

SESSION 5: CHEMISTRY

CHAIRMAN: L.H. BAETSLÉ (BELGIUM))

OVERVIEW OF THE LONG-LIVED RADIONUCLIDE SEPARATION PROCESSES DEVELOPED IN CONNECTION WITH THE CEA's SPIN PROGRAMME

Charles MADIC*1, Jacques BOURGES* and Jean-François DOZOL**

CEA, Direction du Cycle du Combustible

*DRDD, CEN-FAR, B.P. N°6, 92265 Fontenay-aux-Roses, France;

** DESD, CEN-CAD. Cadarache, France.

^{1/} Author to whom correspondance should be addressed.

ABSTRACT :

One possible strategy for eliminating the long-term potential hazards associated with the storage of vitrified high level waste produced by the reprocessing of irradiated nuclear fuels, is the transmutation of the long-lived radionuclides in these wastes into short-lived radionuclides by nuclear means, which requires the prior chemical separation of these long-lived radionuclides from the nuclear waste mixture. To do this, the French CEA launched the SPIN (SÉPARATION-INCINÉRATION) research programme in 1991, under the law passed by the parliament on 30 december 1991.

Research currently under way to develop separation processes for some long-lived radionuclides concerns modifications of the PUREX process, and the development of new solvent extraction processes. The research directions are briefly summarized here.

PUREX process.

Modifications of the operating parameters of the PUREX process can certainly help to separate some long-lived radionuclides like ²³⁷Np and ⁹⁹Tc.

New processes :

Minor actinide separation processes. The strategy for these separations is based either on the extraction of the minor actinides from their stable oxidation states in aqueous nitric acid media (common in the reprocessing industry), or, especially for americium, after oxidation to high oxidation states. This research includes : ° *Minor actinide co-extraction using the DIAMEX process ; ° An(III)/Ln(III) separation ; ° Am selective separation after its oxidation to Am(IV) or Am(VI).*

Cesium extraction process using calixarenes extractants.

This lecture will focus on the latest developments in these research areas.

1. INTRODUCTION

Nuclear-generated electricity accounts for about 17 % of all the electricity produced worldwide. This industry is faced today with a problem of managing the wastes, which is considered acute by public opinion in the different nuclear countries and, in general, by world public opinion. Depending on national policy, these wastes consist either of irradiated fuels, in which case the energy materials (uranium and plutonium) are considered as wastes, or of the mixture of fission products, minor actinides and activation products resulting from the reprocessing of the fuels to recover the uranium and plutonium for recycling. To simplify and to lower the cost of the treatment and conditioning of spent fuel reprocessing wastes, and perhaps also to improve the public acceptance of nuclear power, considerable efforts have been mounted, with the aim of decreasing the unit volume of solid wastes (per ton of fuel reprocessed), particularly those intended for disposal in deep geological repositories. In this field, COGEMA has emerged as the prime mover of this strategy. At the reprocessing plants in La Hague, the unit volume of solid wastes generated in reprocessing operations, which justify deep geological disposal, is around $1.5 \text{ m}^3/\text{t}$ today, or about half of the volume initially defined in the process book. Following modifications to the PUREX process and the application of new processes, this unit volume is due to decrease drastically by the end of the century, when it should be around $0.465 \text{ m}^3/\text{t}$ [1]. The single distinguishing feature of nuclear waste management is their extreme danger, which, depending in particular on the nuclear properties of the radionuclides that they contain, may be spread over considerable periods of time. Faced with the growing opposition of public opinion to very long-term radwaste disposal techniques and the difficulty of the scientists to predict the behavior of the geological barriers for periods exceeding one hundred thousand or even one million years, it has become necessary to study and propose some technical solutions to this problem.

The separation and incineration of long-lived radionuclides by nuclear means, which lies at the source of the problem, in order to convert them to short-lived radionuclides, exhibiting higher activity, but which can feasibly be stored over a short period of time, is considered one possible solution to the problem. The situation is regarded with extreme caution in France, where more than 75 % of the electricity consumed is nuclear-generated. A law was accordingly passed by the French Parliament on 30 December 1991, ordering research to be conducted over a fifteen-year period, aimed in particular to determine the experimental conditions for the conversion of certain long-lived radionuclides present in the nuclear fuels to short-lived radionuclides by nuclear means. In this connection, the CEA launched the SPIN (SéParation/INcinération) program for the definition of long-lived radionuclide separation processes and for their destruction, chiefly by fast-neutron reactors [2]. This "intensive reprocessing" strategy is also being investigated in Japan, which launched the OMEGA program in 1988 [3], with objectives similar to those of the SPIN program.

This paper describes the main research guidelines selected at the CEA, aimed at the separation of long-lived radionuclides, and the latest experimental results obtained are briefly described.

2. PROBLEM ANALYSIS AND RESEARCH OBJECTIVES

The high-level wastes generated by irradiated fuel reprocessing, and intended for disposal in deep geological repositories, today include short- and long-lived radionuclides belonging to the families of fission products, minor actinides and activation products. It is universally acknowledged that the half-life identifying the borderline between short- and long-lived radionuclides is thirty years (half-life of ^{137}Cs). In fact, it is considered possible to develop safe disposal methods for periods of up to three centuries, or ten times the "borderline" period, the time necessary for the "total" decay of the short-lived radionuclides. After three centuries, the radionuclides which subsist in the stored wastes, particularly in the most active among them (nuclear glasses) will be the long-lived radionuclides. For the UOx reference fuel, irradiated to a burnup of 33 GWd/t and cooled for three years, Table 1 lists the long-lived radionuclides present, their abundance and some of their nuclear and radiotoxicological properties [4].

A glance at the data in Table 1 shows that the potential hazard of long-lived radionuclides is chiefly due to the minor actinides, and particularly the americium isotopes. This situation prevails for several tens of thousands of years. Consequently, efforts to develop separation methods will mainly concern the minor actinides, and especially americium. However, another way to tackle the problem is to consider the residual toxicity at the outlet of the geological formations where the nuclear wastes may be stored. This is currently being examined, particularly as part of the European exercise called PAGIS [5]. In this case, the doses delivered to the population in the neighborhood of the disposal site, although considerably lower than the standards currently in force, are mainly due to certain fission products, whose migration rates, with the water vector in the subsoil, are much greater than those of actinides. In consequence, a part of the research efforts is also focused on the separation of certain fission products, particularly technetium and cesium. Since long-lived radionuclides were also certainly not completely destroyed during a nuclear incineration cycle, it is also essential to guarantee the "reprocessability" of the targets or nuclear fuels which will contain these materials.

Table 1. Main characteristics of the long-lived radionuclides present in an irradiated fuel (UO_x type fuel ; burn-up : 33 GWd/t ; cooling time : 3 years)

Radio-nuclide	t½ (years)	Abundance (g/t _{H.M.})	Specific activity (Bq/g)	Dose factor for ingestion (Sv/Bq)	Isotopic %	Total element (g/t _{H.M.})
Fission products						
¹⁴ C	5.7 10 ³	0.13	1.05 10 ¹¹	5.7 10 ⁻¹⁰	100	0.13
⁷⁹ Se	6.5 10 ⁴	4.7	2.58 10 ⁹	2.3 10 ⁻⁹	8.6	54.6
⁹³ Zr	1.5 10 ⁶	714	9.3 10 ⁷	4.2 10 ⁻¹⁰	20.5	3617
⁹⁹ Tc	2.1 10 ⁵	814	6.3 10 ⁸	3.4 10 ⁻¹⁰	100	814
¹⁰⁷ Pd	6.5 10 ⁶	200	1.9 10 ⁷	3.7 10 ⁻¹¹	16.1	1240
¹²⁶ Sn	1.0 10 ⁵	20.3	1.0 10 ⁹	5.1 10 ⁻⁹	39.8	51
¹²⁹ I	1.6 10 ⁷	169	6.5 10 ⁶	2.4 10 ⁻⁸	81.2	208
¹³⁵ Cs	2.3 10 ⁶	1312	4.2 10 ⁷	1.9 10 ⁻⁹	37.2	3521
Minor actinides						
²³⁷ Np	2.1 10 ⁶	434	2.6 10 ⁷	1.0 10 ⁻⁶	100	434
²⁴¹ Am	4.3 10 ²	217	1.3 10 ¹¹	1.2 10 ⁻⁶	66.8	325
²⁴³ Am	7.4 10 ³	102	7.4 10 ⁹	1.2 10 ⁻⁶	31.4	325
²⁴⁵ Cm	8.5 10 ³	1.2	6.3 10 ⁹	1.2 10 ⁻⁶	4.7	25.5
Activation products						
⁵⁹ Ni	7.5 10 ⁴	36.1	3.0 10 ⁹	5.4 10 ⁻¹¹	--	36.1
⁶³ Ni	1.0 10 ²	6.6	2.1 10 ¹²	1.5 10 ⁻¹⁰	--	6.6
⁹⁴ Nb	2.0 10 ⁴	4	6.9 10 ⁹	1.4 10 ⁻⁹	--	4

The objectives of separative chemistry research connected with the SPIN program are listed in Table 2.

Table 2. Research objectives in separation processes [6]

Nature of the objectives	Importance
° Am separation (99 %)	Very important
° Ability for reprocessing	
° MO _x (LWR, FNR)	Very important
° Am targets (FNR ?)	Very important
° Cm, Pu, Np separation (99 %)	Important
° Ability for reprocessing	
° Fuels with Np (FNR ?)	Important
° Cm targets (FNR ?)	Important
° Long-lived F.P. separation	Secondary

3. SEPARATION OF LONG-LIVED RADIONUCLIDES

3.1. Strategy

Before presenting the strategic guidelines concerning the separative methods to be developed for some of the long-lived radionuclides mentioned above, it is essential to review the behavior of these materials in current nuclear fuel reprocessing operations. Table 3 presents this information for the specific case of COGEMA's UP3 plant at La Hague.

