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Separative Technologies for the Removal of Thorium from an Acidic Waste Liquor

H. Eccles[a]; A. Rushton[a]
[a] British Nuclear Fuels plc, Springfields Works Salwick, Preston, Lancashire, UK

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SEPARATIVE TECHNOLOGIES FOR THE REMOVAL OF THORIUM FROM AN ACIDIC WASTE LIQUOR

H Eccles and A Rushton
British Nuclear Fuels plc
Springfields Works
Salwick, Preston, PR4 0XJ
Lancashire, UK

ABSTRACT

Several separative technologies for the removal of thorium isotopes from a waste nitric acid raffinate have been evaluated. The implications of interfering ions and the efficiency of thorium recovery are described.

A comparison of the various techniques studied is reported with particular reference to:

i. Secondary waste.
ii. Scale-up.
iii. Overall best practical environmental option.

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INTRODUCTION

In the production of nuclear fuels by BNFL at their Springfields Works, several sequential processes are necessary to convert uranium ore concentrates (UOCs) to reactor fuel. In one of these processes the uranium, as uranyl nitrate, is separated from impurities present in the UOCs. Generally, the major impurities are the alkali and alkaline earth metals, aluminium, some first and second row transition metals, non-uranic radionuclides and various anionic species such as fluorides and sulphates. The cations and uranium present in the UOCs

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are liberated, predominantly as their nitrates, during the dissolution stage prior to purification of the uranyl nitrate liquor. The latter is achieved using a solvent extraction procedure which, in addition to producing a pure uranyl nitrate solution which is subsequently converted to other uranic compounds, discards an acidic raffinate rich in nitric acid but contaminated with the aforementioned impurities. The radionuclides present in this raffinate, in addition to trace quantities of uranium, are naturally occurring thorium 232 and the uranium daughters thorium 230, thorium 234 and protactium 234.

Although the radioactive environmental impact from these is small and discharges are well within existing site authorisations, it was judged prudent some ten years ago to identify processes for their removal from raffinate in the event of more stringent legislation being imposed in future years.

The work described in this paper relates to the removal of radionuclides, specifically the thorium isotopes, from the aqueous raffinate. Several techniques, namely:

i. precipitation and selective precipitation
ii. ion exchange
iii. biosorption
iv. solvent extraction

were evaluated and one in particular, solvent extraction, was developed to pilot-plant scale.

HISTORICAL BACKGROUND

The data reported in this paper was collected over a ten year period and consequently the composition of raffinate samples used in the numerous investigations varied significantly. With few exceptions, simultaneous and/or parallel comparative studies did not occur and therefore strict comparisons of the five techniques is not advisable but general trends can be formulated.

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However, the more efficient and effective techniques overall can be selected.

At the outset a process specification was formulated against which the five candidate techniques could be judged. Some of the major technical criteria of this specification are:

i. The process should be versatile and capable of accommodating significant variations in the raffinate composition and volumetric arising.

ii. The thorium isotopes should be finally presented in a solid form. The quantity of this solid should be minimised.

iii. The overall environmental impact to both process operatives and general public should be minimised.

The studies associated with each of the candidate techniques generally followed a common pattern, namely:

i. Initial scoping studies to select the best precipitant, ion exchanger, biosorbent, extractant.

ii. Experiments to measure the selectivity of the precipitant, ion exchanger etc for thorium isotopes.

iii. The measurement of the thorium capacity of the ion exchanger, biosorbent, extractant.

iv. The recovery of thorium from the loaded ion exchanger, biosorbent, extractant.

THE RAFFINATE

The raffinate is discarded from a solvent extraction circuit which employs tributyl phosphate dissolved in odourless kerosene as the solvent phase. Generally, about 4.5m^3 of raffinate is generated for each tonne of uranium (as UOC) refined. A refinery with an annual throughput of 5,000t U would discard nearly 23,000m^3 pa and therefore a thorium removal process capable of treating approximately 3.5m^3/hr is required.

