scandium added to Liquor Feed
pH : 1.55
Fe^{3+}: 0.1 g/l

			Test 6	Test 5	Test 4
Flow ratio	aq/org		18	24	30
Sc in extract	g/l (element)		0.69	0.91	1.06
Extraction of scandium in each stage:	% of feed	1st stage	68.0[(a)]	82.0	68.0
		2nd "	28.0	15.0	26.0
		3rd "	3.0	2.7	5.7
		Total	99.0	99.7	99.7

(a) Mixer was operating inefficiently during this test.

13.4 Extraction from Hydrolysed Liquor Slurry

Normally, after reducing ferric ions completely in barren liquor, any hydrolysed solids were separated before extracting from the clear liquor. This could result in appreciable loss of scandium as is shown in Section 12.1 (Table 12). The alternative procedure of maintaining sufficient ferric ions in solution to prevent hydrolysis would not always be desirable, as ferric ions interfered considerably in extraction of certain components.

Preliminary batch tests showed that hydrolysed reduced liquor, in the form of a slurry, could be extracted directly. In addition to extracting scandium from the liquor, some scandium was also recovered from the hydrolysate. This type of extraction, if feasible, would minimise the loss of scandium caused by co-precipitation in the hydrolysate.

A 2-stage continuous extraction test was run for several hours to establish the feasibility of operating with hydrolysed liquor feed. No difficulty was experienced with phase disengagement in the settlers and no emulsion was formed. In fact, less scum and gel collected at the settler interfaces than occurred during extraction from unreduced liquor. Loss of solvent reagent (EHPA) by adsorption or entrainment on solids in the aqueous phase was checked during this test and was shown to be very small. Operation over a longer period would be required to establish the actual level of solvent losses. Scandium assays on hydrolysate solids before and after extraction showed that 60 per cent of the scandium associated with the solids was extracted, in addition to liquor scandium.

13.5 Continuous Stripping Tests

The extracts produced in continuous extraction tests (Section 13.3) were combined to form a bulk feed solution for continuous stripping tests. This solution contained a large proportion of gel precipitate which was kept in suspension by stirring while tests were being run, giving a reasonably uniform proportion of suspended gel in the feed to the stripping tests. Table 30 shows an analysis of the bulk extract.

TABLE 30: ANALYSIS OF BULK EXTRACT
Used for continuous stripping tests

	Total Concentration of Components gel plus clear solution g/l	Proportion of Component in gel %
Sc	0.33	40
Th	0.34	20
Y	0.27	80
Yb	0.38	80
Er	0.07	70
V	0.01	10
Fe	0.45	15
Al	0.02	10
Ti	0.11	10

As scandium tracer had been used in some of the extraction tests, sufficient activity was present in the bulk extract to allow scandium to be determined radiometrically in stripping tests. Other components were determined spectroscopically except iron which was determined colorimetrically.

In each of 4 separate tests, a multi-stage purification stripping section was used to strip most components except scandium, followed by a 2-stage scandium recovery section using alkaline or strong hydrofluoric acid stripping. Conditions for each test are shown with a summary of the results in Tables 31 to 34. At the time these tests were made, it was believed that the purification strip reagent (9$\underline{N}$ H_2SO_4 or 1$\underline{N}$ HF) would completely decompose gel suspended in the extract (Table 18, Section 12.2.6) but, in all tests, unattacked gel accumulated in the settler of the first acid stripping stage. The quantity of accumulated gel was estimated, and a separate sample analysed in each test.

In the final alkaline stripping section (Tests 9 and 10), some entrainment of each phase in the other occurred, considerably reducing stripping efficiency and also contaminating the scandium hydroxide precipitate with phosphate derived from EHPA. At the time these tests were run, detailed studies of alkaline stripping had not been made. Later work showed that most of the trouble could be overcome by using a longer contact time.

TABLE 31: CONTINUOUS STRIPPING TEST 9

Flow ratio:	7 org:1 aq
1st Strip, 5 stages:	9N H_2SO_4
2nd Strip, 2 stages:	2N NaOH
Contact time:	10 min each stage

	Distribution of Components, as Percentage of Feed			
	Gel Accumulated in No. 1 Cell	Stripped by 9N H_2SO_4	Stripped by 2N NaOH	Remaining in Stripped Solvent
Sc	23	2	67.0	8
Th	52	47	0.3	-
Y	68	32	0.02	-
Yb	76	24	0.1	-
Er	74	25	1.0	-
Fe	6	89	5.0	-
Al	56	38	6.0	-
Ti	11	39	49.0	1

TABLE 32: CONTINUOUS STRIPPING TEST 10
Flow ratio: 3 org:1 aq
1st Strip, 5 stages: 9N H_2SO_4
2nd Strip, 2 stages: 2N NaOH
Contact time: 10 min each stage

	Distribution of Components, as Percentage of Feed			
	Gel Accumulated in No. 1 Cell	Stripped by 9N H_2SO_4	Stripped by 2N NaOH	Remaining in Stripped Solvent
Sc	27	3	48	22
Th	46	54	-	-
Y	58	42	-	-
Yb	75	25	-	-
Er	59	40	1	-
Fe	5	94	1	-
Al	39	58	3	-
Ti	10	41	48	1

TABLE 33: CONTINUOUS STRIPPING TEST 11
Flow ratio: 2 org: 1 aq
1st Strip, 2 stages: 1N HF
2nd Strip, 2 stages: 10N HF
Contact time: 10 min each stage

	Distribution of Components, as Percentage of Feed			
	Gel Accumulated in No. 1 Cell	Stripped by 1N HF	Stripped by 10N HF	Remaining in Stripped Solvent
Sc	42	38	19.0	1.0
Th	56	42	2.0	-
Y	79	19	2.0	0.05
Yb	74	22	3.0	0.2
Er	85	13	2.0	0.05
Fe	5	70	25.0	-
Al	18	69	12.0	1.0
Ti	13	82	3.5	1.5

TABLE 34: CONTINUOUS STRIPPING TEST 12
Flow ratio: 3 org: 1 aq
1st Strip, 4 stages: $12\underline{N}\ H_2SO_4$
2nd Strip, 2 stages: $2\overline{N}a_2CO_3$
Contact time: 10 min each stage

	Distribution of Components, as Percentage of Feed			
	Gel Accumulated in No. 1 Cell	Stripped by $12\underline{N}\ H_2SO_4$	Stripped by $2\underline{N}\ Na_2CO_3$	Remaining in Stripped Solvent
Sc	3	11	68.0	18
Th	60	40	-	-
Y	37	62	0.4	-
Yb	37	62	0.4	-
Er	40	56	4.0	-
Fe	14	81	5.0	-
Al	21	72	6.0	1
Ti	5	32	61.0	2

Stripping distribution curves were plotted for each component from assays of samples taken from each phase of each cell in the stripping system while operating in equilibrium. For $9\underline{N}\ H_2SO_4$, results confirmed those obtained by batch tests (Fig. 18 and 19). Stripping with $12\underline{N}\ H_2SO_4$ was less effective than with $9\underline{N}\ H_2SO_4$, although a greater degree of attack on the extract gel was obtained. Distribution curves were drawn for components in HF stripping systems, but these are not presented in this report as it appeared unlikely that HF would be used in preference to the H_2SO_4 and NaOH stripping system.

A further continuous stripping test was made with sulphuric acid at three different concentrations in a fractional stripping system. This test, described in Section 12.5.4, used a clear solvent extract, free from gel, as feed solution, hence no gel accumulation problem was encountered.

14. DISCUSSION OF SOLVENT EXTRACTION RESULTS

Of the barren liquor components extracted by EHPA solutions in kerosene, scandium was the most strongly extracted. This fact could be used to produce a relatively high-grade scandium product by a simple solvent extraction process. Recovery of thorium, yttrium, and heavy lanthanides (lutecium to holmium inclusive) was also shown to be possible by using a greater proportion of solvent. Although Blake and co-workers[8] described the extraction of vanadium with EHPA, this component was difficult to extract from Port Pirie barren liquor. A significant recovery of vanadium could be obtained by extracting with more concentrated EHPA solution (e.g., 0.5M), raising the pH of the liquor to as high a level as practicable, and completely reducing ferric ions in the liquor. The behaviour of vanadium in continuous extraction tests (Tables 25 to 28) showed that some of this component, extracted in the fresh solvent stage, was then displaced back into the liquor by more strongly extracted components introduced in the fresh liquor stage.

Extraction conditions for stated recoveries of particular components (Tables 19 and 20) were obtained from McCabe-Thiele constructions on extraction distribution curves (Fig. 8 to 17). If scandium were the only desired product, a considerable initial concentration could be obtained by extracting at the highest possible flow-ratio of liquor to solvent (30:1) which would permit good recovery of scandium, but would limit the extraction of other components. An alternative method of achieving the same effect would be to extract with EHPA solution at lower concentration (0.01M) which would result in a greater proportion of scandium in the extract load (Fig. 6 and 7).

Fully loaded extracts, both 0.1M and 0.01M EHPA, formed insoluble EHPA gel precipitates requiring special treatment. This is discussed below.

The system of separating components into groups by fractional extraction with successive solvents of increasing EHPA concentration was considered at one stage. However, this would involve repeated treatment, through replicate large extraction equipment, of large volumes of barren liquor. It was decided to adopt the principle of extracting all desired components in one treatment of barren liquor. Fractionation of components could then be more easily and economically achieved in the smaller equipment of the stripping section.

In the extraction process, separation factors of more than 1,000 were obtained between scandium and the major unwanted components, ferrous ions and aluminium. Major contaminants in EHPA extracts were normally titanium and ferric ions. These could be limited in several ways:

i. Complete reduction of ferric ions in barren liquor before extraction, the resulting hydrolysate then being separated, with some loss of scandium and thorium.

ii. Partial reduction of ferric ions to a level just sufficient to prevent hydrolysis of titanium before extraction.

iii. Extraction from barren liquor, untreated, using very short contact times in the extraction mixers.

iv. Extraction at sufficiently high aqueous to solvent flow-ratio such that scandium would displace unwanted components.