Table 3. Behavior of some long-lived radionuclides at COGEMA's UP3 plant at La Hague [4]

Long-lived radionuclide	Behavior
Minor actinides	
^{237}Np	<ul style="list-style-type: none"> ◦ 70 to 90 % extracted in the first U+Pu co-extraction cycle ◦ Np extracted separated in second U cycle ◦ All the Np is finally mixed with FP
$^{241, 243}\text{Am}$ ^{245}Cm	<ul style="list-style-type: none"> ◦ Not extracted, remains with FP
$^{239 \text{ to } 242}\text{Pu}$	<ul style="list-style-type: none"> ◦ 0.12 % of losses with wastes
Fission products	
^{99}Tc	<ul style="list-style-type: none"> ◦ ≈ 30 % of Tc is insoluble in fuel dissolution ◦ Soluble Tc is co-extracted with Zr(IV) and then Pu(IV) (and U(VI)) in the first U+Pu co-extraction cycle, and then separated by special washing and mixing with FP
^{135}Cs	<ul style="list-style-type: none"> ◦ Not extracted, remains with FP

In consequence, the separation strategies adopted are divided into two categories.

* Definition of operating conditions of the PUREX process (in the broad sense of the term) for the separation of some long-lived radionuclides. This strategy concerns ^{237}Np and ^{99}Tc . It could also be applied to ^{93}Zr and ^{129}I .

* Definition of specific separation processes. This concerns $^{241, 243}\text{Am}$, ^{245}Cm and ^{135}Cs .

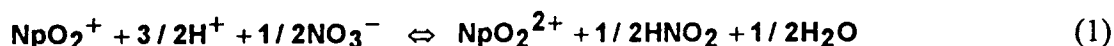
Due to its outstanding ability to solve separation problems in the nuclear industry, all the processes investigated are based on liquid/liquid extraction. For the difficult separation of americium and curium, the process being investigated has several cycles involving different extractants, whereas cesium can be separated using a single extractant.

3.2. Separation of long-lived radionuclides using the PUREX process

²³⁷Np

As stated above, most of the neptunium is extracted in the first U+Pu co-extraction cycle (1CUPu) applied at the UP3 plant in La Hague, and this fraction of extracted neptunium is mainly separated in the second uranium purification cycle (2CU). Hence the current research objective is to determine the physicochemical conditions of the PUREX process required to boost the neptunium extraction yield in 1CUPu. Two types of study are undertaken in this program : consolidation of the PAREX code used to predict the behavior of neptunium in the different steps of the PUREX process, and especially in the 1CUPu and 2CU cycles, and experimental investigations, in the laboratory, aimed to consolidate the knowledge of the redox reactions between the Np(V)/Np(VI) and HNO₂/HNO₃ pairs, and, in a test loop, to qualify the PAREX code for the behavior of neptunium. One may well ask why new studies appear necessary for the new objective, whereas the behavior of neptunium in the PUREX process has been investigated for many years. The answer is that the objectives previously assigned were chiefly aimed to prevent the uranium and plutonium end products from being polluted by neptunium, so that only an "overall" knowledge of neptunium behavior was then necessary, whereas the new objective implies a much closer understanding of this behavior.

The equation of the basic reaction allowing a "rough" interpretation of neptunium behavior in 1CUPu is the oxidation of Np(V) to Np(VI) by nitric acid, a reversible reaction catalysed by nitrous acid produced by reaction.



This reaction, which has been investigated for many years by Siddall and Dukes [7], Swanson [8] and Moulin [9], does not yet appear to have revealed all its aspects. One unanswered question is its kinetics in the presence of highly concentrated uranyl nitrate and of the solvent.

Valid methods nevertheless appear to be developing : increasing the temperature and the nitric acidity during extraction in 1CUPu should help to achieve the objective of quantitative neptunium extraction in 1CUPu without requiring the addition of a special reagent to oxidize the Np(V). This also represents the analysis of Yamana [10].

⁹⁹Tc

The behavior of technetium present in the fuel dissolution liquor (which accounts for about two-thirds of the Tc inventory of irradiated fuel) is unusual (in comparison with the other metallic species) during the operations of the PUREX process. The technetium exists in solution in oxidation state VII, in the form of the TcO₄⁻ ion. In this form, Tc(VII) is co-extracted with Zr(IV) (Tc(VII) playing an identical role to that of the nitrate anions), and then with Pu(IV) and U(VI) after washing of the Zr(IV) contained in the solvent. It is then possible to transfer Tc(VII) to the aqueous phase by washing with concentrated nitric acid (NO₃⁻/TcO₄⁻ competition effect) [11]. The behavior of the soluble fraction of Tc can therefore be considered to be under control. In consequence, research must focus on the understanding of the behavior of Tc in the irradiated fuel dissolution step, in order to identify simple methods that can be used to make the solubilization of the Tc quantitative. Investigations currently under way are designed to determine the precise metabolism of the Tc in the overall PUREX process which is a problem due to analytical difficulties, and to improve the Tc dissolution yield from the dissolution residues.

3.3. Separation of long-lived radionuclides with new processes

3.3.1. Minor actinides

Assuming the implementation of an "intensive reprocessing" strategy, the high-level raffinate leaving the "modified" ICUPu(Np) will only contain, as actinides, in addition to traces of uranium, neptunium and plutonium, the entire fuel inventory of americium and curium. The CEA is investigating two types of process to extract and separate these minor actinides from the FP : the first is based on the extraction of the actinides in their stable oxidation state in nitric medium, i.e. An(III), and the second process is mainly concerned with the separation of americium, and is based on its selective oxidation to Am(IV) or Am(VI) in the presence of a heteropolytungstate ligand, followed by selective extraction (SESAME process).

A common feature of these two processes is that, if they are applied directly to the raffinate from the PUREX process, after being subjected to a minimal modification of its composition. No decrease in the nitric acidity of the effluent is in fact intended, for preventing any risks of undesirable FP precipitation. In the first process, it is necessary to use several extraction cycles to achieve the objectives : first co-extraction cycle of minor actinides by the DIAMEX process (DIAMide EXtraction), applied to the raffinate from the PUREX process. In this step, the lanthanides (Ln(III)), which account for about one-third of all the FP, are co-extracted, and the mixture of An(III) + Ln(III) is obtained, free of strongly hydrolysable ions, such as traces of Pu(IV) and U(VI). The second An(III)/Ln(III) separation cycle uses an extractant with a nitrogen donor atom, such as the alkyl derivatives of tripyridinetriazine or picolinamides, allowing their separation by selective extraction of An(III) the least abundant metallic entities, so that only a minimal extraction capacity is required from the solvent. The third Am/Cm separation cycle could be applied either by the DIAMEX process or by the SESAME process. Note also that, for the first process, all the reagents to be employed (extractants, diluents, chelant reagents present in aqueous solution) will display the feature of being totally incinerable into gases releasable into the environment, thus helping to eliminate any generation of secondary solid waste. Consequently, these reagents will consist exclusively of C, H, N and O atoms.

DIAMEX

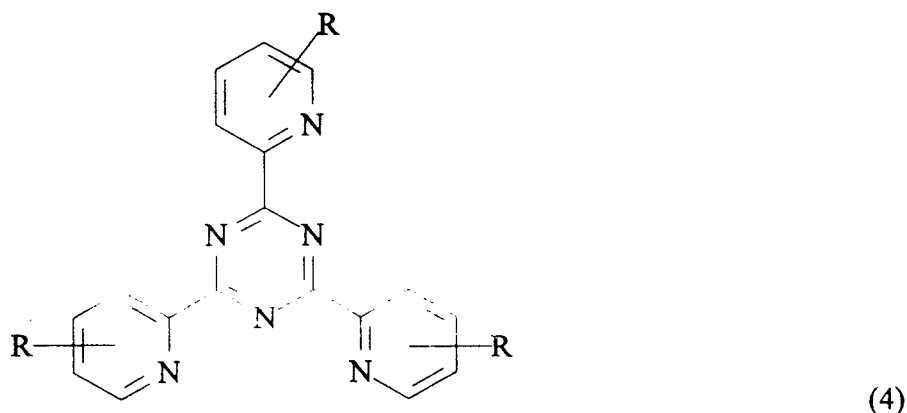
The extraction of the An(III) (Am and Cm) from the high-level raffinate produced by the PUREX process is difficult because of the low extraction capacity of the An(III) nitrates and by the high concentration of nitric acid, which induces strong competition in the extraction of the An(III) nitrates. The diamide extractants, proposed by Musikas [12], and particularly those belonging to the sub-class of malonamides, which have a single carbon that forms a bridge between the two amide groups, offer a solution to this problem of extraction. With the general formula $(RR'NCO)_2CHR''$, where R, R' and R'' are alkyl or oxyalkyl radicals, these compounds are bidentate oxygen donors, forming an extremely stable six-link ring with the metallic ion. The extraction mechanism essentially concerns the extraction of neutral molecules, and corresponds to the following equation :



where E is the diamide extractant (the species present in organic phase are overlined).

The value of n, the number of diamide molecules solvating the An(III) nitrate, is two at saturation of the organic phase. However, using the conventional slope method, the value of n found exceeds two, reflecting the non-ideality of the organic solutions of diamide, an occurrence often encountered in the extractive chemistry of the amides.