A typical composition of raffinate is reported in Table 1. Additionally, the observed ranges of the major constituents are recorded.

TABLE 1

COMPOSITION OF RAFFINATE

Element	Composition Typical	Composition Range
Nitrate	~120g/1	80 - 200g/1
Sulphate	5g/1	2 - 13g/1
Fluoride	2g/1	0.02 - 4g/1
Sodium	500ppm	200 - 2000ppm
Potassium	300ppm	100 - 1000ppm
Magnesium	400ppm	30 - 4500ppm
Calcium	600ppm	150 - 2100ppm
Aluminium	700ppm	200 - 4000ppm
Iron	800ppm	250 - 300ppm
Thorium	800ppm	10 - 2500ppm
Uranium	5ppm	1 - 20ppm
Free nitric acid	~60g/1	50 - 170g/1
α activity	$0.034 GBq/m^3$	
β/γ activity	$5.23 GBq/m^3$	

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Both α and β/γ activities arise from naturally occurring radionuclides and therefore would normally present few occupational hygiene problems. On concentration, however, dose (radiation) uptake to process operatives needs careful consideration.

SELECTION OR SCREENING STUDIES

A variety of precipitants, ion exchange resins, biomasses and liquid extractants were initially studied.

1. Precipitation

The precipitants were:

a. General neutralising type reagents such as sodium hydroxide and lime (essentially hydrated calcium oxide).

b. Oxalic acid, phosphoric acid and fluoride ion.

The thorium removal efficiencies of these reagents from plant raffinate are presented in Table 2.

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TABLE 2

PRECIPITATION OF THORIUM FROM PLANT RAFFINATE

Precipitant	% Removal of Thorium
Sodium hydroxide	>99
Lime	>99
Oxalic acid	37
Phosphoric acid	< 1
Fluoride ions	91

Precipitation conditions:

For sodium hydroxide and lime final pH 9.0.

For the remainder, the thoriam to precipitant ratio (mole/mole) was 1 : > 1,000.

2. Ion Exchange

The chelate ion exchange resin Duolite ES467 which contains amino phosphonic acid groups attached to the polystyrene matrix, was selected in preference to four other commercially available cation exchangers, namely Dowex 50WX2, Dowex 50WX4, Dowex 50WX10 and Amberlite 200. These resins contain the conventional sulphonic acid group.

The initial scoping studies to select the best ion exchange resin involved the measurement of K_{th} values with as received plant raffinate at varying temperatures (25°C, 35°C, 45°C and 55°C). At the lowest temperature the ES467 K_{Th} value was about 150 compared with a mean K_{Th} value for the sulphonic acid resins of approximately 40. At 55°C, the K_{Th} value had increased to nearly 1000 for the chelating resin whereas the corresponding mean value for the cation exchangers was about 80.

Although all five exchange resins were further studied, a significant amount of the data collected has been omitted for brevity, and discussion of ES467 only is reported in this paper.

TABLE 3

THORIUM UPTAKE BY FUNGAL BIOMASS

Strain	Thorium Uptake (g^{-1} dry wt) mmol	Thorium Uptake (g^{-1} dry wt) mg
S. Cerevisiae	0.083	19
P. italicum	0.24	56
P chrysogenum	0.27	63
A Niger	0.25	58
R. arrhizus	0.51	118

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3. Biosorption

Fungal and other microbial biomass have been used success fully in a number of previous instances to remove metallic elements, including actinide elements from aqueous solutions. The use of physiologically active biomass can take advantage of the accumulation of metals by metabolising microbial cells(1,2) or of specific enzymic reactions to detoxify heavy metal wastes(3,4). However, fungal biomass can also take up considerable quantities of heavy metals from solution by adsorption or related processes, even in the absence of physiological activity. This process has been applied to removal of nickel and copper(5) and also to various actinide elements such as thorium, uranium or plutonium(6-9). However, these studies have been conducted almost entirely at pH ranges close to neutrality and hence the application of 'biotechnology' to plant raffinate represents a unique challenge.