Loss of scandium in (i.), due to co-precipitation with the hydrolysate, could be minimised by extracting from the reduced liquor slurry containing suspended hydrolysate (Section 13.4), but the method was not considered to be sound. The main effect in procedures (ii.) and (iii.) would be to lessen extraction of ferric ions, without much effect on titanium extraction. These two procedures were preferred to (i.), being simpler and less likely to cause physical difficulties. Confirmation of the time effect on extraction of ferric ions was shown by the continuous tests (Tables 25 to 28). Much the same quantity of iron was extracted in each stage, as distinct from the behaviour of other components whose distribution was close to equilibrium in each stage. Procedure (iv.) would be suitable where scandium was the only desired product. A further method of limiting titanium extraction by raising the pH of the liquor was suggested by the results in Table 16. It was considered that increasing hydration of the Ti^{4+} ion at higher pH levels caused this reversal of theoretical behaviour, but the utilisation of this property in practice would probably not be feasible due to the tendency for emulsion formation with liquor at pH 2.5 or higher.

Procedure (iv.) would yield a fully loaded extract containing EHPA gel precipitate referred to above. Treatment of such gel suspensions, to reconstitute a clear EHPA solvent phase, required contacting with sulphuric acid of at least $9\underline{N}$ concentration (Table 18). For $0.1\underline{M}$ EHPA extracts, this acid strip was also suitable for removing all components except scandium (i.e., a purification strip, Table 22). However, with $0.01\underline{M}$ EHPA extracts, $9\underline{N}$ H_2SO_4 also stripped a large proportion of scandium, thus an acid purification strip was not possible with the weaker solvent. For this reason, a solvent reagent concentration of $0.1\underline{M}$ EHPA was considered as the minimum which could have practical application. Continuous stripping operations (Tables 31 to 34) showed that stronger acid than $9\underline{N}$ might be required for complete attack of EHPA gel. However, the addition of chloride to the sulphuric acid was beneficial, serving the dual purpose of accelerating attack on EHPA gel and improving the stripping distribution of yttrium, lanthanides, aluminium, and iron. It was considered that $9\underline{N}$ H_2SO_4 containing 1 per cent NaCl would be a suitable reagent for acid purification stripping of a $0.1\underline{M}$ EHPA extract containing gel precipitate.

In continuous multi-stage counter-current operations, any build-up of gel precipitate in the extraction section was successfully prevented by modifying the solvent overflow, so that outgoing solvent extract was drawn from well below the surface of the solvent in the settler. However, the suspended gel entering the acid stripping section was not attacked as expected and accumulated in the settler of the first acid stripping cell. In addition to using stronger acid containing chloride as mentioned above, this difficulty could be partly overcome by diluting the fully loaded extract with fresh hydrogen-form solvent before entering the stripping section. It was shown (Section 12.2.6) that EHPA gel precipitates would gradually dissolve in excess free EHPA solution.

Despite initial difficulties in obtaining a clear stripped solvent phase, stripping with NaOH solution proved to be effective for final recovery of scandium as hydroxide. Long contact times of 30 minutes or more and

NaOH concentrations of 2N to 3N gave the most efficient stripping. Stripped solvent, containing EHPA in sodium-form, could be re-cycled directly to the extraction section if desired, or converted to hydrogen-form by separate acid treatment.

The only acid strip reagent which removed scandium effectively from 0.1M EHPA extract was strong hydrofluoric acid (10N). Difficulties of handling and of recovering scandium from the fluoride solution were such that alkaline stripping was preferred.

Losses of EHPA and nonanol to the aqueous solutions could not be measured in small-scale tests. A small loss of EHPA to alkaline stripping solutions was expected, but this was known to decrease with increasing concentration of alkali. Blake, Brown, and Coleman[8] determined the solubility of EHPA as 300 ppm in 0.5M NaOH and only 7 ppm in 2.5M NaOH. Entrainment in the raffinate would probably be the most significant loss, and this could be determined only be continuous operation on a larger scale for a suitable period.

15. CONCLUSIONS ON SOLVENT EXTRACTION

15.1 General

Solvent extraction from Port Pirie barren liquor, using EHPA solution in kerosene, has been shown to be a feasible process for recovery of scandium alone or, alternatively, scandium plus thorium, yttrium, and heavy lanthanides. The only pre-treatment of liquor required is partial or complete reduction of ferric ions by contacting the liquor with metallic iron. Conditions for extraction and stripping, and strengths of reagents, can be chosen to achieve various separations, resulting in several types of products. Outlines of the two main suggested processes are given below.

15.2 Possible Solvent Extraction Processes

15.2.1 Scandium Production

Figure 21 shows a simplified flow-diagram for a proposed scandium recovery process. Main steps in this process would be:

1. Reduction of ferric ions in barren liquor to as low a level as possible without causing titanium to precipitate. Concentration of ferric ions would be reduced from approximately 4 grams per litre to 0.5 grams per litre.
2. Extraction from reduced barren liquor with 0.1M EHPA in kerosene containing 2 per cent nonanol. Three counter-current stages, each with a contact time of 30 seconds or shorter, and a flow ratio of 30 aqueous to 1 organic, would extract essentially all of the scandium.

Other extractable components would be only partly recovered. Major contaminants in the extract would be iron and titanium.

3. Dilution of the extract with an equal volume of hydrogen-form solvent to assist in dissolving the gel precipitate.

4. Purification of the extract by stripping with 9<u>N</u> or stronger H_2SO_4 containing 1 per cent NaCl. Five or more counter-current stages, with a flow-ratio of 3 organic to 1 aqueous and a contact time of 5 minutes in each stage, would strip essentially all components except scandium and part of the titanium.

5. Stripping of scandium with 2<u>N</u> NaOH solution. Several mixers in cascade, followed by one separator, would provide the necessary length of time of contact. Clear stripped solvent would be re-cycled to the extraction section via an acidification section (to provide hydrogen-form EHPA for extract dilution).

6. Recovery of hydroxide product by centrifuging or filtering the caustic soda slurry from the stripping section. Clear NaOH solution could be made up to volume and strength and re-cycled. Filtered scandium hydroxide would probably require further treatment before drying and ignition as a scandium oxide product.

15.2.2 Scandium, Thorium, Yttrium, and Heavy Lanthanide Production

Recovery of these components could be achieved by a similar process to that for scandium alone, with the following modifications:

1. Complete reduction of ferric ions in barren liquor. This would result in formation of a titanium hydrolysate.

2. Extraction from reduced liquor with hydrolysate in suspension. Three stages, as above, but with a flow ratio of 1 organic to 1 aqueous, would completely extract scandium, thorium, yttrium, and lanthanides heavier than holmium.

3. Fractional acid stripping. Several different products containing yttrium, thorium, and heavy lanthanides could be recovered by fractional stripping with sulphuric acid of several different strengths (Section 12.5.4), or by complete stripping of these components with strong sulphuric acid followed by fractional re-extraction of the loaded strip solution to separate the various products. Other fractional stripping systems, using reagents such as oxalic acid and hydrofluoric acid, could also be considered here. Scandium product would be recovered by final alkaline stripping as in the process for scandium alone.

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FIGURE 1: PRECIPITATION AS HYDROXIDES
Port Pirie Barren Liquor

