SOME IMPLICATIONS OF PARTITIONING PROCESSES
FOR HIGH LEVEL WASTE

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ABSTRACT

The concept of partitioning and transmutation (P/T) of actinides is based on the removal of long-lived actinides from high level waste (HLW) before it is vitrified, and their incineration. The argument for P/T is that it reduces the long-term toxicity of vitrified HLW. The more significant criterion of its effect on the radiological dose to mankind resulting from releases from the repository also needs to be addressed.

Considerations of the long-term radiotoxicity of the radionuclides present in HLW, and also of their radiological dose implications, lead to the conclusion that the important chemical elements that need to be removed from HLW in an effective P/T strategy are: Np, Pu, Am and Tc. Zirconium should also be considered, because of the long half-life of the isotope ^{93}Zr.

The performance of alternative processes needs to be judged against their effectiveness in removing these elements. Candidate processes for the partitioning of HLW have been analysed, in as quantitative a manner as data permit. None of them can achieve a perfect separation. The processes require plant and equipment of comparable scale to the chemical separation section of the original reprocessing plant. The actinide products are obtained in high volume aqueous streams, which would require further processing to provide targets for incineration or transmutation. Secondary waste streams containing actinides will be produced from the partitioning processes and also from the subsequent treatment of the products and the fabrication of targets. These secondary wastes may present new problems in waste management and should be considered in a comparative assessment of alternative processes.

It is concluded that P/T remains a complex and expensive process that would change, but not improve, current waste management strategies.

1.   INTRODUCTION

The partitioning and transmutation (P/T) of actinides and other long-lived radionuclides is an advanced concept in the management of high level radioactive waste (HLW) arising from nuclear fuel reprocessing operations. It involves the separation of actinides and long-lived fission products from HLW, and their conversion into fuel or targets. These can then be irradiated in a reactor or accelerator to transmute the separated nuclides into products of greatly reduced half-lives.

It is claimed that in this way the long term toxicity of HLW for disposal is reduced, and that this will make the disposal of HLW more acceptable to the public. However, analysis of the behaviour of radionuclides in HLW repositories in the absence of P/T and their release to the environment show that, under the proposed strategy of vitrification and disposal to a deep geological repository, doses to mankind are very low and are dominated by the radionuclides ^{99}Tc and ^{135}Cs rather than the actinides[1].

The view of the UK nuclear industry was summed up in the 1992 report of the Topic Group on Decommissioning and Waste Management of the Nuclear Utilities Chairmen's Group[2]: ·

"International reviews of the potential of PTA* came to the conclusion that there will be no significant reduction in potential long-term radioactive risk. These are dominated by isotopes unaffected by PTA and the wastes would therefore still require geological disposal. It was also concluded that the resources needed for the work would be extremely large".

In accordance with this view, there is no major programme of research and development on P/T in the UK. There is, however, a commitment to evaluate long term waste management options including P/T and to keep the topic under review. This paper describes the comparative assessments of the efficiencies and costs of alternative schemes for the partitioning of long-lived nuclides from HLW.

2.   THE REFERENCE PUREX PROCESS

For the purposes of this study, the fuel to be reprocessed in the reference PUREX process is taken to be standard LWR fuel at a burn-up of 4.7% and a post irradiation decay time of 4 years. The actinide and fission product content of the fuel at reprocessing were calculated using the FISPIN code. No allowances have been made for loss of fuel during the dissolution process, although it is recognised that some of the inventory of long-lived radionuclides of interest do occur in the dissolver insolubles, or are associated with the fuel cladding.

A hypothetical PUREX process has been assumed comprising:

* first cycle, extraction/scrub and U-Pu partition using U(IV);

* two cycles of Pu purification, each cycle comprising extraction/scrub and strip, and two parallel cycles of U purification, each comprising a U feed evaporation step followed by extraction/scrub and strip;

* solvent phase consisting of 30% tributyl phosphate in a hydrocarbon diluent.

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* PTA - partitioning and transmutation of actinides

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It has been assumed that in the co-processing stages the loss of U and Pu to the high level aqueous raffinate is U $0.005gl^{-1}$, Pu $0.001gl^{-1}$. These values are typical of current PUREX operations. For the purposes of this assessment it has been assumed that all the neptunium in the fuel passes to the HLW.