Following an extensive literature review and screening studies, further evaluations concentrated on biomass from five fungal species. The actinide uptakes from a 3mM thorium - 1M nitric acid solution are reported.

TABLE 4

SOLVENTS AND THEIR THORIUM EXTRACTION EFFICIENCIES

0.1M solvent in odourless kerosene (batch studies - single contract)

Solvent	% Th Extraction
Tri-n-octyl phosphine oxide (TOPO)	99.9
Di-2-ethyl hexylphosphoric acid (D2EHPA)	98.8
Dibutyl phosphonate (DBBP)	39.0
Bis-2-ethylhexyl phosphite (bis 2EHP)	50.5
Hexyl ethyl hexyl (ethyl hexyl phosphite) (HEH(EHP))	95.6
Trioctylamine (TOA)	44.3
Amberlite LA2 (an unspecified secondary amine)	37.3
Aliquat 336 (an unspecified quaternary ammonium salt)	43.5
Tributyl phosphate (TBP)	34.5
Cyanex 923 (a mixture of trialkyl phosphine oxides)	99.6

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Biomass from filamentous fungi took up greater amounts of thorium than yeast biomass. Interestingly, the thorium uptake by biomass in 1.0M HNO_3, ie pH value approximately 0, is as great as those obtained at higher pH(8). There are several possible explanations for this: Either different thorium binding sites may be available at pH 0 than at pH 2 to 4 or the low pH of the HNO_3 solution may lead to chemical differences in the dominant species of thorium in solution. This point is discussed in more detail in the next section.

4. Solvent Extraction

Various solvents had been identified from earlier work(10,11) and from a subsequent literature search(12). The thorium extraction efficiencies of ten solvents were measured and the values are reported in Table 4. These initial trials showed that the four solvents with the highest extraction efficiencies and therefore the greatest potential to achieve the target figure were:-

TOPO
D2EHPA
HEH(EHP)
and Cyanex 923 (a mixture of trialkyl phosphine oxides, including TOPO).

The last solvent was eliminated from further studies as at the time Cyanex 923 was still under development and was not available in commercial quantities. Another, HEH(EHP), was eliminated following equilibrium curve studies, ie HEH(EHP) had an irregular and impractical curve.

Although both TOPO and D2EHPA were further evaluated, only the additional data collected for TOPO systems are reported in this paper.

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SELECTIVITY STUDIES

1. Precipitation

A thorium selective separation process is needed if the quantity of final solid product is to be minimised. Neutralisation of plant raffinate with either sodium hydroxide or lime results in the precipitation of all heavy metals as their hydroxides in conjunction with the thorium isotopes. This situation is exemplified by reference with the thorium isotopes. This situation is exemplified by reference to Figure 1. The bulk of the thorium isotopes (measured as β activity) is removed from the solution initially by pH value 3.0, co-precipitated and/or adsorbed onto metal hydroxide flocs. However, 20kg of solids (dry weight) are produced for each te of uranium refined, of which only 10% would be associated with thorium; an impractical solution.

As other metals such as magnesium and calcium can form insoluble compounds with oxalic acid, phosphoric acid and fluoride, the thorium selectivity of these three precipitants was determined. This was achieved by measuring the

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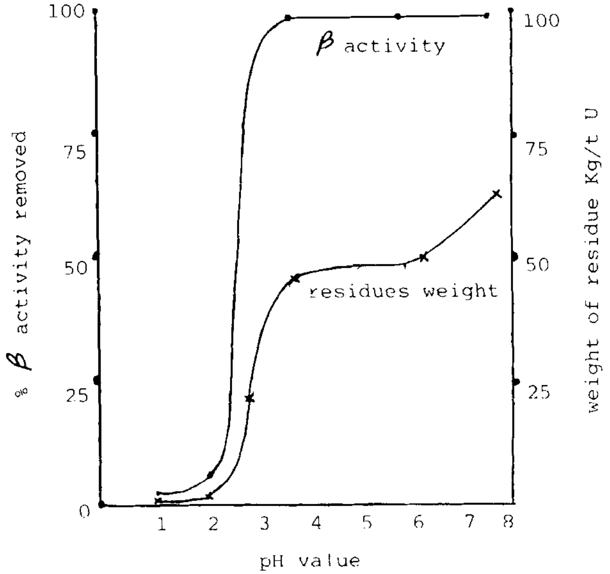