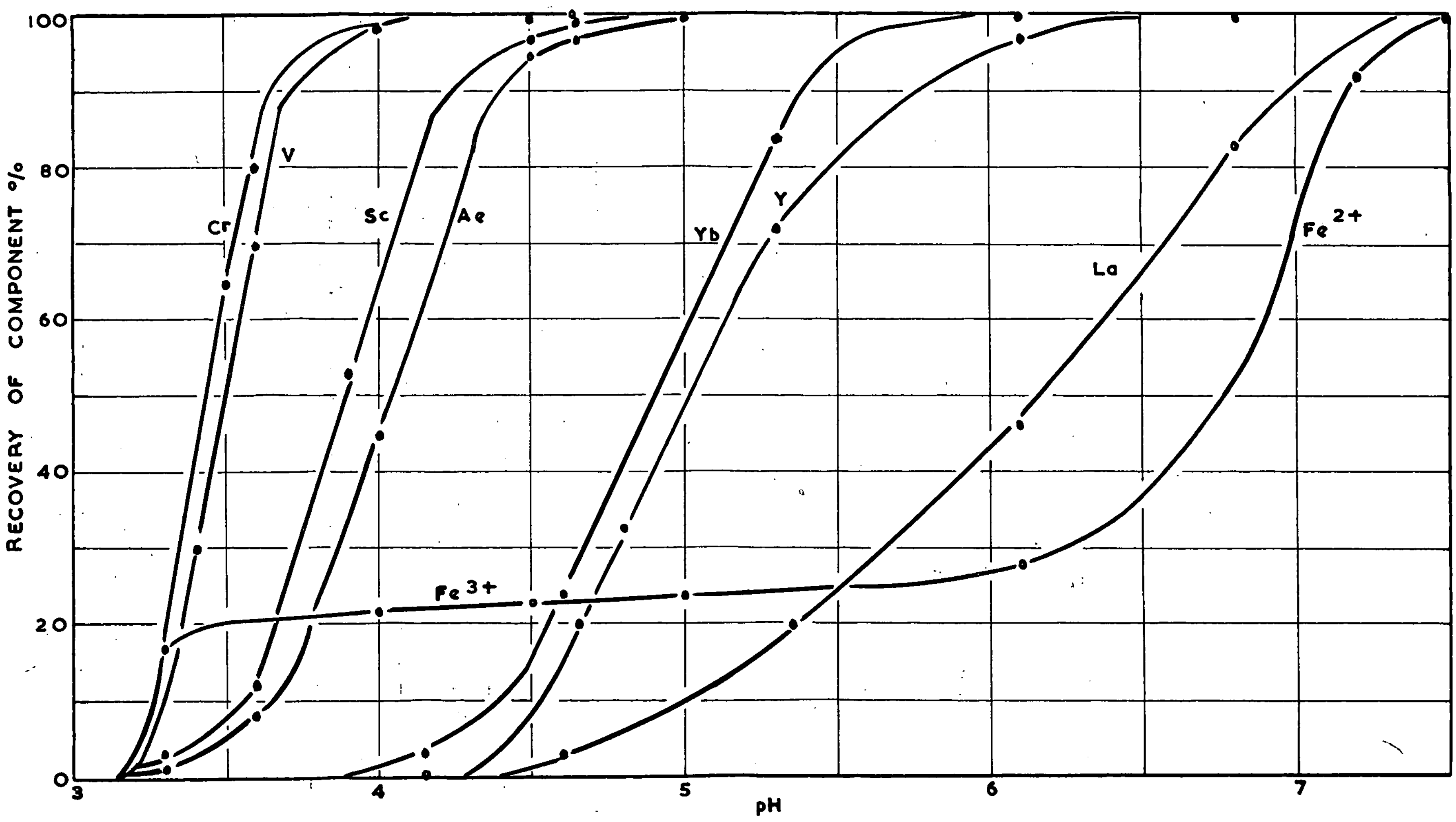


FIGURE 2: LEACHING OF IGNITED PRECIPITATES WITH 0.05$\underline{M}$ HCl AT 20°C

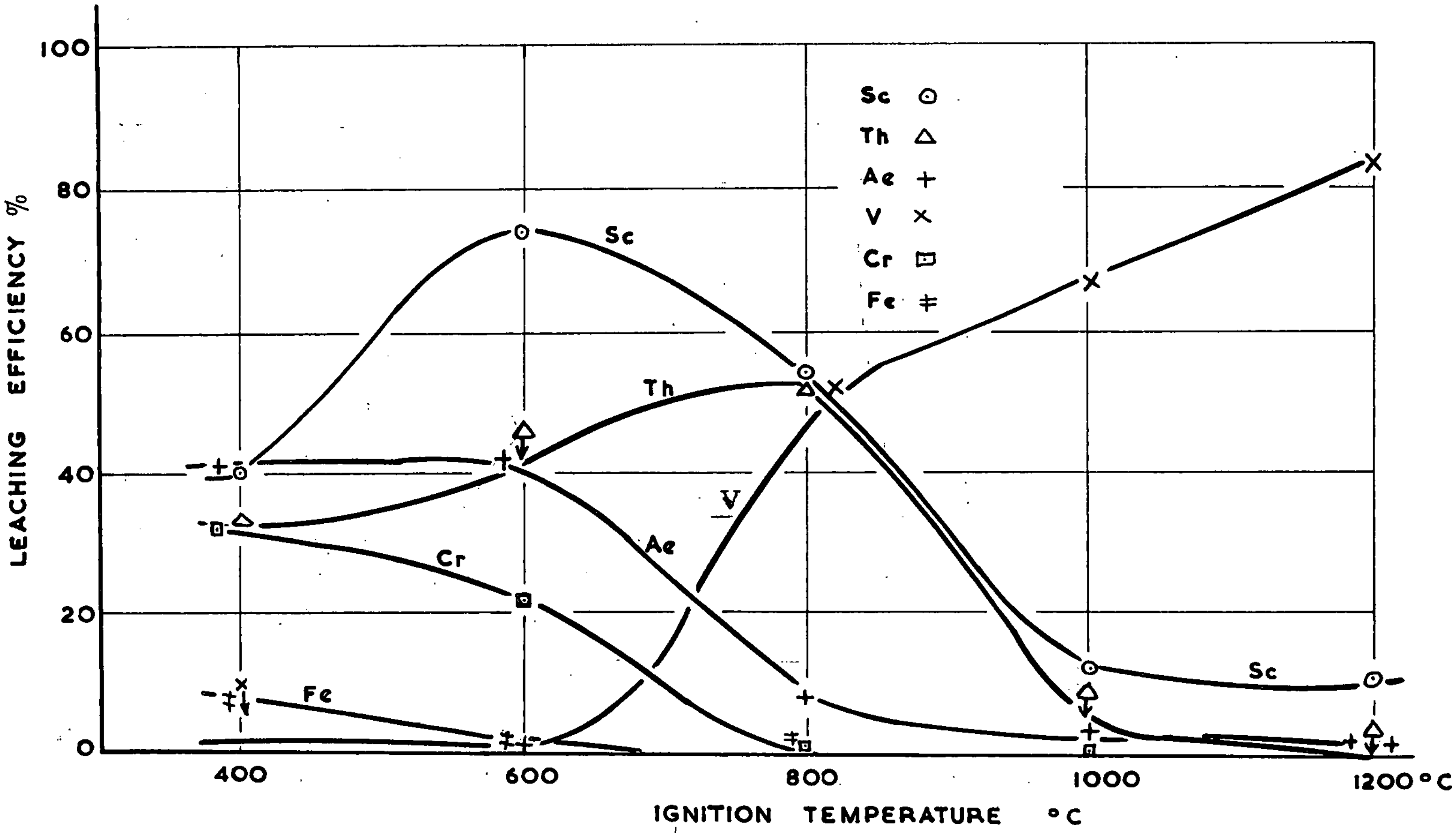
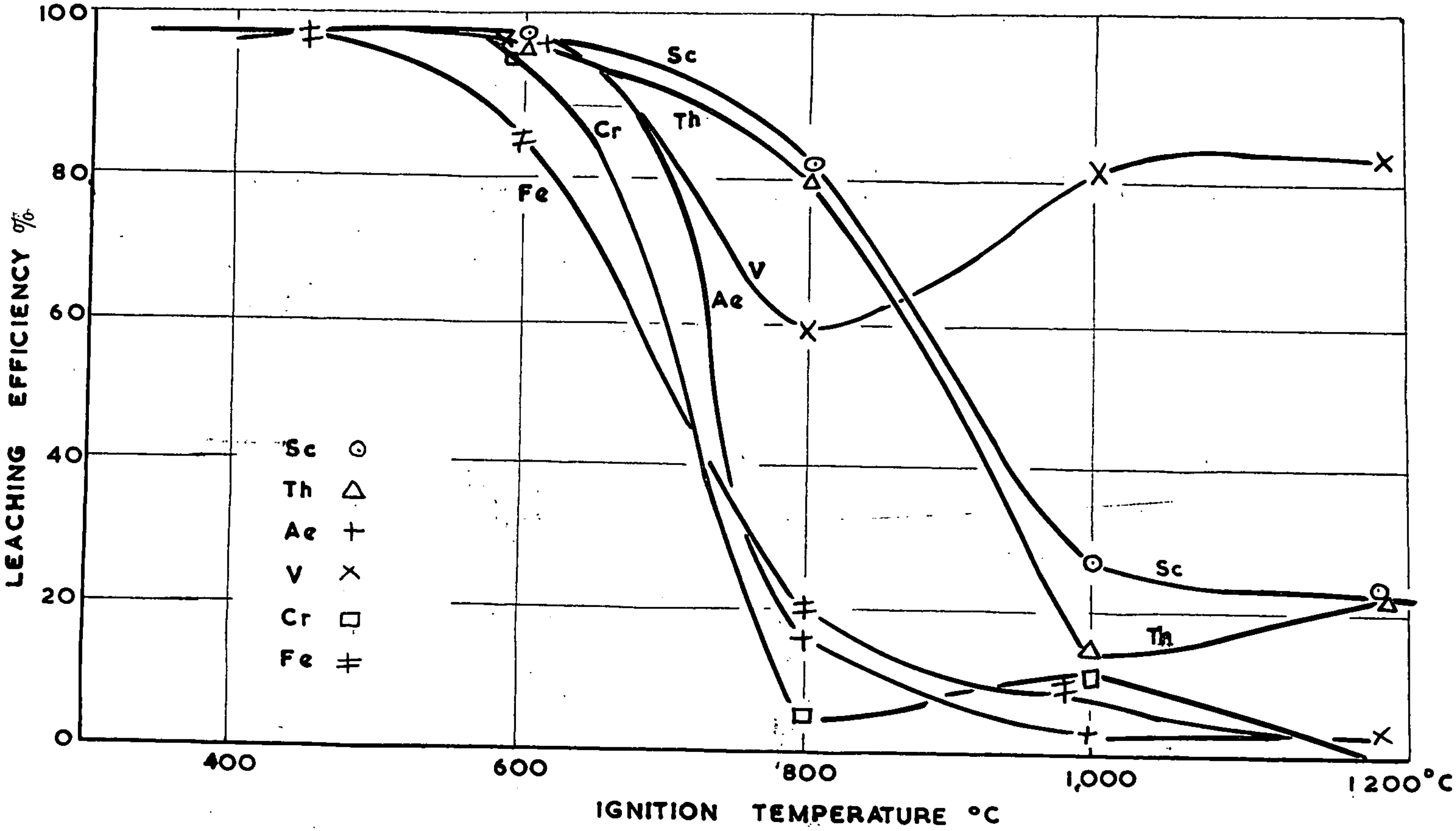