Of the waste streams that will arise from the operation of the reference process the high active raffinate (HAR) stream is the one usually receiving most attention since it is the precursor of HLW and contains the greatest inventory of higher actinides. However, in a complete P/T scheme other wastes containing actinides and long-lived fission products will also have to be considered.

For this assessment it has been assumed that low and intermediate level liquid waste streams containing plutonium at 0.001g/l are evaporated (10 fold) and added to the HLW liquid, which is also evaporated by a factor of 2. The combined liquors constitute the feed to a candidate partitioning process, with the composition shown in Table 1.

Table 1: Composition of the HLW Feed to the Candidate Partition Processes
(Basis: 5te U per day)

Volume	$17.5m^3$/day
Nitric Acid	4-5M
Key elements (g/day)	
U	130
Pu	60
Np	2700
Am	2170
Zr	24800
Tc	5700

3. RADIONUCLIDES TO BE SEPARATED

Three factors need to be considered in deciding which radionuclides should be separated from HLW (for eventual transmutation or storage):

- long term radiotoxicity

- long term radioactivity

- contribution to the dose to mankind resulting from release from an HLW repository

From the standpoint of repository safety, these factors need to be assessed over a long time scale (10^4 - 10^6 years). In order to eliminate the long-term impact of a specific radionuclide, it is necessary to separate not only the nuclide itself but its precursors in the relevant radioactive decay chain that are present in HLW. On this basis the contribution of a particular element present in HLW now to the radioactivity of the HLW in the long term can be calculated, by taking account of the contributions by the daughter products of each isotope of the element concerned.

Table 2: Contributions of Key Elements (and their Daughters) to the Total Radioactivity of HLW in the Long Term

Element	Contribution to Total Activity (%) after (years)			
	10^4	10^5	10^6	10^7
Zr	8	19	34	13
Tc	30	56	8	0
Np	1	7	29	27
Am	41	7	18	33
Pu	13	3	0	1
Total	94	91	89	73

Table 2 shows the contributions of key elements initially present in HLW to the long-term radioactivity. It shows that most of the long-lived radioactivity of HLW could be eliminated by removing the elements shown from HLW after reprocessing.

Table 3 shows the contributions of key elements to the long-term radiotoxicity of HLW on the same basis. The figures have been derived using the Annual Limit of Intake (ALI) by ingestion for each radionuclide[3] to calculate its contribution to the total number of ALIs present at various times. The effect of removing an element now has then been assessed by taking account of the contribution of the element and its daughters, in the same way as for the radioactivity calculation.

Table 3: Contribution of Key Elements (and their Daughters) to the Total Radiotoxicity (Ingestion) of HLW in the Long-Term

Element	Contribution to Total Radiotoxicity (%) after (years)			
	10^4	10^5	10^6	10^7
Zr	0.0	0.1	0.1	0.0
Tc	0.1	1.0	0.1	0.0
Np	2.0	37.0	61.0	40.0
Pu	16.0	1.0	0.0	0.2
Am	81.0	60.0	38.0	49.0
Total	99.9	99.0	99.0	89.6

Table 3 shows that the long-term radiotoxicity of HLW can be dramatically reduced by removing the actinide elements, particularly neptunium and americium, before disposal.

Zirconium-93, although a major contributor to long-term activity, has a much lower toxicity than the actinides. Other fission products (^{99}Tc, ^{135}Cs, ^{126}Sn) also have lower toxicities, but they are nevertheless important for partitioning considerations, because of their contributions to the dose to mankind resulting from releases from a repository[1]. It is assumed that ^{129}I is absent from HLW.

The contribution of zirconium to long-term radioactivity comes entirely from its ^{93}Zr isotope, and this only accounts for 20% by weight of fission zirconium. Similarly, the long-lived activity of caesium comes from ^{135}Cs which accounts only for some fraction of the total caesium. In the absence of expensive isotopic separation processes, these elements would be inconvenient substrates for transmutation and many proposed partitioning schemes do not address their separation.