The first is based on the use of derivatives of tripyridinetriazine R_3 TPTZ [14], answering to the following semi-developed formula :

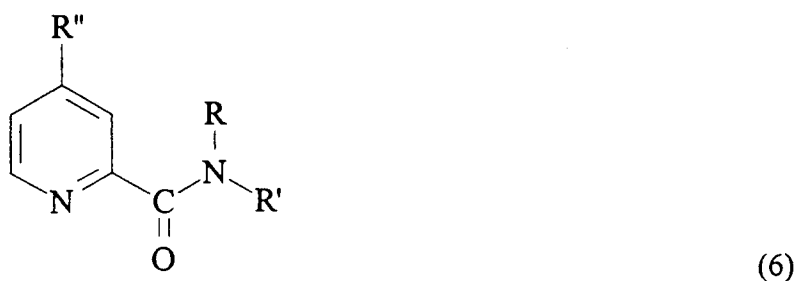


To be effective, the extractant R_3 TPTZ must be employed in synergistic combination with an HA acid extractant, a source of more lipophilic anions than nitrate ions. The extraction equation is then written :



The current research direction, pursued jointly with the team of Dr. M.J.Hudson of the University of Reading (UK), concern the synthesis of alkyl derivatives of TPTZ that are sufficiently hydrophobic and the synthesis of HA acids with low pK_a .

The second system concerns the use of picolinamide extractants, answering to the following general semi-developed formula :



As demonstrated by Cordier [15], pyridine 2 carboxamide, for which R, R' and R'' = H, a soluble reagent in the aqueous phase, is a selective chelatant of Am(III) with respect to Nd(III). The grafting of alkyl groups, R, R' and R'', helps to reinforce the lipophilic properties of the molecules and accordingly to enhance their ability as selective extractant for An(III).

The extraction equation is written :



Current research directions in this area are aimed to strengthen the affinity of picolinamides for An(III) nitrates, particularly in order to counteract the strong competition due to the extraction of nitric acid.

SESAME (Selective Extracting Separation of Americium by Means of Electrolysis)

Another alternative to separate americium, either directly from the raffinate produced by the PUREX process, or from the An(III)/Ln(III) mixture produced by the DIAMEX process, or even from the Am(III)+Cm(III) mixture, consists of its selective oxidation to Am(IV) or Am(VI) followed by its extraction. The chief difficulty to be overcome in this connection is the oxidation of Am(III) in nitric medium with acidity greater than 1 mol/l. In the case of the Am(III)/Am(IV) pair, in fact, this impossibility is thermodynamic (E_0 Am(III)/Am(IV) = 2.6 V/NHE), whereas it is rather kinetic in the case of the Am(III)/Am(VI) pair. By contrast, it is possible to oxidize Am(III) by chemical or by electrochemical means, subject to the presence in aqueous solution of a powerful ligand belonging to the heteropolytungstate family. For example, the ligand $P_2W_{17}O_{61}^{10-}$ is extremely effective for this purpose. Present in a concentration higher than of Am(III), it allows the oxidation of the americium to Am(IV), whereas for molar ratios lower than 1, the americium is oxidized to Am(VI). Other heteropolytungstate ligands are also satisfactory, such as silicotungstates. After oxidation, the americium can be extracted, either by amine salts in the case of Am(IV), or by bis-2,6 dimethyl-4 heptyl phosphoric acid for Am(VI). In these conditions, neither the lanthanides (except for cerium) nor the curium is oxidized, and is therefore easily separated from the americium. This is the basis of the SESAME process [16].

Active tests of the SESAME process are currently under way at Fontenay-aux-Roses, on raffinates from the PUREX process, and on an An(III)/Ln(III) mixture generated in 1993 during active tests of the DIAMEX process.

3.3.2. Fission products

Among the long-lived fission products that need to be separated, only ^{135}Cs is now the subject of intensive study at the Cadarache Nuclear Center, for the definition of a separation process. The extractant molecule expected to permit the separation of Cs(I), either from a 1 mol/l nitric acid solution, concentrated with sodium nitrate (4 mol/l), like the solution generated by evaporation processes for radioactive effluents, or a high-level raffinate produced by the application of the PUREX process, has been selected in the family of calixarenes. These molecules, in the form of a calix (hence their name) are pre-organized structures which, by the grafting of adequate functional groups, either on the upper rim or on the lower rim of the structure, help to define specific chelatants for ionic species considered as targets. The use of these substituents also makes it possible to impart hydrophilic or lipophilic properties to the molecules, thus enabling them to act as chelatants or extractants. The research project, conducted jointly with several European universities under a contract with the CEC, consisted of a screening of the different synthesized calixarenes for their aptitude for Cs(I)/Na(I) separation followed by the extraction of Cs(I) from nitric solutions. Spectacular performance was observed in these two areas with the following calixarenes : mono-ring calix[4]arenes and bis-ring-n calix[4]arenes. Very high separation factors $SF_{\text{Cs/Na}}$ close to $4 \cdot 10^4$ were obtained with certain molecules[17]. These molecules lend themselves well to extraction in the form of supported liquid membranes (SLM), which therefore help to perform separations with a very small quantity of extractant.

Research under way at Cadarache in this area is concerned with :

- * the demonstration of the feasibility of the extraction of ^{135}Cs (in a mixture with the other cesium nuclides) from a high-level effluent produced by the PUREX process,
- * the search for specific calixarenes for the minor actinides, allowing selective separation of An(III)/Ln(III).

4. CONCLUSIONS

Studies under way at the CEA in connection with the SPIN program aimed at the separation of long-lived radionuclides for their subsequent nuclear "incineration" (P & T strategy) have yielded promising results, both in the areas of the DIAMEX and SESAME processes, and in the selective separation of cesium. Yet the road is a long one before the definition of the flow diagrams of a facility that would implement these intensive reprocessing technologies. While it is possible to reasonably predict the feasibility of a process such as DIAMEX, this cannot be said of An(III)/Ln(III) separations, which are certainly more difficult to achieve, or of the SESAME and "calixarene" processes, which are still in the basic research or early development stage. It also appears clear that economic considerations will have to be taken into account when the process decisions are made. For the time being, criteria of simplicity and reliability will certainly prevail in these decisions. While it is possible to predict that the chemists will find solutions to these complex problems of long-lived radionuclide separation, it is also clear that considerable efforts will have to be made to develop industrially-viable solutions.

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Note : A similar lecture was presented in July 1994 at the ADIT Conference (Las Vegas, N, M, USA).

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DEVELOPMENT OF PARTITIONING PROCESS AT JAERI

M. KUBOTA, Y. MORITA, R. TATSUGAE, T. FUJIWARA and Y. KONDO

Japan Atomic Energy Research Institute
Tokai-mura, Ibaraki-ken, 319-11, Japan

ABSTRACT

One of the methods to manage HLLW generated from nuclear fuel reprocessing is to partition long-lived transuranic elements (TRU) and heat-generating nuclides such as Sr-90 and Cs-137 from HLLW, and then to transmute TRU to shorter-lived or stable nuclides by a fission process and to fix Sr-90 and Cs-137 in mineral-like stable compounds.

Since 1985, much efforts have been directed to developing an advanced partitioning process for separating elements in HLLW into four groups; TRU, Tc-platinum group metals (PGM), Sr-Cs and the other elements. The most recent studies on the separation of the TRU group with diisodecylphosphoric acid (DIDPA) will be described in our presentation.

DEVELOPMENT OF PARTITIONING PROCESS AT JAERI

M. KUBOTA, Y. MORITA, R. TATSUGAE, T. FUJIWARA and Y. KONDO

Japan Atomic Energy Research Institute
Tokai-mura, Ibaraki-ken, 319-11, Japan

1. Introduction

Partitioning of nuclides such as transuranium elements (TRU), Tc-99, Sr-90 and Cs-137 in a high-level liquid waste (HLLW) generated in nuclear fuel reprocessing and transmutation of long-lived nuclides by nuclear reactions are expected to increase the efficiency of high-level waste disposal and will seek the utilization of existing resources in a spent fuel.

Since 1985, much efforts have been directed to developing an advanced partitioning process for separating elements in HLLW into four groups; TRU, Tc-platinum group metals (PGM), Sr-Cs and the other elements. The most recent studies on the separation of the TRU group with diisodecylphosphoric acid (DIDPA) will be described in the present paper.

2. Separation of TRU, especially Np

Effectiveness of DIDPA for the complete extraction of Am, Cm, Pu and U had been already demonstrated with an actual HLLW before 1984. Therefore much attention has been given to how to increase the Np extraction with DIDPA. The penta-valent Np, which is dominant in HLLW, is the TRU most difficult to extract with general organic solvents. We found that the addition of hydrogen peroxide to the TRU extraction with DIDPA accelerated the pentavalent Np extraction. Through the experiments on a counter-current continuous extraction using a mixer-settler, more than 99.96% of penta-valent Np was found to be extracted when hydrogen peroxide was fed at a level to compensate for its decomposition as shown in Fig. 1

The behavior of fission and corrosion products in the continuous counter-current extraction with DIDPA was experimented with a simulated HLLW. Table 1 shows that more than 99.99% of Nd, which was used as a stand-in for rare earths, Am and Cm, was recovered by back-extraction with 4 M nitric acid. Most of Fe was extracted with DIDPA, but not back-extracted with 4 M nitric acid. Therefore, Fe could be separated from Nd with a decontamination factor of about 100. About 6% of Ru and 11% of Rh were extracted in this experiment. Their extraction behavior might be changed in a practical application because their chemical forms seem to differ in an actual HLLW. Almost all Cs and Sr were transferred to the raffinate fraction and Nd was found to be completely separated from these heat generating nuclides in HLLW.