FIGURE 3: LEACHING OF IGNITED PRECIPITATES WITH 1$\underline{M}$ HCl AT BOILING TEMPERATURE



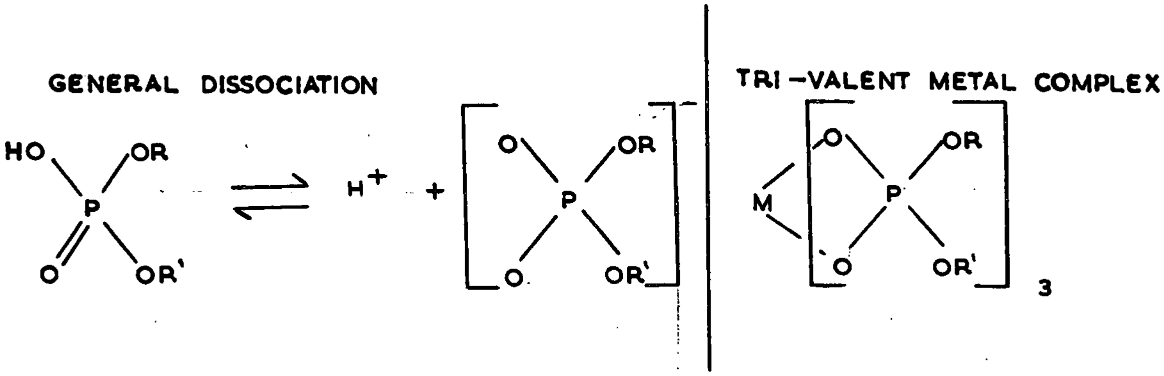


FIGURE 4: POSTULATED EXTRACTION MECHANISM WITH EHPA

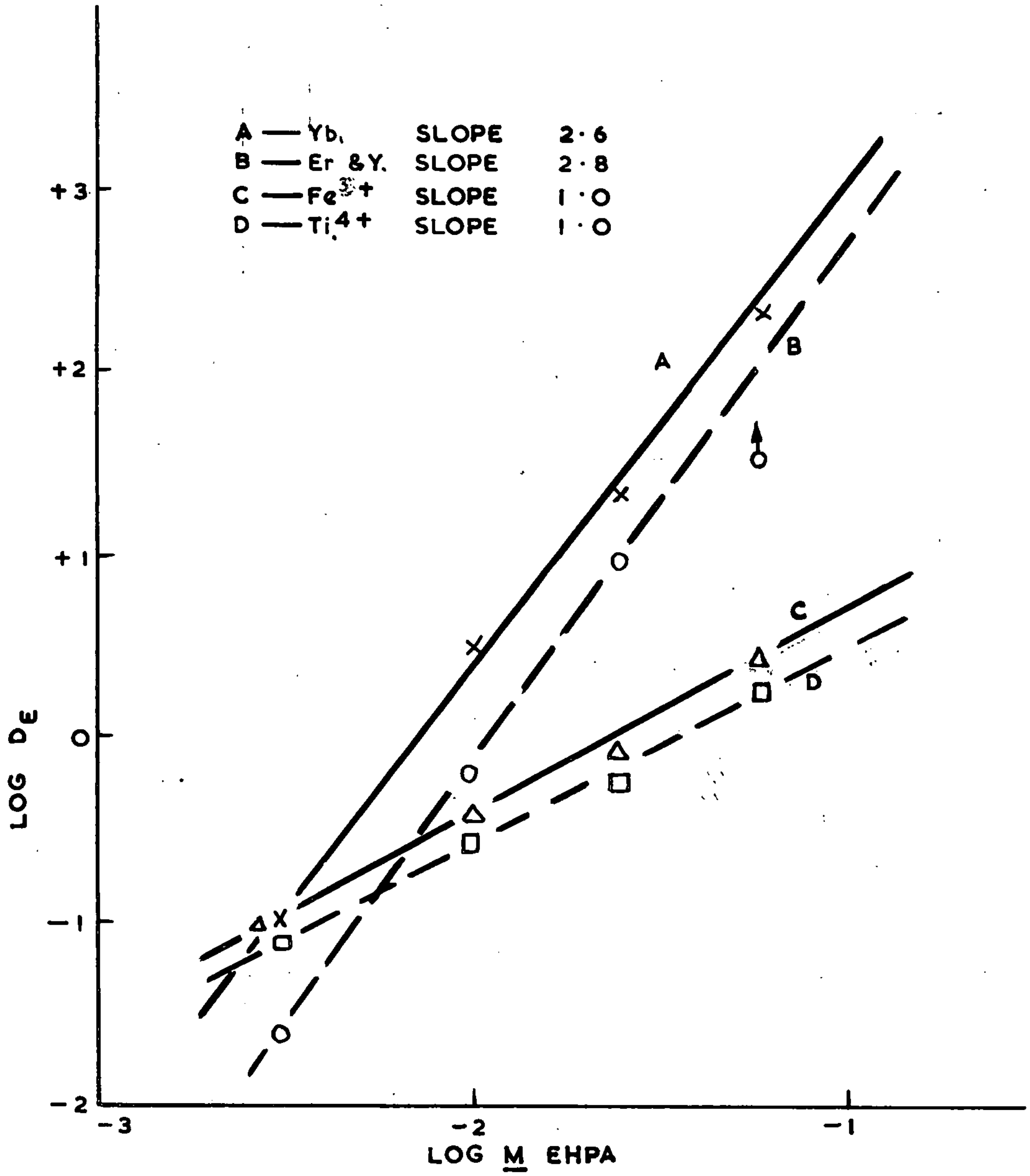


FIGURE 5: EFFECT OF CONCENTRATION OF EHPA ON EXTRACTION OF COMPONENTS

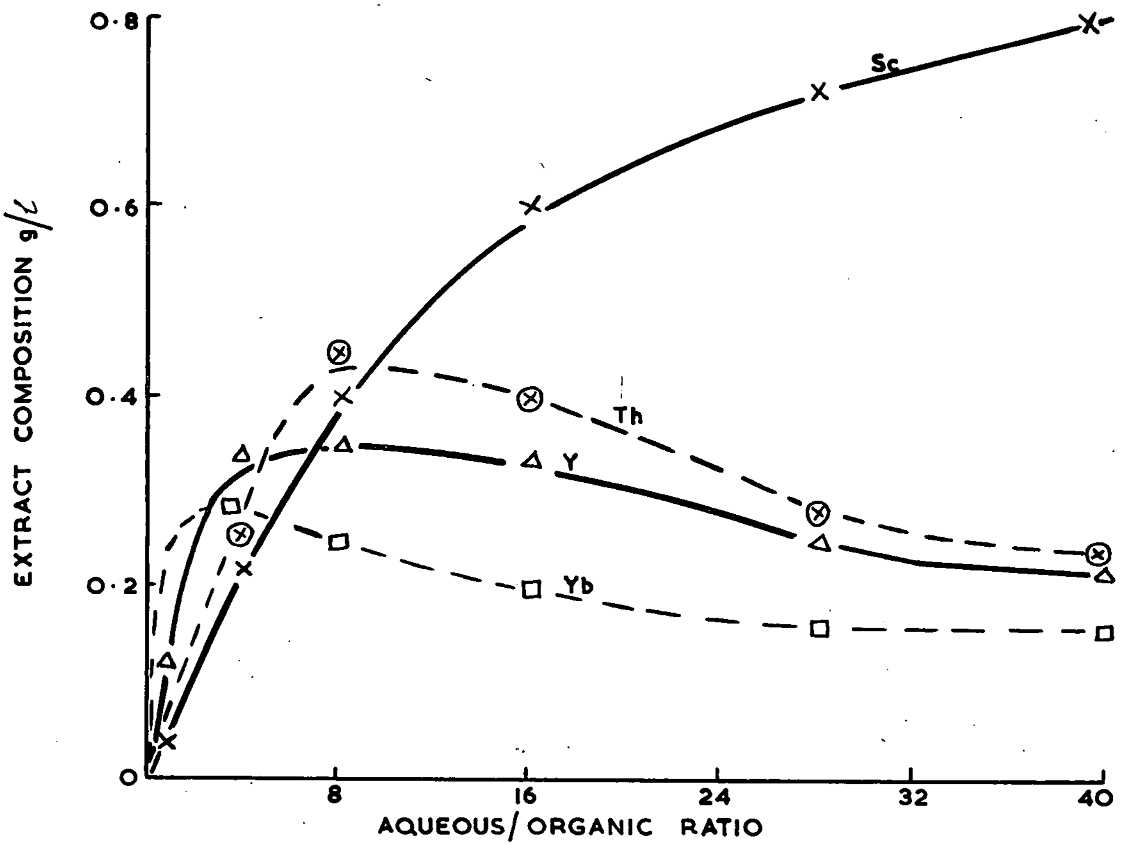


FIGURE 6: EXTRACTION WITH 0.1M EHPA - EFFECT OF VOLUME RATIO ON EXTRACT COMPOSITION