This paper evaluates alternative partitioning processes in terms of their effectiveness in removing neptunium, plutonium, americium and technetium. Some attention is also given to zirconium. However, it is important to recognise that removal of these elements merely reduces the long-term radiotoxicity and radioactivity of HLW. It does not necessarily reduce the radiological dose to mankind resulting from releases from a repository. This radiological impact depends on the location and design of the repository for the HLW, but it is generally dominated by fission products, eg, ^{99}Tc, ^{135}Cs and ^{126}Sn. Thus, of the elements considered in this assessment, only technetium is significant from the radiological dose standpoint. If it were desired to reduce even further the very low doses to mankind from waste repositories, it would be necessary to focus attention not only on ^{99}Tc but also on ^{135}Cs and ^{126}Sn in HLW. These present far more difficult problems for partitioning and for transmutation. Moreover, it has been calculated[1] that the doses resulting from release of ^{36}Cl and ^{129}I from intermediate level waste repositories are higher than those resulting from HLW disposal. The difficulties of separating and transmuting these isotopes would be immense, and to do so would not be cost effective in the light of the very low reduction in doses achieved.

4.   EVALUATION OF CANDIDATE PARTITION PROCESSES

4.1   The Treatment Processes

Three representative partition processes from the literature have been selected in order to make a comparative evaluation of them.

1)   The TRPO process, developed in the People's Republic of China and based on the extractant trialkylphosphine oxide[4,5].

2)   The TRUEX process developed in the United States of America and using the extractant octyl(phenyl)-N,N-di-isobutylcarbamoylmethylenephosphine oxide (CMPO)[6].

3)   The DIAMEX process developed by the CEA in France[7], based on the diamide extractant, dimethyldibutyltetradecylmalonamide.

In recent work, the TRPO process has been tested in active batch experiments[5] and in an active flowsheet demonstration using centrifugal contactors[8]. A version of the TRUEX process was also demonstrated in the centrifugal contactor rig[8]. The CEA[7] have demonstrated the DIAMEX process in the CYRANO active facility. The illustrative flowsheets shown in Figures 1, 2 and 3 are based on the data for these active trials.

4.2 Volumetric Arisings and Plant Requirements

Table 4 shows the relative volumes of the key product and waste streams from each of the candidate processes, as multiples of the volume of the feed to the process, as used in the active experimental studies.

Table 4: Estimated Relative Volumes (per unit volume of Feed) of Product Streams from Candidate Processes

Stream	Relative Volume		
	TRPO	TRUEX	DIAMEX
Raffinate	1.15	1.4	1.7
Am product	0.4	1.25	1.5
Np, Pu product	0.5	0.55	
U product	0.5	0.55	
Total	2.55	3.75	3.2

It can be seen that the volumetric capacity, and hence the scale of the plant required, for the first sections of any of the processes considered is similar to that of the cycle 1 section of the reference PUREX process. The shielding requirements will also be similar, since essentially the same fission product inventory is being handled.

For the processes considered, the total volume of aqueous products and wastes is two to four times greater than the volume feed to the process. The feed to the process needs in some cases to be at a lower acidity than the HLW feed described in Section 2. If this reduction in acidity is achieved by dilution, there will be a further increase in volume in the product streams from the partitioning process. However, alternative methods of reducing the acidity, eg denitration, electrolytic reduction, have been suggested[4] and would result in smaller volume changes.

4.3 The Performance of the Candidate Processes

Table 5 gives details of the distribution of the key radionuclides between the product streams for each of the candidate processes considered. The data are based on the available information from active trials[5,7,8].

Table 5: Separation Performance of Candidate Processes
(% of Total Element in Feed)