FIGURE 1. Fractional Precipitation of Thorium using Sodium Hydroxide.

initial and final concentrations of Mg and Ca in plant raffinate. Within experimental error, their concentrations remained constant at 760ppm and 320ppm respectively for all three precipitants. However, analysis of filtrates indicated a lower than expected fluoride concentration, thus suggesting additional metal ions were being precipitated or fluoride thorium adducts were being formed.

Further analysis revealed that the precipitation of thorium by fluoride from plant raffinate results in the formation of a NaF-ThF_4 double salt.

As near-selective precipitation of thorium as thorium tetrafluoride was the most effective, whilst achieving a small quantity of solid, the other precipitant processes were ultimately discarded.

TABLE 5

THE EFFECT OF CATION CONCENTRATION ON THE K_{Th} VALUE FOR DUOLITE ES467

Metal Ion in Equilibrium with the Resin

	Na			Ca			Fe		
Initial metal ion concen- tratopm g/l	0.45	1.2	5.0	0.78	1.9	6.5	0.72	1.8	5.8
K_{Th} value	176	162	200	176	212	200	176	70	13

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2. Ion Exchange

The influence of nitric acid, sulphuric acid and various metal ions on the selectivity of ES467 for thorium was studies. The influence of nitric acid on the K_{Th} value was positive, ie increasing acidity from 1M to 6M increased this value from ~130 to ~ 230. Increasing the sulphate concentrate of plant raffinate from 4.4g/l to 38.0g/l (~ 0.4M) had little or no effect on the K_{Th} value. However, for sulphonic acid resins the corresponding K_{Th} values were reduced.

These observations can be justifiably explained since increasing the nitric acid content of the solution reduces the number of discrete hydrated Th^{4+} ions in solution. At high nitric acid values (4 to 6M) the majority of the thorium species are present as $Th(NO_3)_5^-$ and $Th(NO_3)_6^{2-}$. Similarly, the major thorium species in ~0.4M sulphuric acid solution are $Th(SO_4)_2$ and $Th(SO_4)_3^{2-}$. The concentration of such species increases with sulphate content.

However, the formation of the resin-thorium complex is apparently greater than the stability of either thorium-nitrato or thorium sulphato complexes.

The influence of sodium, calcium and ferric ions on the K_{Th} value is illustrated by data reported in Table 5.

TABLE 6

THORIUM UPTAKE BY FUNGAL BIOMASS IN THE PRESENCE OF CATIONS

Strain	Metal Ion in Equilibrium with the Biomass					
	Control	Na	Mg	Ca	Fe	Al
		Initial Metal Ion Concentration mg/l				
	0	460	240	400	1116	270
S. Cerevisiae	0.083	0.083	0.085	0.085	0.046	0.060
P. italicum	0.24	0.22	0.22	0.21	0.19	0.24
P. chrysogenum	0.27	0.29	0.35	0.31	0.27	0.34
A. niger	0.25	0.26	0.27	0.21	0.21	0.26

values in mmol/g dry wt of biomass control 3mM thorium in 1M HNO_3

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Sodium and calcium ions had little or no effect on the affinity of Duolite ES467 for thorium. However, increasing the iron (111) concentration of the liquor gradually reduced the selectivity of the resin for thorium.