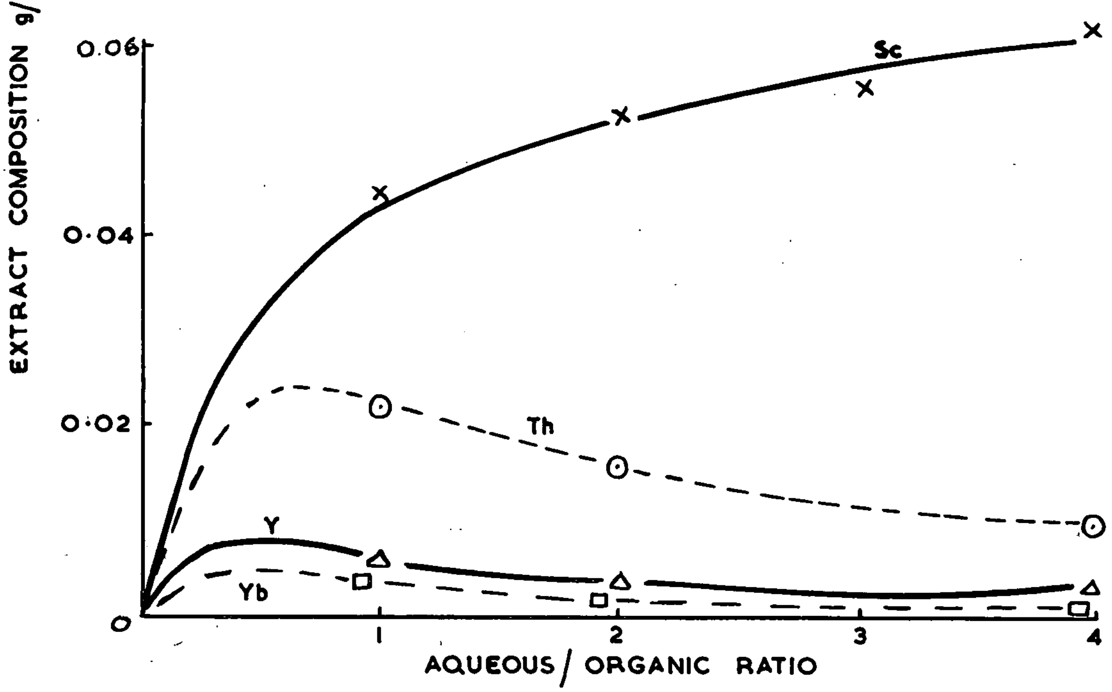


FIGURE 7: EXTRACTION WITH 0.01M EHPA - EFFECT OF VOLUME RATIO ON EXTRACT COMPOSITION

FIGURE 8: SCANDIUM DISTRIBUTION CURVE - EXTRACTION WITH 0.01$\underline{M}$ EHPA

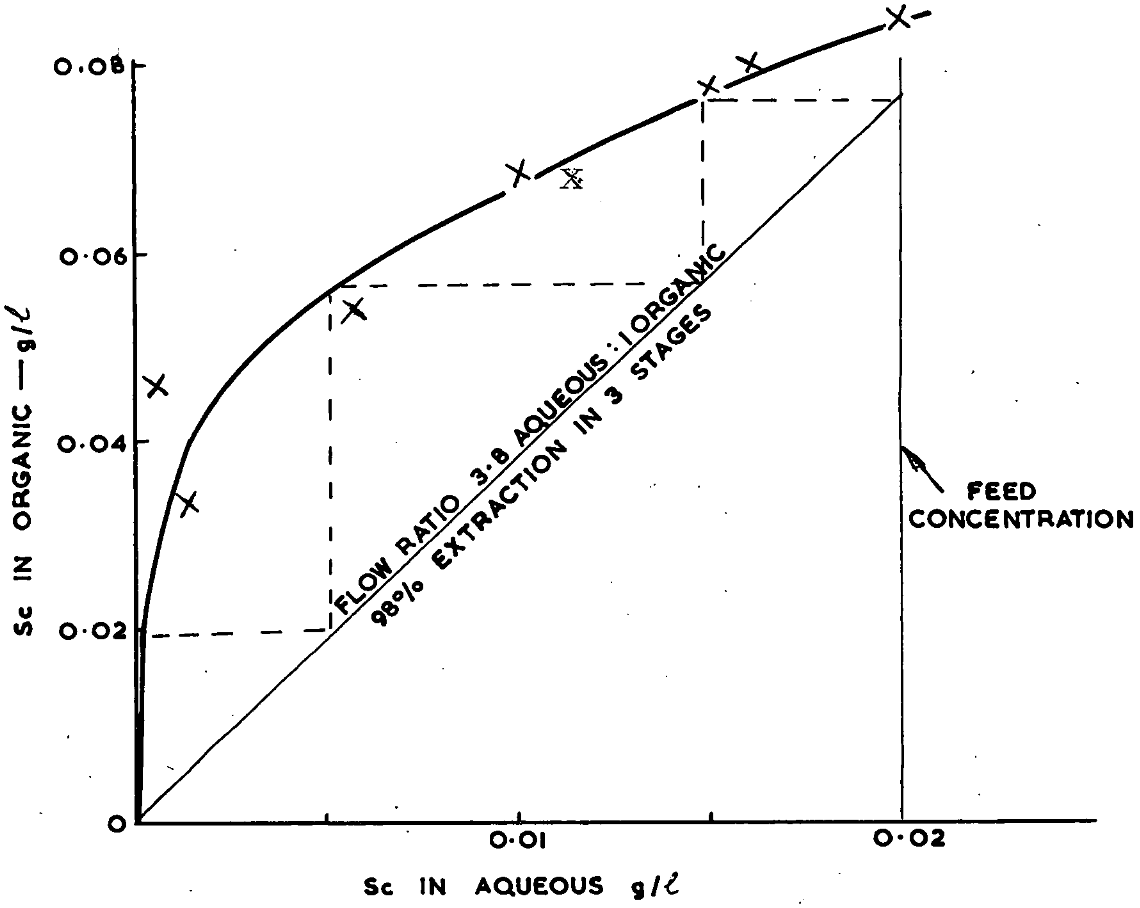


FIGURE 9: SCANDIUM DISTRIBUTION CURVE – EXTRACTION WITH 0.1M EHPA

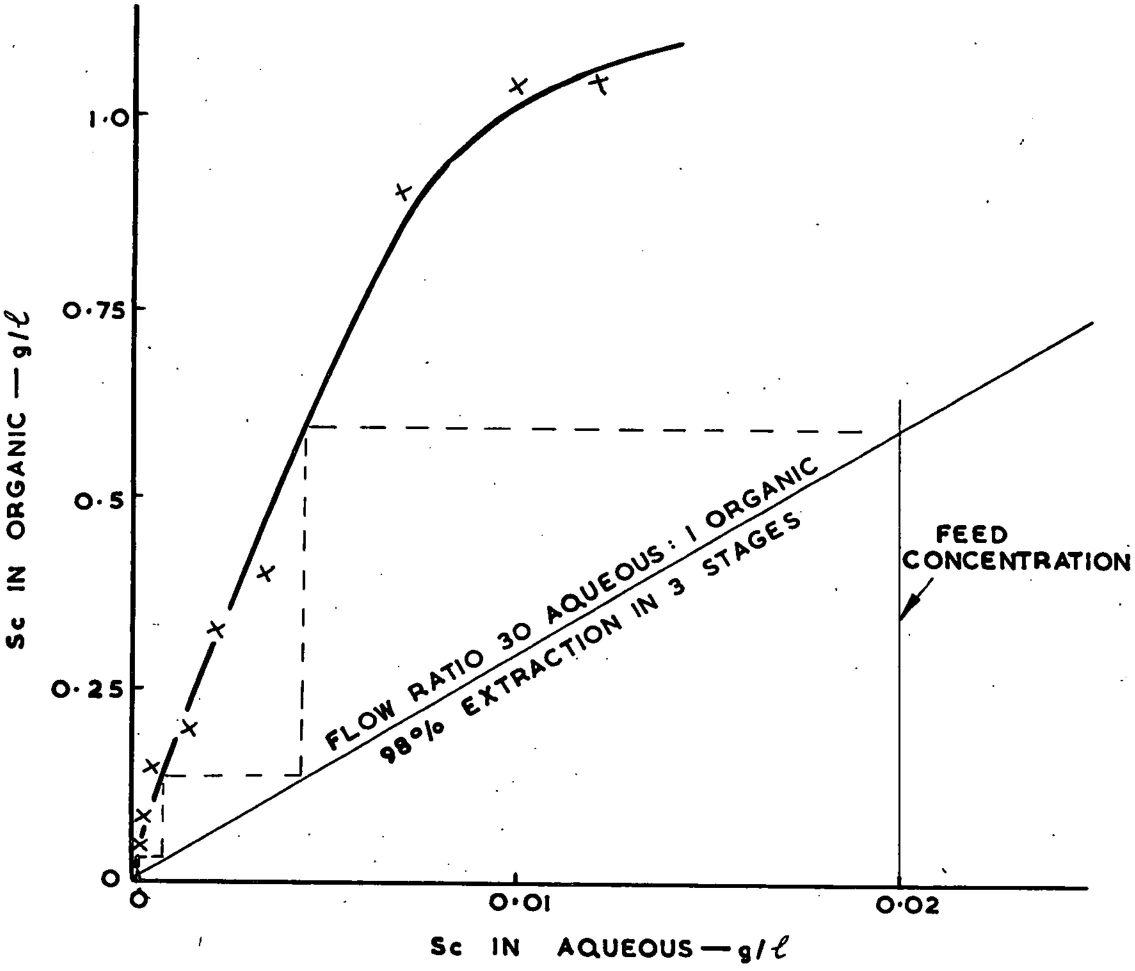


FIGURE 10: THORIUM DISTRIBUTION CURVE - EXTRACTION WITH 0.1$\underline{M}$ EHPA