Product Stream	Raffinate	Am/Cm Product	Np/Pu Product	U Product	Recycle Solvent
TRPO Process					
Zr[a]	5.0	5.0	43.0	0.4	42.0
Tc[b]	0.1	-	-	-	-
U[b]	-	-	0.1	99.8	0.1
Np[b]	9.8	Trace	89.5	0.1	0.5
Pu[b]	0.2	-	99.6	0.2	Trace
Am[b]	-	99.7	0.1	0.1	Trace
TRUEX (CMPO) Process[b][c]					
Tc	0.6	-	-	-	-
Ln[d]	-	8.6	10.7	3.9	0.3
U	-	0.1	0.4	98.9	0.1
Np	-	7.7	2.2	2.6	0.1
Pu	-	12.3	3.5	1.3	-
Am	-	7.2	6.7	4.9	0.4
Cm	0.1	13.0	10.3	7.0	0.6
DIAMEX Process[e]					
Fe	34.0	66.0	-	-	-
Zr	100.0	-	-	-	-
Mo	27.0	73.0	-	-	-
Ru	50.0	39.0	-	-	11.0
Ln[d]	-	100.0	-	-	-
U	-	100.0	-	-	-
Pu	-	100.0	-	-	-
Am	0.5	99.5	-	-	-

Notes

[a]   Estimated from data in Reference (5). In addition, 5% is estimated to pass to the scrub raffinate.

[b]   From Reference (8).

[c]   Complete mass balance was not obtained. Some of constituents of the feed accumulated in the contactors.

[d]   Lanthanide fission products.

[e]   From Reference (7) (Run 2).

4.3.1 The TRPO Process

The TRPO process has been demonstrated in an active facility at JRC Karlsruhe[8], and was shown to operate very effectively. Comprehensive data for technetium behaviour were not obtained in the active trial, but estimates of its distribution are available from earlier studies[5]. It appears that most of the technetium and zirconium will be extracted and may contaminate the product streams. The behaviour of neptunium was also not completely satisfactory: about 10% of it occurred in the raffinate, probably because of the presence of different valency states in the feed. An important conclusion is that the raffinate will not be free of long-lived radionuclides.

The mixed Np, Pu product contains oxalate. Presumably it would have to be separated if Np was to be transmuted. An oxalate destruction step followed by valence state conditioning and a solvent extraction cycle would probably be required. Similarly, there is sodium carbonate in the U product, and this would need to be taken into account in a process for uranium purification.

The feed to the TRPO process needs to be 1M in nitric acid in order to achieve extraction of the actinides. This could be accomplished[4] by denitration and electrolytic reduction. This will involve additional capital expenditure and active plant; but the alternative would require considerable dilution of the PUREX HLW stream, and a corresponding increase in the volume of the HA raffinate. Conversely, a high acid strip is used for the Am, Cm product. This product will also contain the lanthanide elements. Before transmutation of Am can be undertaken, some separation of the lanthanides and actinides in this stream will be necessary. Many of the possible schemes for such a separation require dilute acid conditions, so that the problem of dilution, volume increase, and waste production may again be significant.

The data available indicate that there will be no large accumulation of solutes in the solvent stream except for zirconium (42%). A solvent washing contactor will have to be supplied in order for solvent to be recycled, and this will lead to a further aqueous waste stream containing traces of long-lived radionuclides. Eventually spent solvent will require destruction and disposal. The presence of phosphorus would need to be allowed for in any scheme involving incineration. Schemes involving acid or alkaline hydrolysis (as proposed for phosphate ester extractants) are inapplicable to a phosphine oxide. It is likely that incineration would lead to the production of a phosphate-containing waste stream from the off-gas treatment system.

4.3.2 The TRUEX Process

A trial of the TRUEX process (CMPO extractant) has been conducted on real HLW at the JRC Karlsruhe and preliminary results are available[8]. Mass balances were not complete and it appeared that substantial fractions of some of the long-lived radionuclides accumulate in the system. The process cannot be successfully applied unless this problem is resolved. There appears to be extensive cross-contamination of the product streams.

The problems inherent in dilution of the feed to reduce the acidity, and in the management of spent solvent are similar to those noted for the TRPO process.

4.3.3 The DIAMEX Process

This process has been the subject of intensive development by the CEA, and an active trial has been reported[7]. The process is designed to accept as feed an HLW feed from a modified PUREX

process, such that the feed is free of technetium and neptunium. The DIAMEX reagent extracts trivalent actinides and lanthanides from this stream. It also extracts molybdenum and zirconium and these are dealt with by the incorporation of suitable reagents (hydrogen peroxide and ketomalonic acid respectively) into the scrub liquor. The results in Table 5 are for a run in which ketomalonic acid only was used in the scrub section. This successfully suppressed zirconium extraction. Extraction of molybdenum could also be reduced using hydrogen peroxide in the scrub, but the two reagents react with each other, so that some zirconium is then extracted. Further development of the scrub system is required.