3. Separation of Am and Cm from rare earths

In order to develop a more continuous process, we are developing a preferential back-extraction of Am and Cm, leaving rare earths in the DIDPA solvent. Figure 2 shows the comparison of distribution ratio of Am with those of rare earths. The distribution ratio of Sm was the nearest to that of Am. Figure 3 shows the pH dependence of the distribution ratio of Am and Nd in the back-extraction from the DIDPA solvent with diethylenetriaminepentaacetic acid (DTPA). The separation factor between two elements became more than 10.

The pH of the stripping solution, which contains 0.05 M DTPA, 1 M lactic acid and ammonium, changes stage by stage in continuous back-extraction because of the extraction of ammonium. Figure 4 shows the pH profile in the continuous back-extraction. The profile could be estimated by calculation from batch experimental data of ammonium extraction. Good agreement between observed and calculated values makes it possible to design and optimize the process flow sheet from the batch experimental data of distribution ratio.

Figure 5 shows the Am concentration profile obtained in the continuous back-extraction experiment with the DIDPA solvent containing only Am. About 99.9% of Am was back-extracted from the solvent and the Am concentration profile was in fair agreement with calculated profile as shown in Fig. 6.

The continuous back-extraction experiment was performed with the DIDPA solvent containing Nd and La, which are stand-ins for Am-Cm and rare earths respectively. The experimental results as shown in Fig. 7 revealed that more than 99.9% of Nd was back-extracted, while more than 98% of La was left in the solvent, and the Nd and La concentration profiles agreed very closely with calculated profiles.

These findings show that the estimation of the back-extraction behavior of Am, Cm and rare earths by calculation would be valid enough for the optimization of the back-extraction process.

Figure 8 shows calculated concentration profiles of Am and Nd in the optimized process. The calculation shows that 99.995% of Am is back-extracted and only 1.7% of Nd or 1.1% of rare earths accompanies Am. As the weight ratio of Am and Cm to rare earths is only 3.3% in HLLW, it would become about 75% after separation.

We are going to confirm this estimation by performing the continuous experiment with the solvent containing both Am and rare earths.

4. Back-extraction of U

After the Am and Cm back-extraction with DTPA solution, all of rare earths and other TRU (Np and Pu) can be back-extracted with 4 M nitric acid and 0.8 M oxalic acid solution, respectively. As for the back-extraction of U, effectiveness of phosphoric acid has been already studied. However, it has some difficulties in practical use.

We are developing on the application of a sodium carbonate solution to the U back-extraction from the DIDPA solvent.

Batch experiments showed that the distribution ratio of U became lower than 0.1 when the 0.8 to 2 M sodium carbonate solution was used as back-extractant. However, the emulsion was formed. We found that it could be avoided by increasing temperature and/or adding alcohol.

Table 2 shows required temperature to avoid the emulsion. If the temperature was increased to 65 °C, no emulsion was observed. If ethanol was added with a ratio of 15 vol%, the temperature can be lowered to 15°C.

Figure 9 shows the distribution ratio of U under the condition that no emulsion was formed. Because of the low distribution ratio, U would be back-extracted in a small number of stages in a mixer-settler.

5. Construction of partitioning process

Through these fundamental studies, the advanced partitioning process for the TRU separation from HLLW has been constructed as shown in Fig.10 and its effectiveness will be demonstrated with an actual HLLW at the NUCEF (Nuclear Fuel Cycle Safety Engineering Research Facility) in the near future.

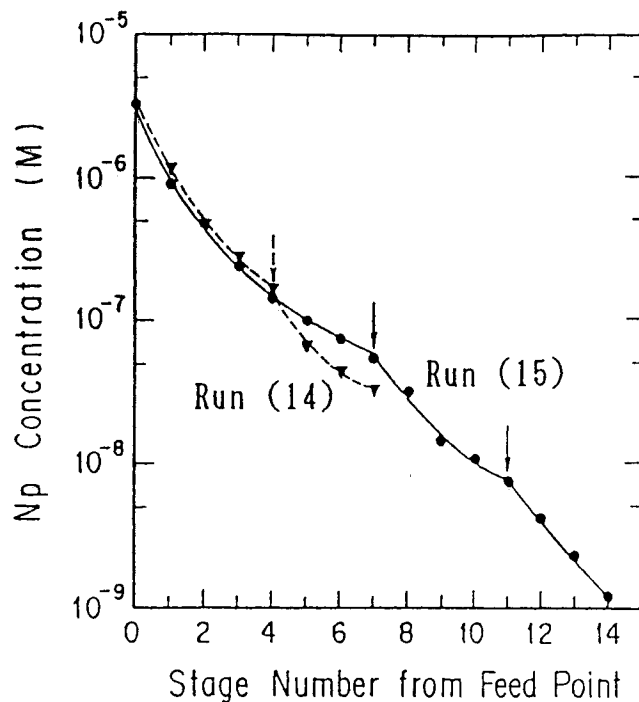


Fig.1 Concentration profile of Np in aqueous phase at the extraction section 45°C. Downward arrows show the points where H₂O₂ is added.

Run (14) (7-stages) : 99.0% recovery.

Run (15) (14-stages): over 99.96% recovery

Table 1 Behaviors of fission and corrosion products

- Ratios (%) of each element in the three fractions. 45 °C.

7-stages extraction with the DIDPA solvent
 4-stages scrubbing with 0.5M HNO₃ - 0.5M H₂O₂
 5-stages stripping with 4M HNO₃

Element	Raffinate	4 M HNO ₃ (Product I)	Organic Fraction
Na	>99.6	0.31	<0.1
Cr	>99.5	0.38	<0.1
Fe	0.13	0.1	99.77
Ni	>99.5	0.44	<0.1
Rb	>99.97	<0.02	<0.01
Cs	>99.99	<0.005	<0.002
Sr	>99.95	0.042	<0.004
Ba	>99.94	0.027	<0.04
Ru	93.53	0.98	5.49
Rh	88.30	1.86	9.84
Pd	>99.5	0.43	<0.02
Nd	0.002	>99.99	<0.006

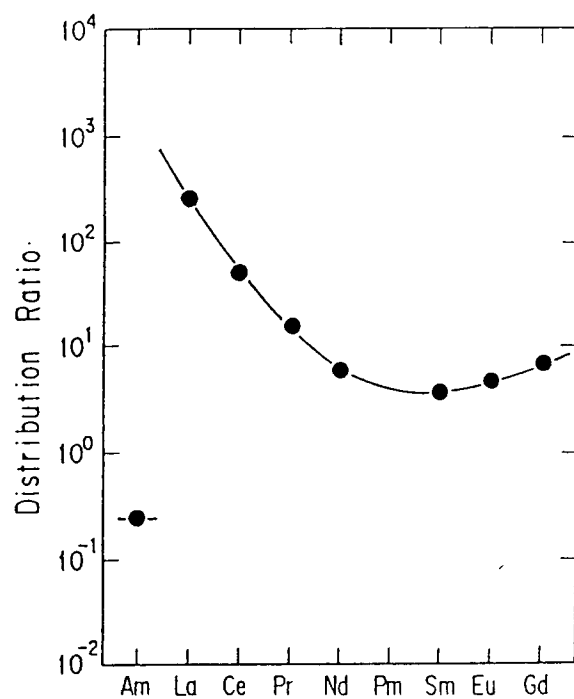


Fig.2 Comparison of Am distribution ratio with that of rare earths
 Org. : 0.5 M DIDPA - 0.1 M TBP in n-dodecane
 Aq. : 0.05 M DTPA - 1 M lactic acid - NH₄OH, pH 3.6 after back-extraction

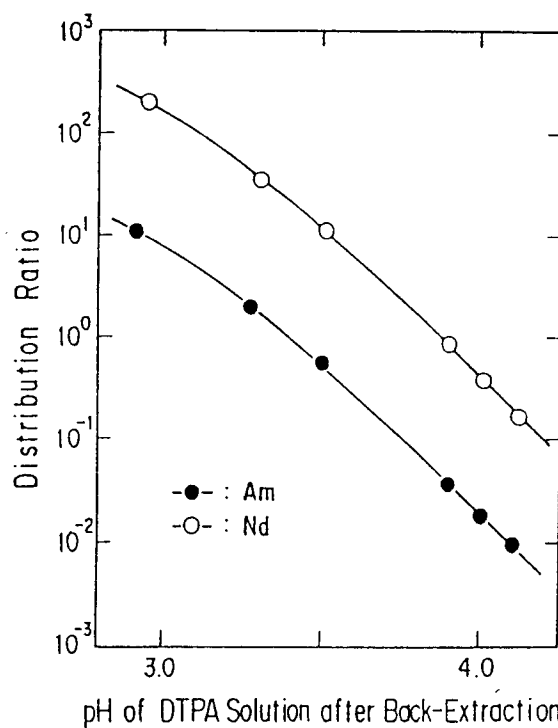


Fig. 3 pH dependence of distribution ratio of Am and rare earths in back-extraction from DIDPA solvent with DTPA
 Org. : 0.5 M DIDPA - 0.1 M TBP in n-dodecane
 Aq. : 0.05 M DTPA - 1 M lactic acid - NH₄OH