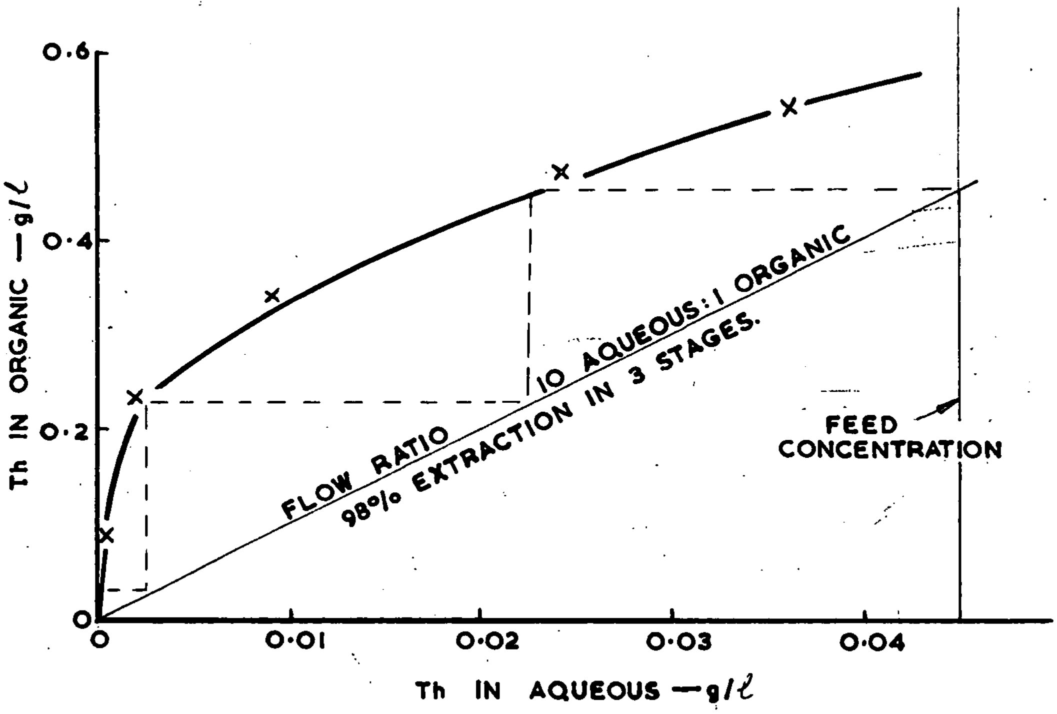
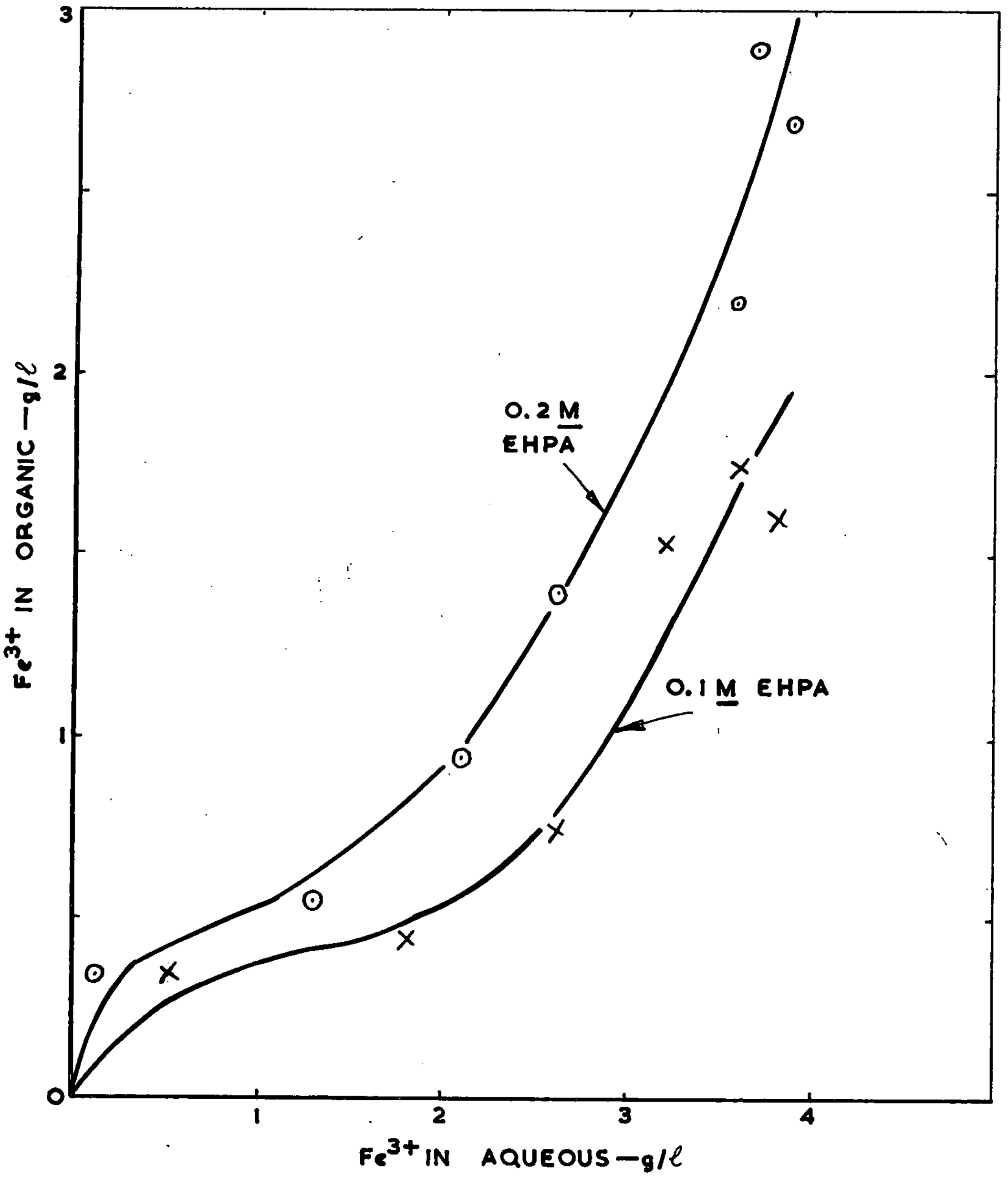


FIGURE 11: DISTRIBUTION CURVES FOR EXTRACTION OF Fe^{3+} WITH EHPA
Barren Liquor containing 4g/l Fe^{3+}



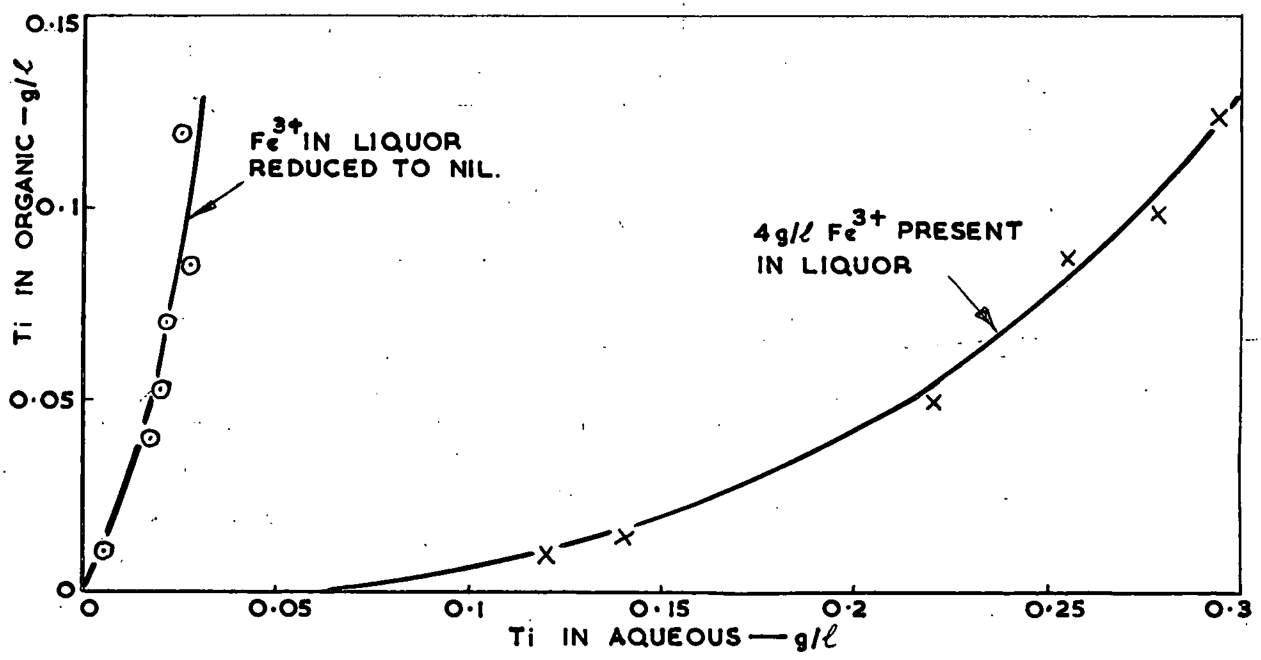


FIGURE 12: TITANIUM DISTRIBUTION CURVES - EXTRACTION WITH 0.1M EHPA

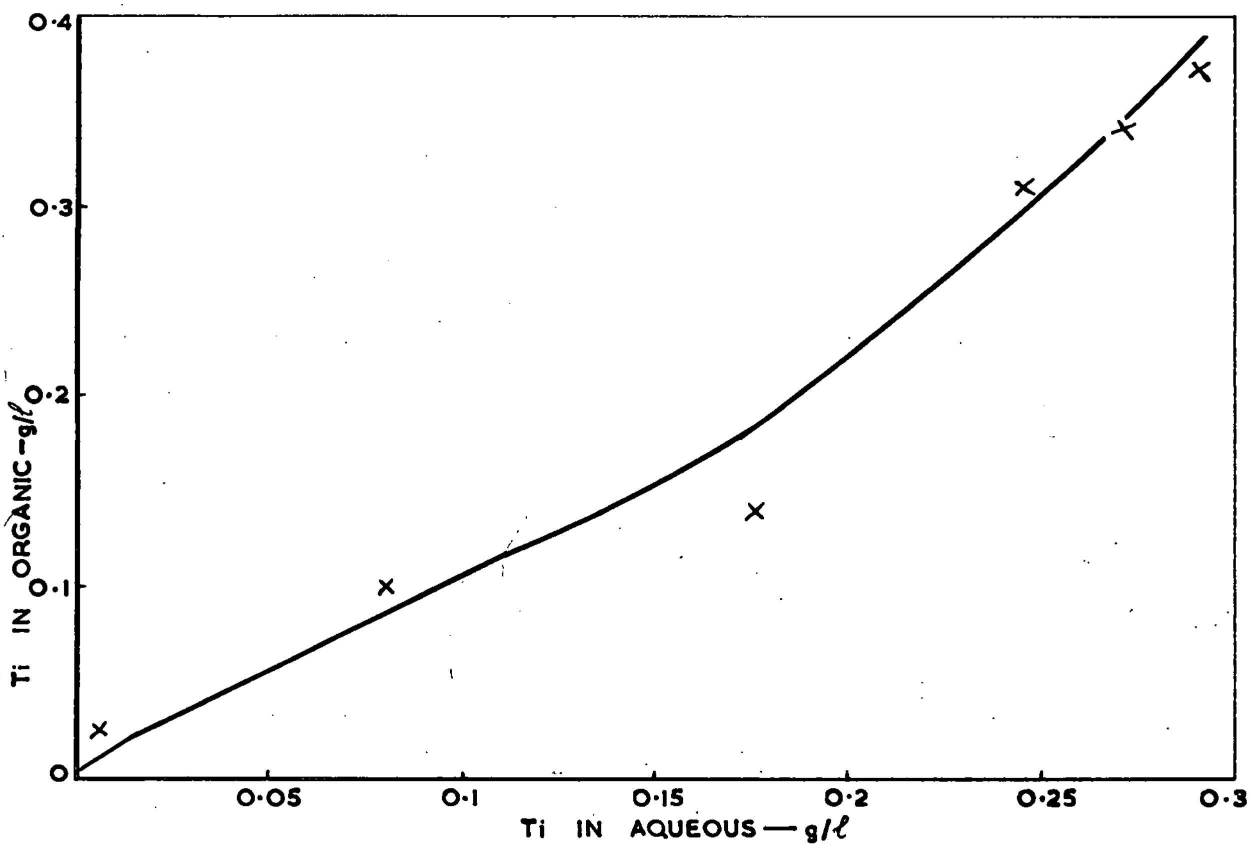


FIGURE 13: TITANIUM DISTRIBUTION CURVE - EXTRACTION WITH 0.2M EHPA
Barren Liquor containing 4 g/l Fe^{3+}