3. Biosorption

The uptake of thorium by fungal biomasses from 1M nitric acid solution in the presence of a number of cations is shown in Table 6. Within experimental control, sodium, calcium and magnesium ions did not inhibit uptake, whereas aluminium on occasions improved the uptake, whilst iron (111) significantly reduced uptake for S. Cerevisiae and P italicum.

However, it should be emphasised that although thorium uptake was generally uninhibited by the presence of these cations, it is possible some may also have been extracted by the biomasses.

TABLE 7

THORIUM SELECTIVITY RATIOS FOR 0.1M TOPO/CYCLOHEXANE

Free Acidity of Aqueous Phase	Temperature	Thorium Selectivity Ratios (10^3)		
M HNO_3	°C	Fe	Al	Mg
1	25	32	8.3	49
	60	7.6	3.4	20
3	25	4.9	2.4	13
	60	3.2	1.2	6.9

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4. Solvent Extraction

The influence of aqueous phase acidity and temperature were examined to validate the versatility of the TOPO solvent to process fluctuations. Experimental data for a 0.1M TOPO/cyclohexane system showed that increasing the nitric acid acidity of the aqueous phase, which contained 4000ppm of thorium, from one to three molar reduced the thorium distribution value from 36 to 11. This behaviour was expected as nitric acid is generally coextracted as $HNO_3$2 TOPO with the thorium nitrate-TOPO adduct $Th(NO_3)_4$2 TOPO. A similar decrease in the K_{Th} value, ie from 36 to 14, was also measured if the temperature of the solution was increased from 25°C to 65°C. The selectivity of TOPO for thorium in preference to ferric iron, aluminium and magnesium was also examined and the results are reported in Table 7.

Previous published data indicated that iron (111), aluminium and magnesium nitrates are not extracted by TOPO from 1M nitric acid solutions. However, our studies revealed that these metals are extracted albeit in trace quantities. Typical K values for these metals were of the order 10^{-3} with aluminium the most extractable and magnesium the least.

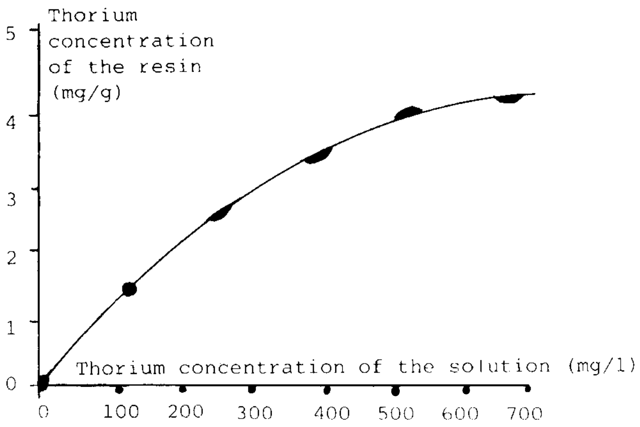

FIGURE 2. Thorium Loading of Duolite ES467 for Plant Raffinate

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CAPACITY STUDIES

Thorium capacities of Duolite ES467, biomasses and TOPO were measured but, as non standard experimental conditions were employed, the following results can only be regarded as indicative and not directly comparable.

1. Precipitation

Generally, about 4.3g of fluoride ion are required to effectively precipitate (>95%) thorium ions from plant raffinate (initial thorium concentration ~200ppm). This equates to 50mg thorium per g of fluoride.

2. Ion Exchange

The thorium capacity of Duolite ES467 using as received plant raffinate is represented graphically in Figure 2. The maximum thorium loading under realistic operational conditions, ie plant conditions, is 4mg/g of resin, ie about

TABLE 8

MAXIMUM LOADING OF THORIUM BY FUNGAL BIOMASS

Strain	Maximum Loading mg/g dry wt
Saccharomyces cerevisiae	58
Penicillium italicum	116
Penicillium chrysogenum	186
Aspergillus niger	162
Rizopus arrhizus	162

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8mg/g of dry resin. This value is significantly lower than the manufacturer's technical information of >40mg Ca/g of resin but the experimental conditions are not comparable.