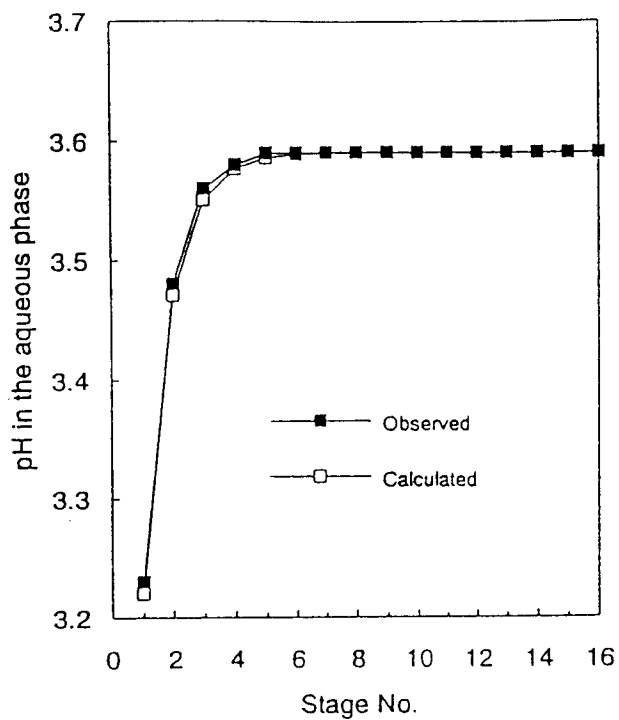


Fig. 4 pH profile in the back-extraction process with the DTPA solution

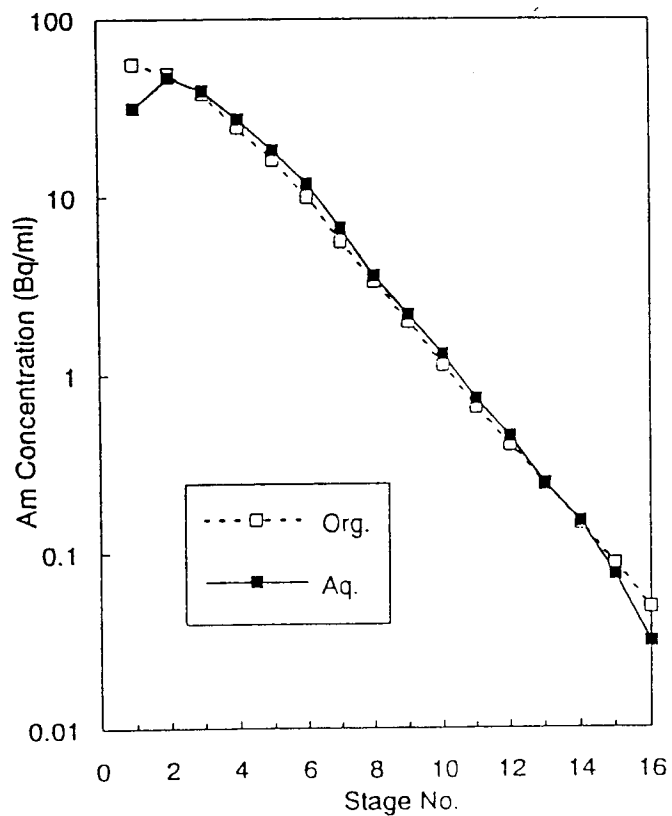


Fig. 5 Concentration profile of Am observed in continuous back-extraction with DTPA

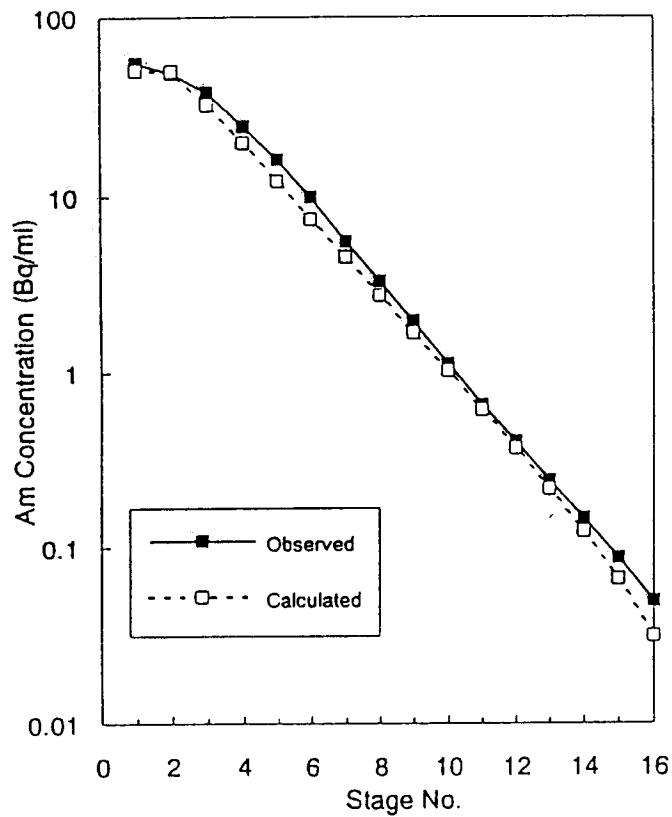


Fig. 6 Comparison of the observed and calculated concentration profiles of Am in the organic phase in continuous back-extraction with DTPA

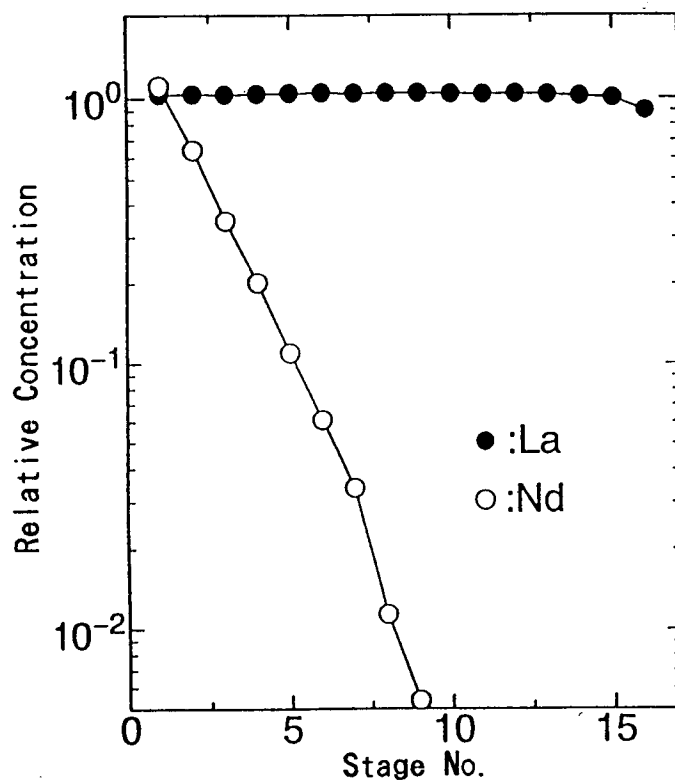


Fig. 7 Observed cocentration profiles of La and Nd in the organic phase in continuous back-extraction with DTPA

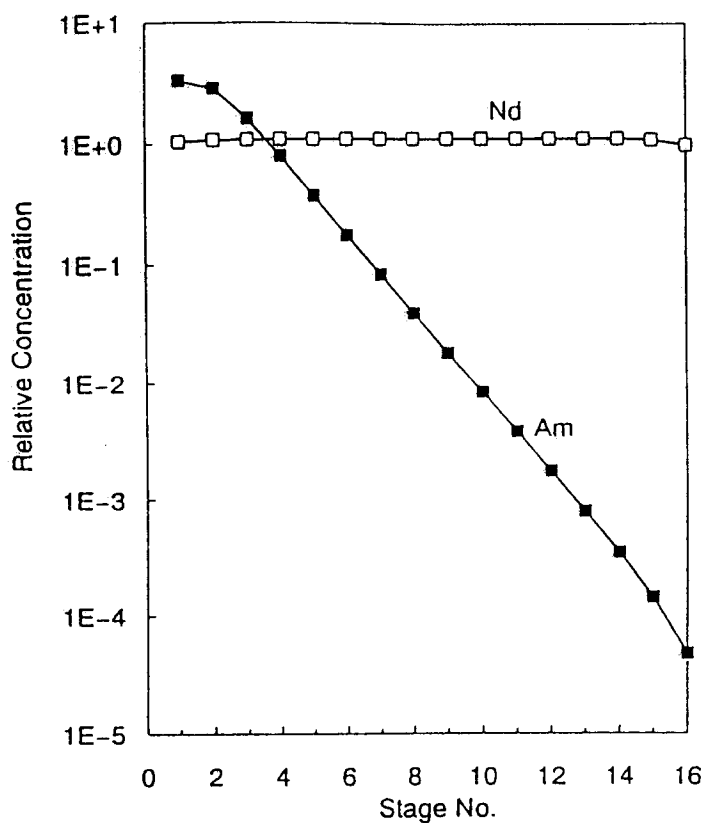


Fig. 8 Calculated concentration profiles of Am and Nd in the organic phase in continuous back-extraction with DTPA

Relative flow rate: Org. feed 100
 DTPA soln. 100
 Initial pH of DTPA soln.: 3.52

Table 2 Required temperature to avoid the formation of emulsion

Na ₂ CO ₃ (M)	Ethanol (v/o)	Temperature (°C)
0.5	0	> 70
1.5	0	> 65
1.5	5	> 45
1.5	10	> 30
1.5	15	> 15
0.5	15	> 25

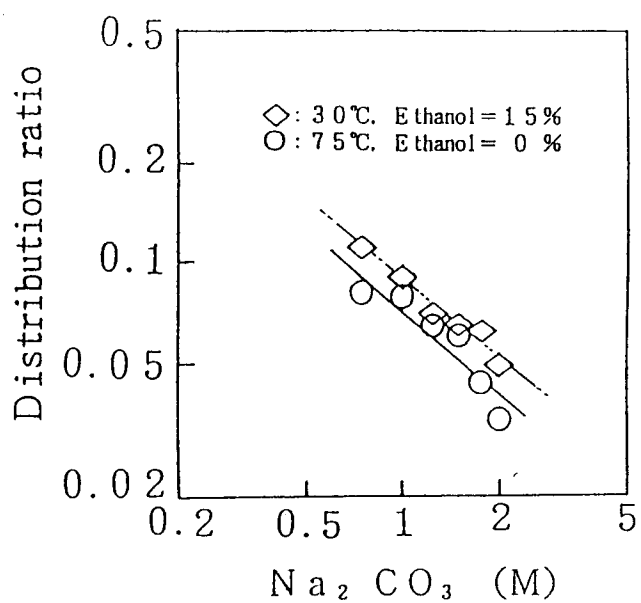


Fig. 9 Distribution ratio of U in back-extraction with Na_2CO_3 from DIDPA solvent