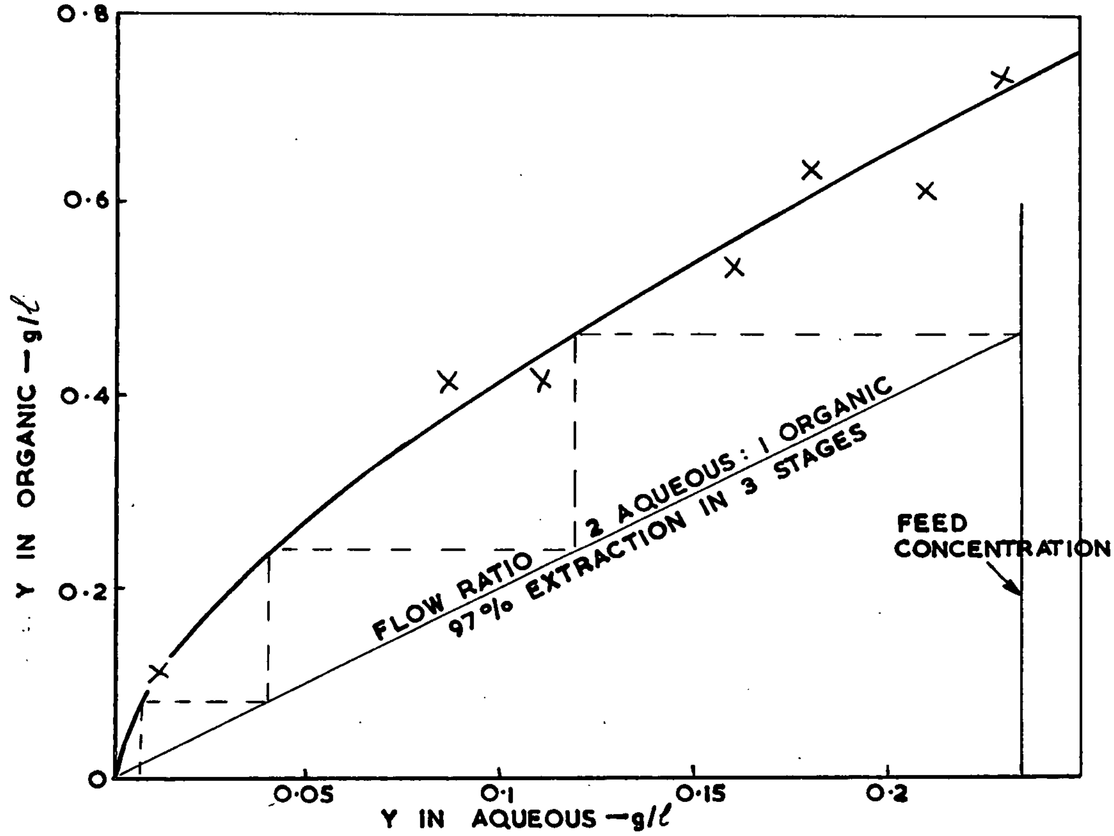


FIGURE 14: YTTRIUM DISTRIBUTION CURVE – EXTRACTION WITH 0.1M EHPA

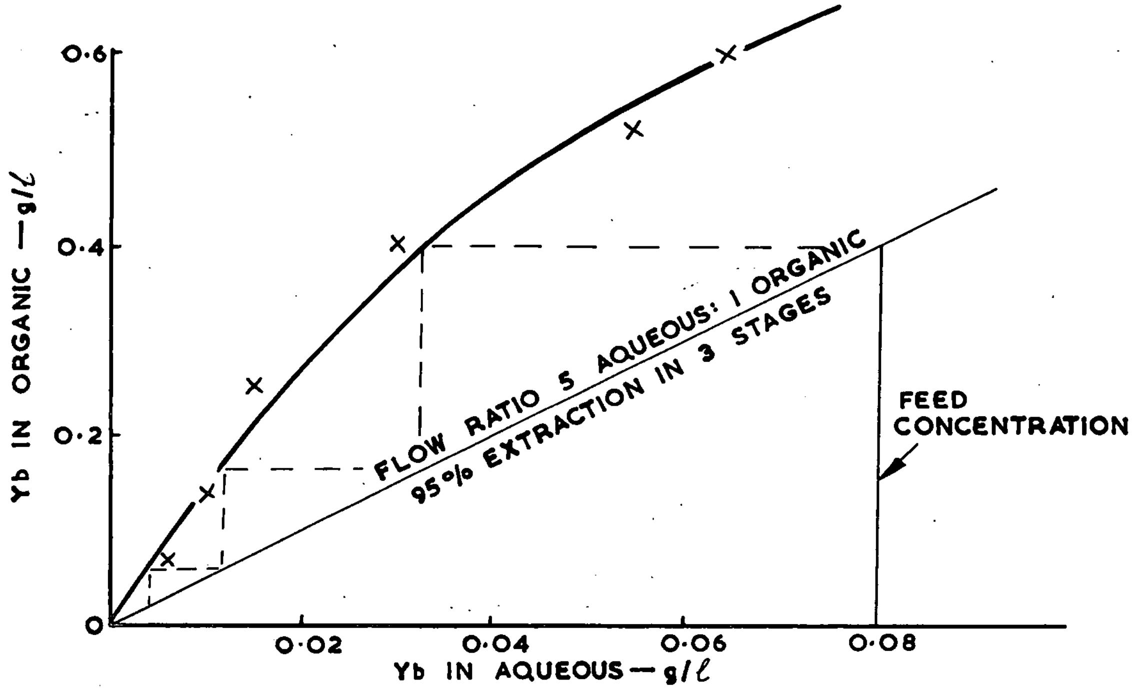


FIGURE 15: YTTERBIUM DISTRIBUTION CURVE – EXTRACTION WITH 0.1M EHPA

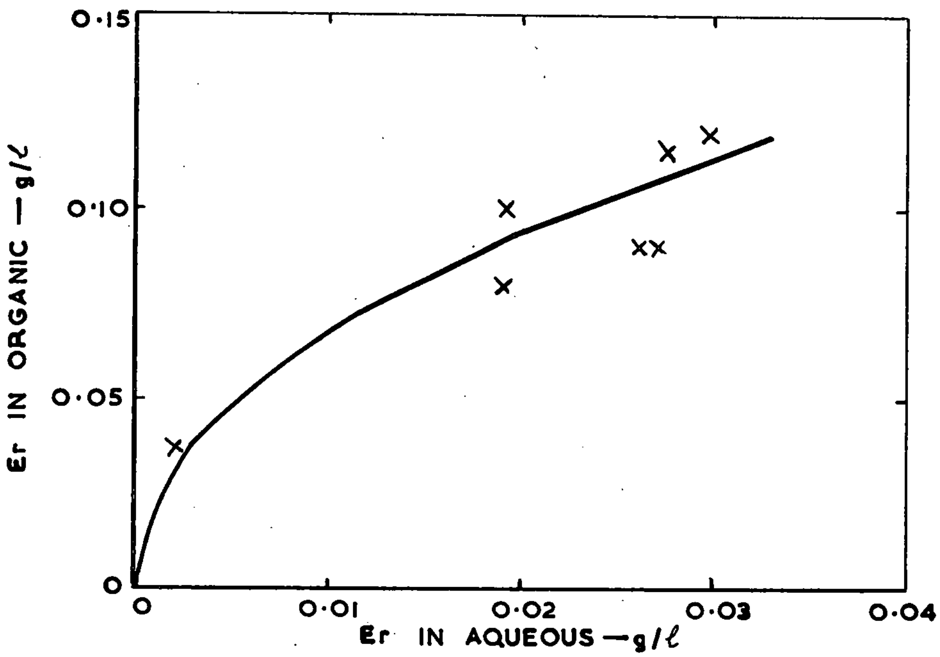


FIGURE 16: ERBIUM DISTRIBUTION CURVE - EXTRACTION WITH 0.1M EHPA

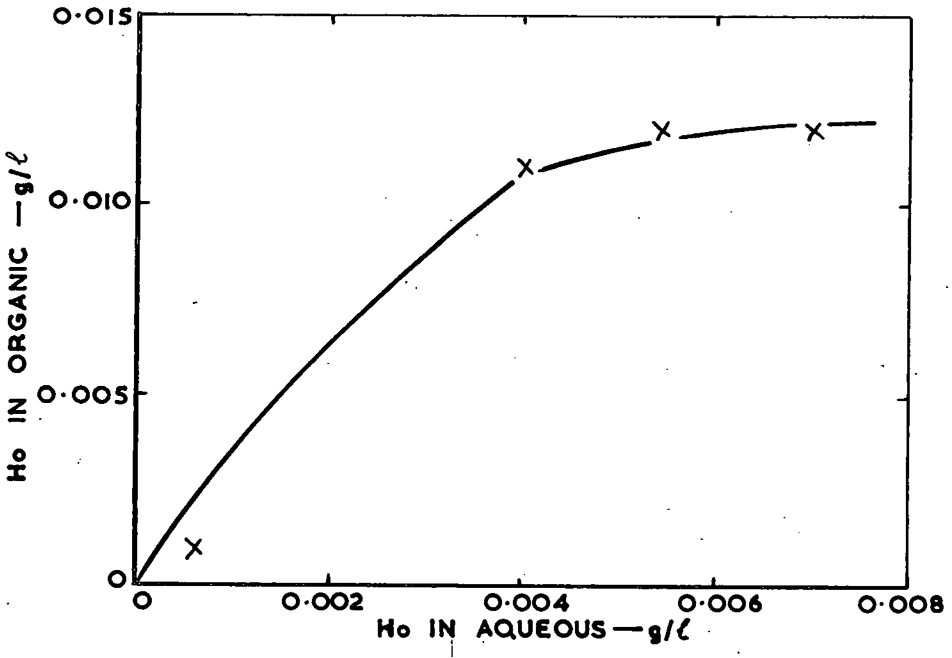


FIGURE 17: HOLMIUM DISTRIBUTION CURVE - EXTRACTION WITH 0.1M EHPA