Good extraction and stripping performance were observed for the actinides and lanthanides. Extraction takes place from 4M acid, and stripping is achieved with 0.5M nitric acid. Thus no adjustment of the feed activity is needed and the low acidity of the product stream is appropriate for subsequent actinide/lanthanide separation procedures.

It will be important to ensure that excessive quantities of Ru, Fe, Zr and Mo do not accumulate in the solvent. This would rise to a solvent wash raffinate containing these elements. However, their removal earlier in the flowsheet may also lead to the creation of secondary wastes.

The destruction of spent DIAMEX solvent by incineration will lead to complete conversion to carbon dioxide, nitrogen and water. This is an important advantage of extractants that do not contain phosphorus.

4.4 Product Conversion

The three partitioning processes reviewed above generate the required products in aqueous solution in various degrees of chemical and radiochemical purity. If the required elements are to be converted into targets for irradiation/transmutation, or into a form suitable for long-term storage, the product streams from the TRPO, TRUEX and DIAMEX process will require further chemical processing to obtain the appropriate materials (eg, oxides). These conversion processes will require further chemical plant and generate further waste streams containing low levels of the long-lived radionuclides.

5. DISCUSSION

The analysis in this paper rests solely on the authors' interpretation of published information on the candidate partitioning processes considered. It may not take full account of recent developments and improvements to these processes.

Within these constraints, none of the processes studied claims to achieve a complete separation of all the radionuclides of interest. This may not be important in some cases. However, extensive cross-contamination between product streams will exacerbate the difficulty of processing them to give fuel pellets or targets for irradiation, and may lead to the creation of troublesome secondary waste streams.

In all cases several liquid streams are created in place of the original HLW without significant increases in concentration. The overall volume of liquid at the end of the process is at least two times greater than at the beginning.