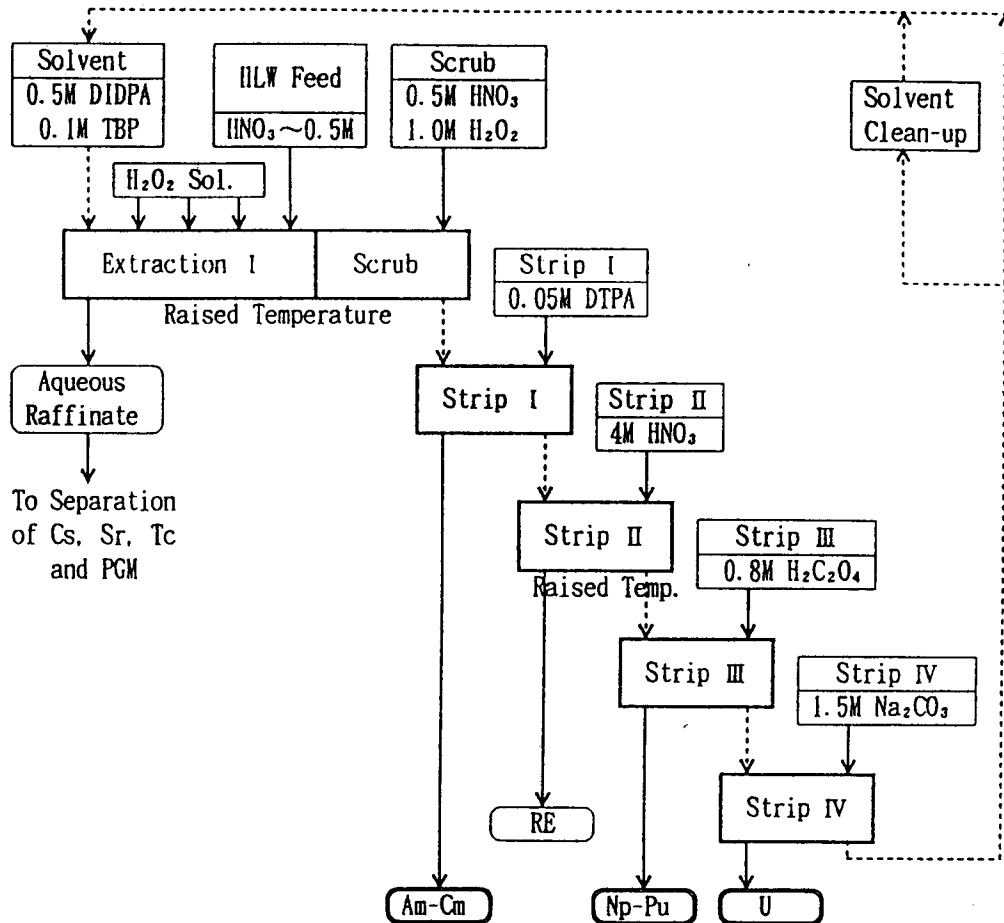


Fig.10 Process flowsheet for TRU separation by extraction with DIDPA solvent followed by selective back-extraction

Pyrometallurgical partitioning of minor actinides and lanthanides in LiCl-KCl eutectic molten salt / liquid metal system

M. Kurata, Y. Sakamura and T. Inoue

Central Research Institute of Electric Power Industry
Iwadokita 2-11-1, Komae, Tokyo 201, Japan

Abstract

Distribution coefficient of actinides and rare earth elements were measured in LiCl-KCl eutectic molten salt / liquid cadmium system and in LiCl-KCl eutectic molten salt / liquid bismuth system. According to separation factor experimentally determined, the LiCl-KCl / bismuth system is also preferable to separate the actinides and the rare earth elements, nevertheless cadmium can be a candidate solvent if electrorefining has a excellent capability of separation of these elements.

1. Introduction

High level radioactive waste (HLW) from reprocessing of spent fuels of light water reactors contains a small amount of long-lived nuclides, mainly minor actinides (MA), which remain radioactive toxicity for more than one million years. If the MA could be separated from the HLW and transmuted to short-lived nuclides, it is expected that this technology could substantially reduce the isolation period of the HLW from biosphere and could simplify the disposal of the HLW, and thus, that would have a potential to provide an ideal nuclear fuel cycle strategy, by which the long-lived toxic elements could be imprisoned in the nuclear fuel cycle. Pyrometallurgical partitioning of the MA, which is expected to produce a lower amount of secondary radioactive wastes and to favor compact facilities although the products have lower purity as compared with the conventional aqueous processes, is being developed by Central Research Institute of Electric Power Industry (CRIEPI) [1]. The pyrometallurgical partitioning can be combined with the transmutation of the MA in the U-Pu-Zr metallic fuel by the addition of the extracted MA.

Fig. 1 represents the flow diagram of the pyrometallurgical process for the partitioning of the MA from the HLW proposed by CRIEPI. This process mainly consists of (1) denitration of the HLW to oxides by heating, (2) chlorination of the oxides, (3) reductive extraction of noble metals from the molten chlorides using Cd, (4) reductive extraction to separate the MA from molten chlorides using Li and (5) electrorefining to increase purity of the recovered MA. Both the denitration and chlorination steps are pre-processing for partitioning. The main separation of the MA is performed both in the reductive extraction and in the electrorefining, in which the most important parameter is the separation factor between the MA and the rare earth elements (RE) which are existed 10 times large amount of the actinides in the HLW. The calculated composition of the HLW after chlorination step is represented in table 1. According to the preliminary estimation [1], the comparable weight of the lanthanides can be accompanied with the MA in the U-Pu-Zr alloy based metallic fuel.

The separation factor of the actinides and the RE are largely affected by (1) temperature, (2) composition of the molten chloride, (3) the sort of liquid metal solvent. In the reductive extraction process, relatively low temperature, around 500 °C, is preferable because the difference of the formation of Gibbs energy of chloride of actinides and lanthanides becomes large along with decrease in temperature. The chlorides from the chlorination step are dissolved in LiCl-KCl eutectic salt to maintain the liquidus temperature of the mixed chlorides less than 500 °C. Cd, Zn, Pb, Bi or others is available as liquid metal solvent from the point of the melting temperature. However, the solubility of actinides and lanthanides in Zn and Pb is very low, then Cd or Bi can be selected as the candidate solvent. The difference of the separation behavior of some actinides and lanthanides using LiCl-KCl/Cd or -/Bi system is studied and material balances of both systems are also investigated.

In this study, the separation factors between neodymium and four actinides (U, Np, Pu, Am) and seven lanthanides (Y, La, Ce, Pr, Sm, Eu, Gd) and those between neodymium and two actinides (U, Np) and seven lanthanides are experimentally determined in the LiCl-KCl/Cd system and in the LiCl-KCl/Bi system, respectively.

2. Experimental

2.1 Reagents

Polarographic grade LiCl-KCl eutectic salt (59:41mol%) and unhydrated lanthanide trichlorides obtained from the Anderson Physics Laboratories, U.S.A., were used for the experiment. The actinide trichlorides were made by the oxidation of the actinide metals dissolved in liquid Cd or Bi by the addition of CdCl₂ or BiCl₃. The Cd and Bi metal with a purity of 99.9999 % obtained from the Rare Earth Products, U.S.A., were melted at 500 °C along with LiCl-KCl eutectic salt in the argon atmosphere glove box for thorough removal of oxygen in the metals and then the surface of the metals were mechanically polished after cooling. Li-Cd and Li-Bi alloy were used as the reductant and CdCl₂ or BiCl₃ as the oxidant in this experiment.

2.2 Apparatus

The measurement was carried out by setting the apparatus shown in Fig. 2 in the furnace well of an argon atmosphere glove box. The oxygen content and dew point in the glove box were maintained less than 0.5 ppm and -80 °C, respectively.

2.3 Procedure

The weighed salt was loaded in an alumina crucible (SSA-S) which was placed at the bottom of the reaction cell. The cell was then heated to melt the salt and then the Cd or Bi was added in the crucible. After melting the metal, an agitator was, then, lowered into the liquid metal phase and the melt was stirred continuously at 60 rpm. The distribution of the lanthanides and actinides was controlled by the incremental addition of the Li-Cd or Li-Bi alloy or the addition of CdCl₂ or BiCl₃ to the system. Preliminary experiments indicated that the equilibrium was attained in less than 4 hours after the addition of reductant or oxidant when the liquid metal phase was not saturated with the rare earth elements [4].

After the attainment of equilibrium, the samples of the salt and metal were taken by inserting a Pyrex glass tube into the salt or metal phase and then by withdrawing into the tube with a glass syringe. The salt samples were dissolved in 1 N HNO₃, while the metal samples were washed with water for removal of salt contamination, and then were dissolved in 1 N HNO₃ by heating at about 100 °C. The lanthanides and actinides in these solutions were analyzed by ICP, and Li and K by atomic absorption spectroscopy.