3. Biosorption

Adsorption of thorium by biomass of all strains showed saturation kinetics with respect to thorium concentration. Simple adsorption models did not produce a good fit to these results, unlike adsorption at moderate pH to which the Freundlich isotherm showed a good fit(13). The maximum thorium uptake by the different strains was estimated graphically and is shown in Table 8.

4. Solvent Extraction

Equilibrium curves were constructed for TOPO/OK systems from batch experimental data in the conventional manner and are presented graphically in Figure 3. The maximum loading for a 0.1M TOPO/OK system for a plant raffinate containing 400ppm was approximately 4300mg, ie 110mg thorium/g of TOPO.

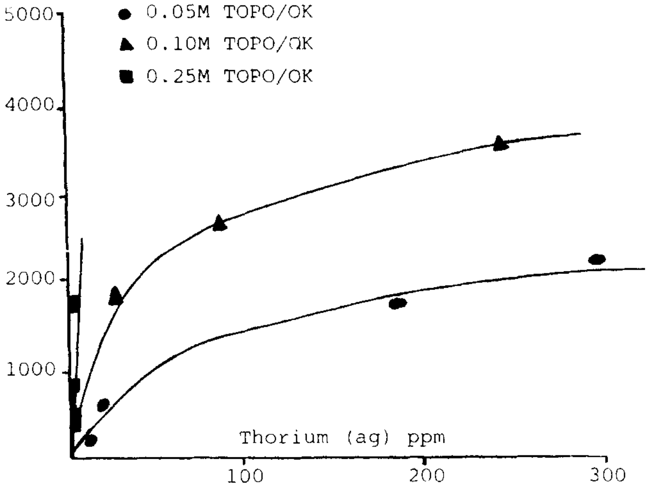

FIGURE 3. Thorium Equilibrium Curves for TOPO/OK Systems at Ambient Temperature

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DESORPTION/BACKWASHING STUDIES

1. Precipitation

Although this particular section is irrelevant to the removal of thorium isotopes from plant raffinate by precipitation with fluoride ion, it is worth mentioning that the separation of ThF_4NaF from the acid liquor is not easy. A significant proportion of the studies, not reported here, were associated with this problem.

2. Ion Exchange

Various eluants, namely ammonium acetate, oxalic acid, a mixture of hydrochloric and hydrofluoric acids, and ammonium citrate have been used to recover thorium from cation exchange resins. These reagents, with the exception of the last, had little or no ability to recover thorium from Duolite ES467. Ammonium citrate (0.5M) removed only a small

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TABLE 9

DESORPTION OF THORIUM FROM LOADED FUNGAL BIOMASSES

Eluant	% Desorption of Thorium from Loaded Biomass	
Biomass	P. chrysogenum	P. italicum
Distilled water	~2	~1
Na_2CO_3	85	83
Na_2HPO_4	1	~2
NaH_2PO_4	<1	<1
$(NH_4)_2CO_3$	71	76
$NH_4H_2PO_4$	<1	<1

Concentration of all eluants 0.2M

quantity (~3%) of the thorium from the resin. The superior eluant studied was ammonium carbonate (0.5M) which recovered in total approximately 10% of the adsorbed thorium.

Although the recovery of thorium from the chelating resin was relatively poor, the results did indicate that lower temperatures favoured the elution process.

3. Biosorption

The desorption of thorium from fungal biomass by the different solutions evaluated showed much the same pattern for all species (Table 9). Very little thorium was eluted by distilled water, or by sodium or ammonium phosphates. However, both sodium and ammonium carbonate eluted a large proportion of the adsorbed thorium (70-85%). There was no apparent difference between the percentage of adsorbed thorium which was eluted by these two compounds.