None of the processes discussed could be applied without substantial further development, and work to verify its detailed performance. In addition it has been shown that the additional costs (capital and operating) of adopting a HLW partitioning process are likely to be comparable with the costs of reprocessing by the PUREX process in the reference system.
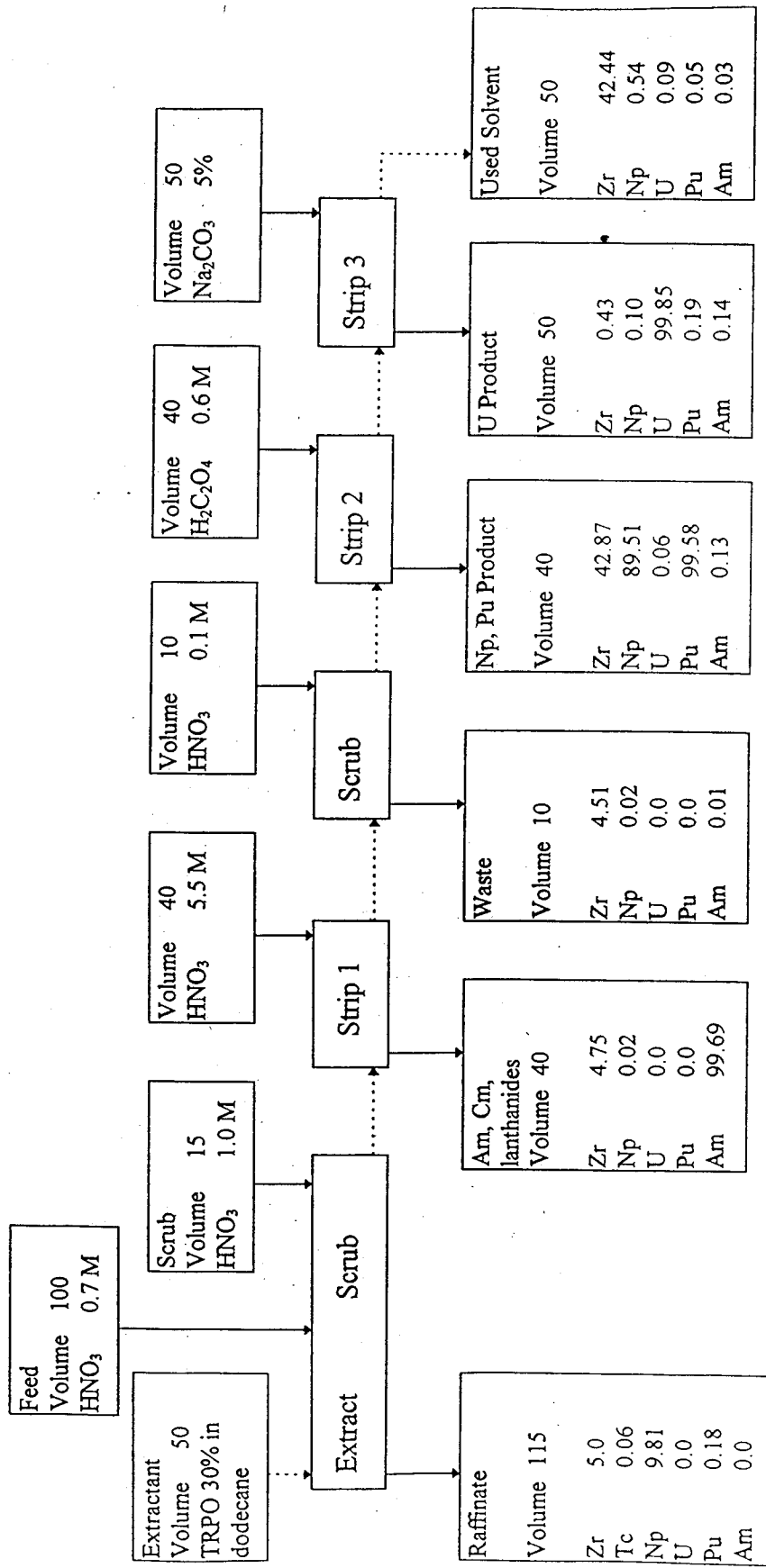
The present paper does not consider the recovery/conversion of the products from partition into targets for irradiation/transmutation. The conversion processes will require process plant and will generate further waste streams. The conversion processes are not 100% efficient.
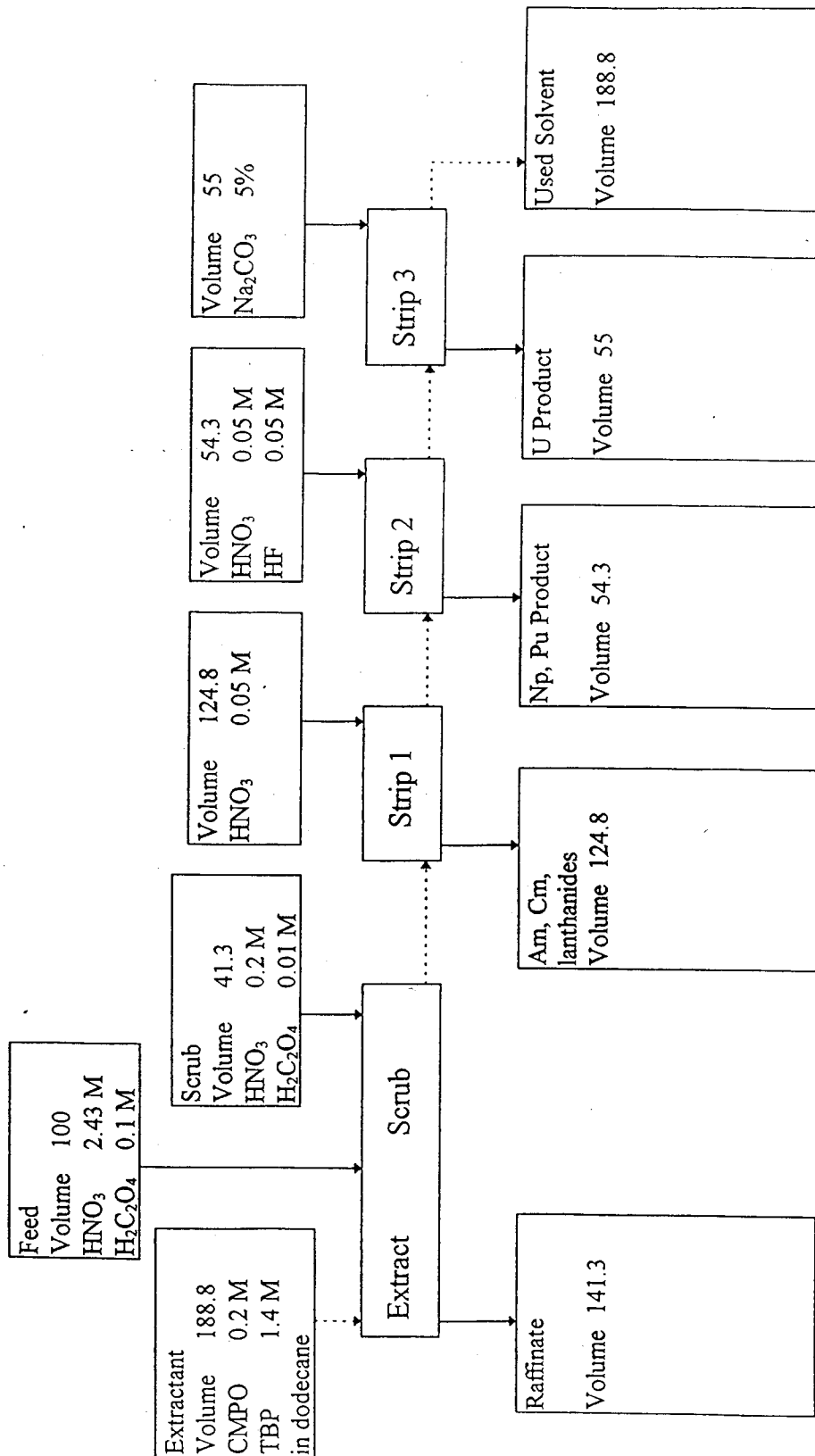
6. ACKNOWLEDGEMENTS