3. Results and discussion

3.1 Determination of distribution coefficients for lanthanides and actinides

The distribution of a trivalent element, such as the lanthanides and actinides, between molten LiCl-KCl eutectic salt and liquid metal can be expressed by the following reaction:



The suffix A and B represent two different heavy metals with same valence. The equilibrium constant K can be written as

$$K = \frac{a_{M^B\text{Cl}_3} a_{M^A}}{a_{M^A\text{Cl}_3} a_{M^B}} = \frac{\gamma_{M^B\text{Cl}_3} \gamma_{M^A}}{\gamma_{M^A\text{Cl}_3} \gamma_{M^B}} \cdot \frac{X_{M^B\text{Cl}_3} X_{M^A}}{X_{M^A\text{Cl}_3} X_{M^B}}, \quad (1)$$

in which a, X and γ denote activity, mole fraction and activity coefficient, respectively. If the activity coefficients are constant in the system followed by Henry's law, an apparent equilibrium constant K' is given by

$$K' = K \cdot \frac{\gamma_{M^B\text{Cl}_3} \gamma_{M^A\text{Cl}_3}}{\gamma_{M^B} \gamma_{M^A}} = \frac{X_{M^B\text{Cl}_3} X_{M^A\text{Cl}_3}}{X_{M^B} X_{M^A}}. \quad (2)$$

When the distribution coefficients are defined as

$$D_M = \frac{X_M}{X_{MCl_3}}, \quad (3)$$

eq. (2) can be written in logarithmic form as

$$\log (D_{M^A}) = \log (D_{M^B}) + \log (K'). \quad (4)$$

Thus, a relationship of logarithm of distribution coefficient of two trivalent heavy metals should give a straight line having a slope of unity. The separation factor of element B to element A is defined as

$$SF = \frac{D_{M^B}}{D_{M^A}}. \quad (5)$$

Fig. 3 shows the relationship of the distribution coefficient of the various heavy metals and that of Nd in LiCl-KCl/Cd system. The slope of each line is almost unity with the exception of Sm, Eu and Am which behave as a divalent element in LiCl-KCl molten salt [2]. It suggests that the actinides and the rare earth elements behave as trivalent and that activity coefficient of each element is nearly constant both in the LiCl-KCl molten salt and in the liquid Cd in the concentration measured. From the results, the reductivity of the elements into the liquid Cd is an order of

$$U > Np > Pu > Am > Pr, Nd > Ce > La > Gd > Y.$$

Fig. 4 shows the relationship of the distribution coefficients in the LiCl-KCl/Bi system. The slopes are almost unity with the exception of Sm and Eu and the order of the reduction in the LiCl-KCl/Bi is the same as that in the LiCl/KCl/Cd system, however, the SF between the elements becomes larger in -/Bi than in -/Cd.

3.2 Separation factor of actinides and lanthanides

The separation factors of various elements versus Nd both in the LiCl-KCl/Cd and in the LiCl-KCl/Bi system are summarized in table 2. The separation factor of U and Np versus Nd is rather smaller in the LiCl-KCl/Bi than in the LiCl-KCl/Cd and that of the heavy lanthanides (Y, Gd) is larger, nevertheless, that of light lanthanides (La, Ce, Pr) is similar in the both systems.

3.3 Material flow in LiCl-KCl/Cd system and -/Bi system

Material flow of the lanthanides and actinides during the Li reduction step in the LiCl-KCl/Cd and LiCl-KCl/Bi system is calculated for the HLW concentration shown in table 1, using the separation factor of the elements under the condition that 99 % of Am and Np are extracted from molten salt into liquid metal. The relatively poor capability of the separation between the actinides and the rare earth elements in the LiCl-KCl/Cd system requires the multistep reductions and extractions to obtain improved purity of the actinides. Fig. 5 (a) shows the extracted ratio of the elements as a function of the number of Li reduction step in the LiCl-KCl/Cd system. After the first reduction step, ca. 90 % for Ce, Pr and Nd, ca. 70 % for La and Gd and 7 % for Y are accompanied with actinides and then, after the second step, ca. 60 % for Ce, Pr and Nd and ca. 25 % for La and Gd are accompanied. The amount of the lanthanides accompanied gradually decreases along with increase in the number of the step, however, even after the eighth step, ca 40 % for Ce, Pr and Nd and about 10 % for La and Gd still come along with the actinides. The composition of the rare earth elements and the actinides between before the Li reduction and after the eight times Li reduction step is compared in table 3. About 5 times larger amount of the rare earth elements is still accompanied with the minor actinides after the eight times Li reduction and it suggests that further separation step, e. g. the electrorefining, should be required to improve the purity of the final products.

On the other hand, when the LiCl-KCl/Bi is employed for the separation between the rare earth elements and the actinides, the relatively high capability was attained. Fig. 5 (b) shows the extracted ratio of the elements as a function of the number of the reduction steps in the LiCl-KCl/Bi system. After only two steps of the reduction the accompanied amount of the rare earth elements is rather low when the actinides were reduced more than 99 %. The composition of the final products using the LiCl-KCl/Bi system is compared with using the LiCl-KCl/Cd system in table 3.

3.4 Designing of pyrometallurgical partitioning process

Several options for pyrometallurgical partitioning process can be designed, because of the large flexibility of the system. Two types of typical block diagram of the process using the LiCl-KCl / Cd system or the - / Bi system are represented in figures 6 and 7. The number of the Li reduction steps would be smaller in the LiCl-KCl / Bi system than in the - / Cd system.

4. Conclusions

The separation factor between the actinides and the rare earth elements is experimentally measured in the LiCl-KCl / Cd and in the LiCl-KCl / Bi system. The multistep Li reduction and further separation after Li reduction would be required when Cd was used as the solvent. On the other hand, Bi has the high capability for separating the actinides from the rare earth elements and the composition of the final products after two steps could be provided for the transmutation. Two types of the process flow are proposed.

Acknowledgment

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- [5] T. Hijikata et. al., Proc. of Future Nuclear Systems : Emerging Fuel Cycles and Waste Disposal Options, GLOBAL '93, Seattle, Washington, Sep. 12-17, 1993, p. 1074.

Table 1 Composition of fission products after chlorination step (based on the calculation by ORIGEN-II) .

group	composition(wt%)
U	10.3
MA	3.2
alkali	9.0
alkaline	7.6
lanthanide	32.3
Zr	10.9
Mo	10.5
noble metal	16.3

Table 2. Separation factor of various elements to Nd
at 500 C.

element	LiCl-KCl/Cd	LiCl-KCl/Bi
U	0.022	0.00091
Np	0.043	0.0095
Pu	0.056**	0.012***
Am *	0.067**	0.014***
Pr	0.91	0.77
Nd	1.0	1.0
Ce	1.1	0.91
La	2.8	2.8
Gd	3.8	11
Y	110	710
Sm *	1400	3700
Eu *	2600	7700
Li*	2800	1300

* where $\log D(\text{Nd}) = 0$

** measured at 450 C

*** estimated value

Table 3 Comparison of calculated composition after Li reduction step by using LiCl-KCl/Cd or LiCl-KCl/Bi system .

element	starting composition (at%)	after 8th step using LiCl-KCl/Cd (at%)	after 2nd step using LiCl-KCl/Bi (at%)	CRIEPI target (at%)
U	15.0	37.7	71.0	62.1
Np	2.3	5.7	10.8	as total of MA
Pu	0.2	0.4	0.8	18.9
Am	2.1	5.4	10.1	
actinide;total	19.6	49.2	92.7	81.1
Y	5.3	0.1	0.0	
La	9.5	3.1	0.7	
Ce	18.3	14.2	3.9	
Pr	8.5	7.5	2.0	
Nd	30.5	25.5	5.9	
Sm	5.9	0.0	0.0	
Eu	1.1	0.0	0.0	
Gd	1.2	0.3	0.0	
lanthanide;total	80.4	50.8	7.3	18.9

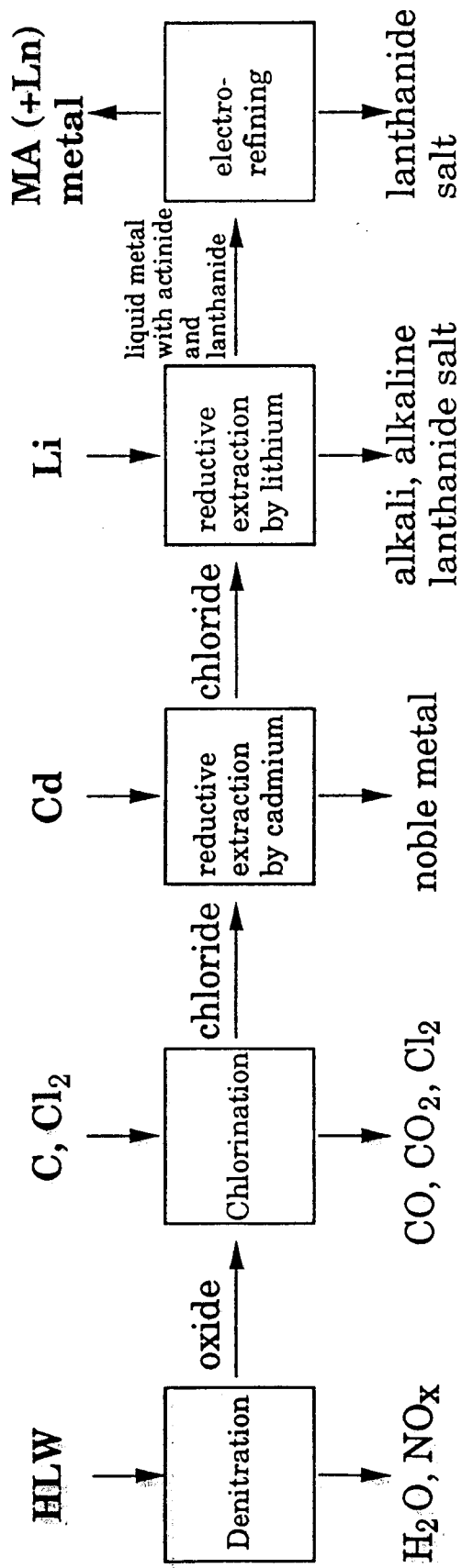


Fig. 1 Flow diagram of pyrometallurgical process for partitioning of MA from HLW.