FIGURE 18: DISTRIBUTION CURVES FOR Sc, Ti, Fe AND Yb - STRIPPING WITH 9N H_2SO_4 FROM 0.1M EHPA EXTRACT

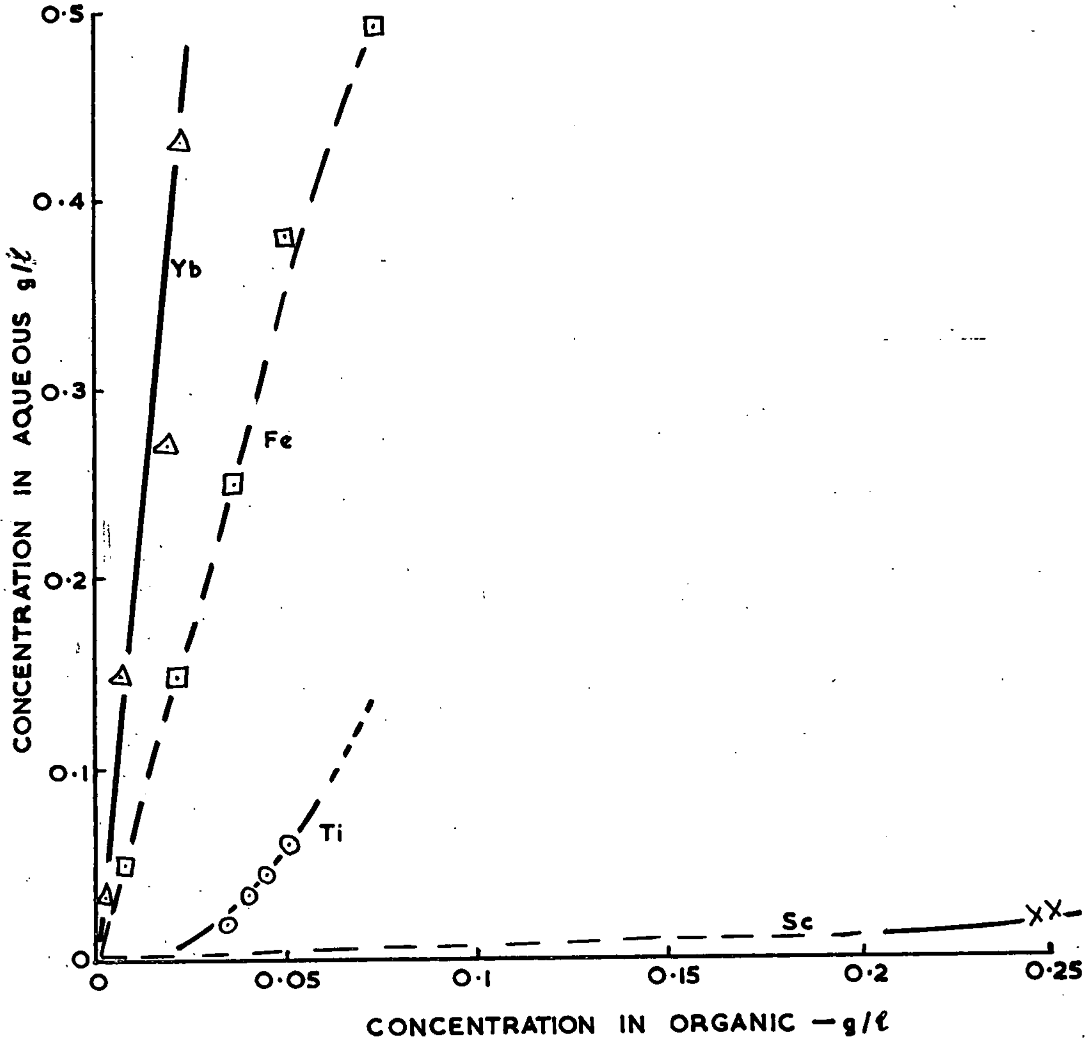


FIGURE 19: DISTRIBUTION CURVES FOR Er, Y, AND Th STRIPPING WITH 9N H_2SO_4 FROM 0.1M EHPA EXTRACT

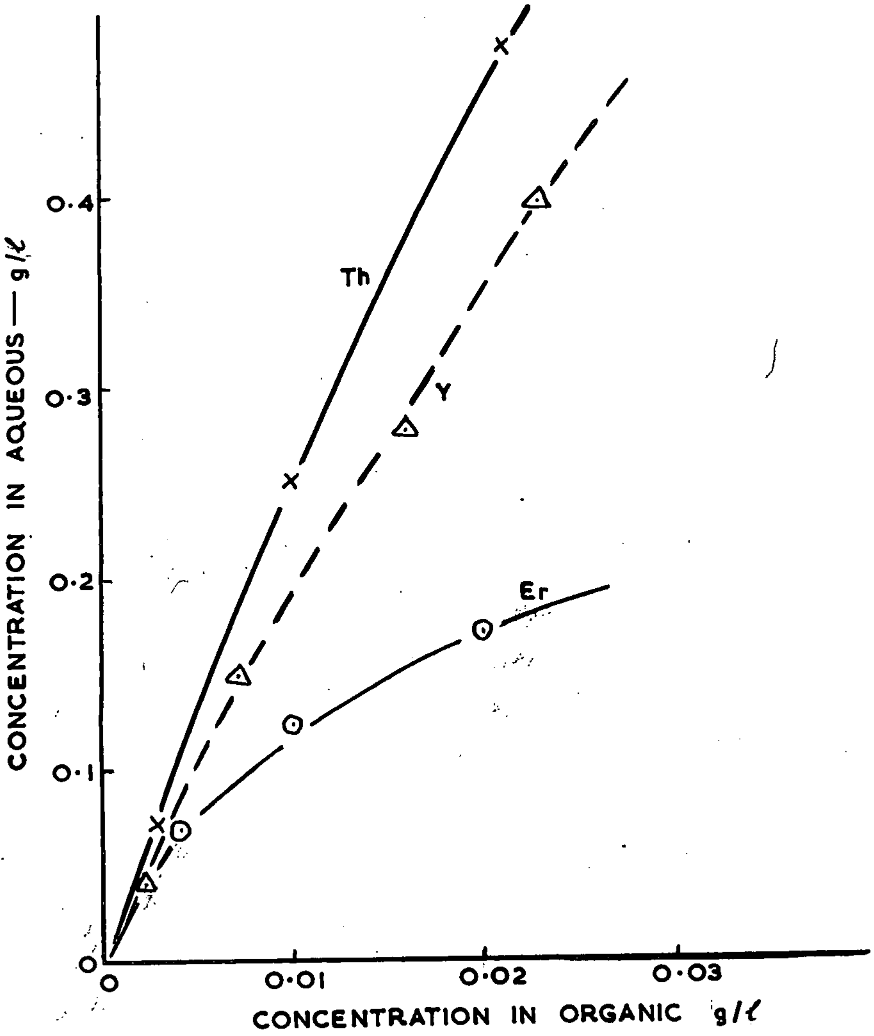


FIGURE 20: SMALL MIXER-SETTLERS
2-Stage counter-current extraction

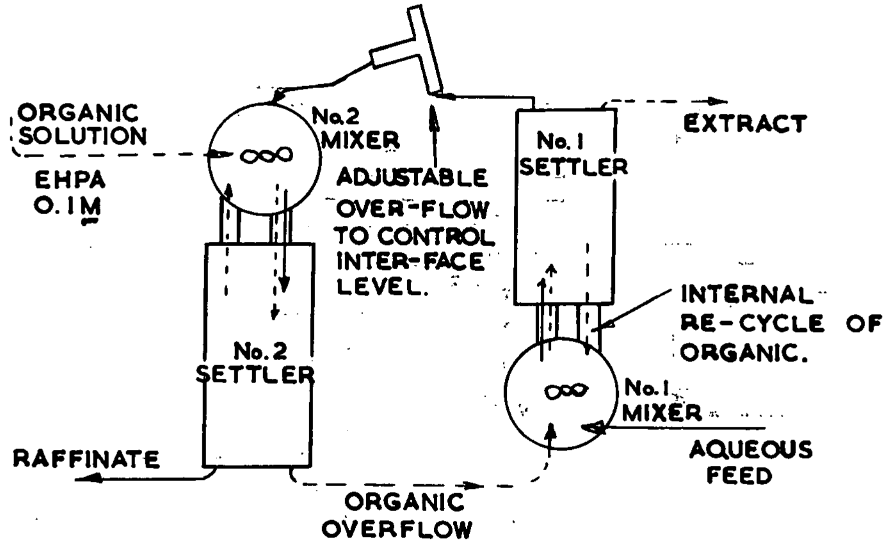


FIGURE 21: PROPOSED FLOW-SHEET FOR SCANDIUM PRODUCTION