4. Solvent Extraction

The co-extraction of nitric acid with thorium nitrate influenced the selection of a back extractant for the recovery of thorium from the loaded 0.1M TOPO/OK solvent system. Several potential back extraction reagents were

TABLE 10

THORIUM BACK EXTRACTION EFFICIENCIES FOR LOADED 0.1M TOPO/OK

Back Extraction Liquor	%Th Backwashed from Solvent
0.1M EDTA	80
1.0M Tri-potassium citrate	86
1.0M Tartaric acid	18
3.0M Sulphuric acid	89
1.0M Sulphuric acid	83
0.3M Sulphuric acid	78
1.0M Na_2SO_4/1.0M H_2SO_4	91
2.0M K_2CO_3	85

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examined, initially using a batch procedure. Some of these reagents and the corresponding results are reported in Table 10.

Following further batch and continuous studies using a 10-stage laboratory size mixer-settler unit, a 4M potassium carbonate solution was ultimately selected.

PILOT PLANT STUDIES

The 0.1M TOPO/OK solvent extraction process was eventually selected for pilot-plant studies. This decision was based on:-

i. Precipitation of thorium from plant raffinate using either sodium hydroxide or lime results in a significant volume of solids for ultimate disposal.

ii. At the time the problems of $NaF \cdot ThF_4$ solid-liquid separation had not been resolved nor had the process been optimised for all anticipated plant raffinate compositions. furthermore, the potential problems of handling a solid 1000 times per unit volume more radioactive than the plant raffinate, had not been fully addressed.

TABLE 11

PILOT PLANT DATA

Plant Raffinate Thorium Content	Solvent to Aqueous Ratio		Thorium Extraction Efficiencies (%)		Thorium Content of Back Extraction Liquor
ppm	Forward	Back	Forward	Back	ppm
165	1 : 10	10 : 1	99.5	99.9	16401
1125	1 : 3.5	10 : 1	99.9	99.9	39296
1210	1 : 3.5	10 : 1	99.8	99.8	42181
905	1 : 5	10 : 1	99.9	99.7	45069

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iii. The chelate ion-exchange resin Duolite ES467 had a poor thorium capacity and eluation of the actinide from the loaded resin was difficult.

iv. The use of microbes/biomasses for the treatment of plant raffinate and/or waste effluents in general, is an infant but emergent technology. However, the biomasses evaluated had superior thorium uptakes and elution characteristics and comparative selectivity compared with the chelate ion-echange resin.

Resulting from the initial batch studies and a series of continuous countercurrent trials using a twenty stage laboratory size mixer-settler unit, a process flowsheet was produced. This flowsheet was validated at pilot-plant scale with an aqueous feed throughput of 100 litres/hr generating a back extraction liquor of 1 litre/hr(14).

The following extraction efficiencies were achieved for the corresponding conditions (Table 11).

REVIEW OF CANDIDATE PROCESSES

Although the removal of thorium isotopes from plant raffinate can be achieved simply and effectively using a cheap alkali such as sodium hydroxide, a comparatively large volume of secondary waste (metal hydroxides) is produced. This problem is overcome if the actinide is precipitated as the insoluble double salt $NaF{\cdot}ThF_4$ but at the expense of efficiency and simplicity. Although only about 30t of dry solids would be produced, their separation and handling requires careful consideration.

The adsorption of thorium onto conventional sulphonic acid resins and even the chelating ion exchange resin Duolite ES467 is impractical due to low thorium capacities and poor elution characteristics. Furthermore, thorium would require precipitation from any eluant liquor.

The proposed use of fungal biomasses for the removal of thorium from plant raffinate was speculative but the results obtained from our studies were very encouraging and warrant a more detailed and extensive examination. The application of biotechnology to waste management issues is a potential growth industry.

Not surprisingly, a solvent extraction process was selected for pilot-plant evaluation. Not only was this decision based on data gathered during the five year solvent extraction project but also since BNFL has a wealth of experience in both design and operation of solvent extraction plants. Nevertheless, the thorium from the backwash 4M potassium carbonate liquor requires recovery. A precipitation technique was developed, but this adds to the complexity of the overall removal process.

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