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Feed
Volume 100
HNO₃ 0.7 M

Scrub
Volume 15
HNO₃ 1.0 M

Extractant
Volume 50
TRPO 30% in dodecane

Volume 40
HNO₃ 5.5 M

Volume 10
HNO₃ 0.1 M

Volume 40
H₂C₂O₄ 0.6 M

Volume 50
Na₂CO₃ 5%

Extract — Scrub — Strip 1 — Scrub — Strip 2 — Strip 3

Raffinate
Volume 115

Zr	5.0
Tc	0.06
Np	9.81
U	0.0
Pu	0.18
Am	0.0

Am, Cm, lanthanides
Volume 40

Zr	4.75
Np	0.02
U	0.0
Pu	0.0
Am	99.69

Waste
Volume 10

Zr	4.51
Np	0.02
U	0.0
Pu	0.0
Am	0.01

Np, Pu Product
Volume 40

Zr	42.87
Np	89.51
U	0.06
Pu	99.58
Am	0.13

U Product
Volume 50

Zr	0.43
Np	0.10
U	99.85
Pu	0.19
Am	0.14

Used Solvent
Volume 50

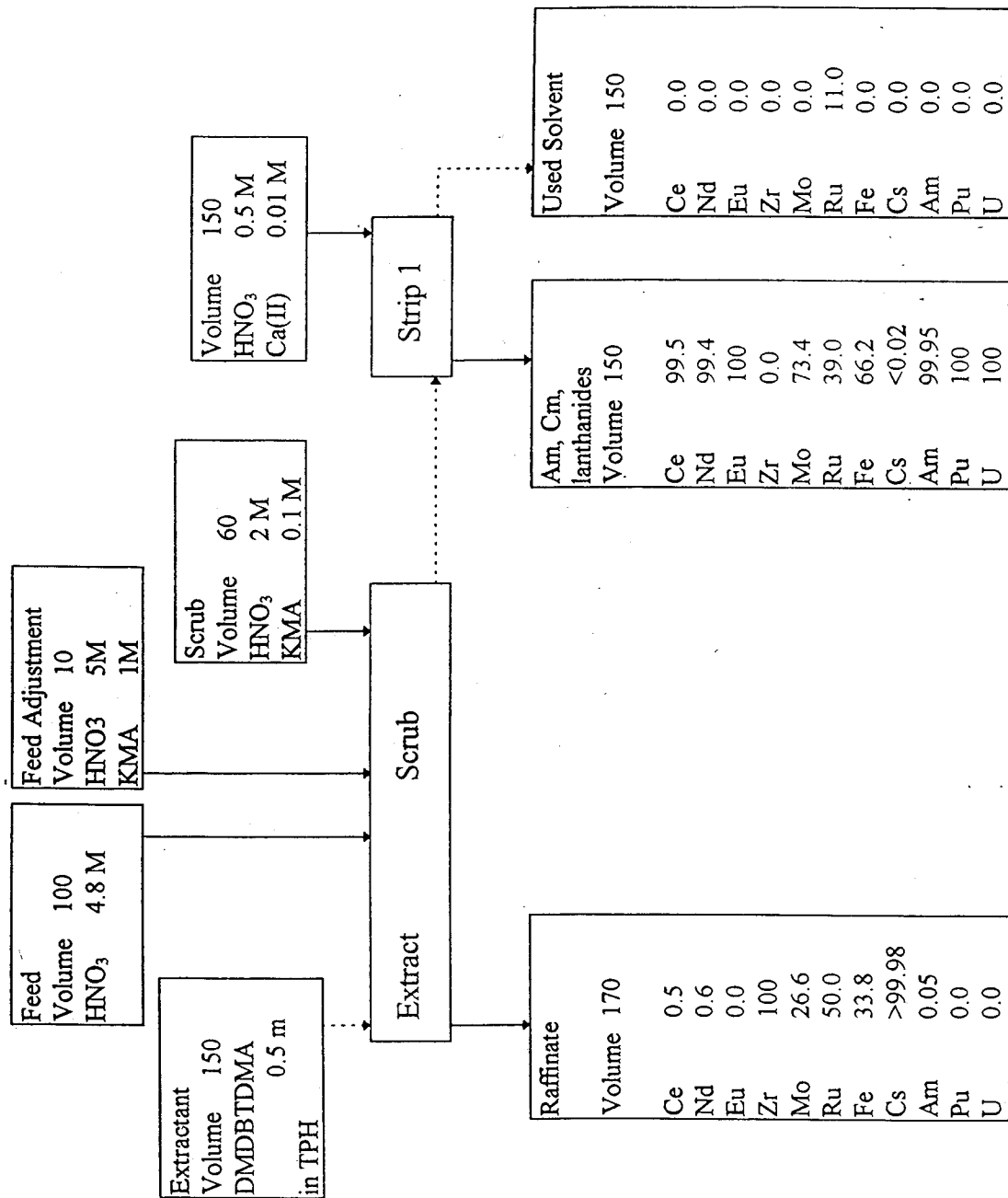|	
Zr	42.44
Np	0.54
U	0.09
Pu	0.05
Am	0.03

Figure 1 TRPO Process Flowsheet
Note. Data for solutes are expressed as percentages of the mass in the feed. Volumes are normalised to 100 units feed.

Feed
Volume 100
HNO_3 2.43 M
$H_2C_2O_4$ 0.1 M

Extractant
Volume 188.8
CMPO 0.2 M
TBP 1.4 M
in dodecane

Scrub
Volume 41.3
HNO_3 0.2 M
$H_2C_2O_4$ 0.01 M

Volume 124.8
HNO_3 0.05 M

Volume 54.3
HNO_3 0.05 M
HF 0.05 M

Volume 55
Na_2CO_3 5%

Extract

Scrub

Strip 1

Strip 2

Strip 3

Raffinate
Volume 141.3

Am, Cm,
lanthanides
Volume 124.8

Np, Pu Product
Volume 54.3

U Product
Volume 55

Used Solvent
Volume 188.8

Figure 2 Truex (CMPO) Process Flowsheet
Note. Volumes are normalised to 100 units feed.

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Figure 3 Diamex Process Flowsheet

Note. Data for solutes are expressed as percentages of the mass in the feed. Volumes are normalised to 100 units feed.