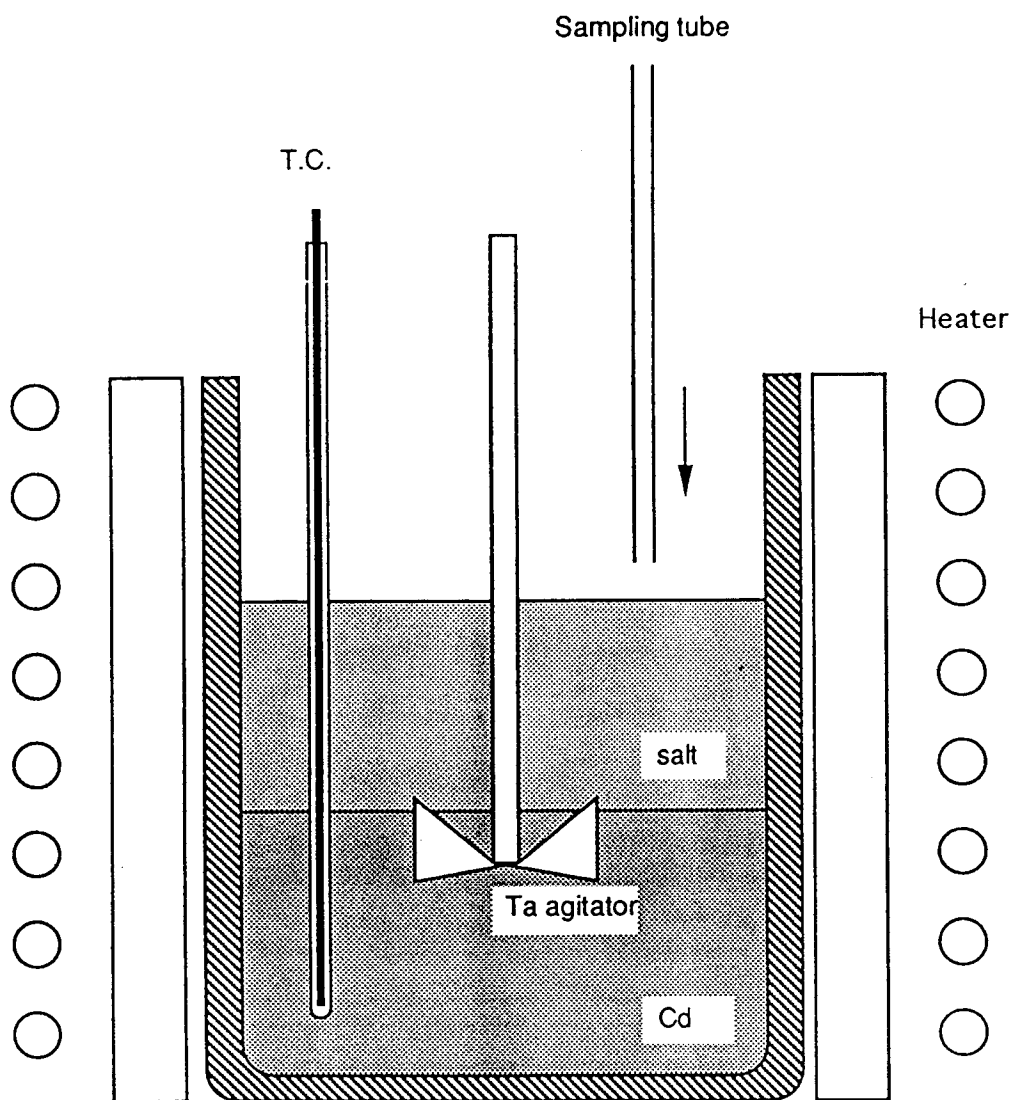


Fig. 2 Reaction cell

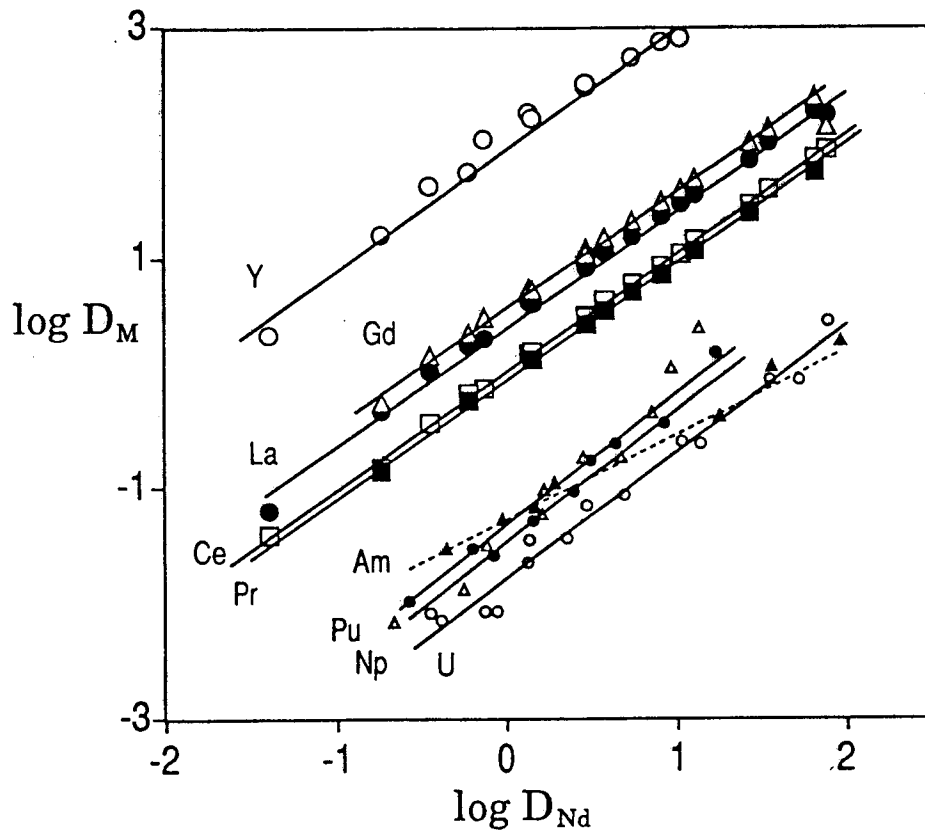


Fig. 3 Distribution coefficient of various elements vs. distribution coefficient of neodymium between LiCl-KCl eutectic molten salt and liquid cadmium at 500 °C. (The coefficients of Np, Pu and Am were measured at 450 °C)

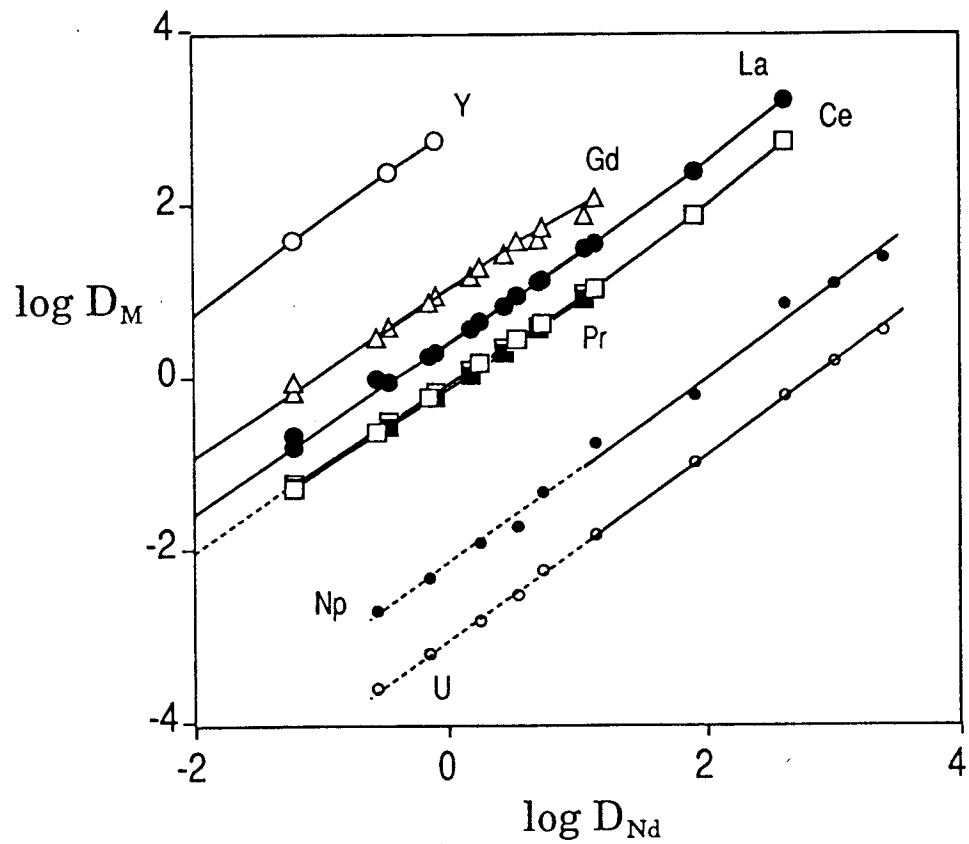


Fig. 4 Distribution coefficient of various elements vs. distribution coefficient of neodymium between LiCl-KCl eutectic molten salt and liquid bismuth at 500 °C.

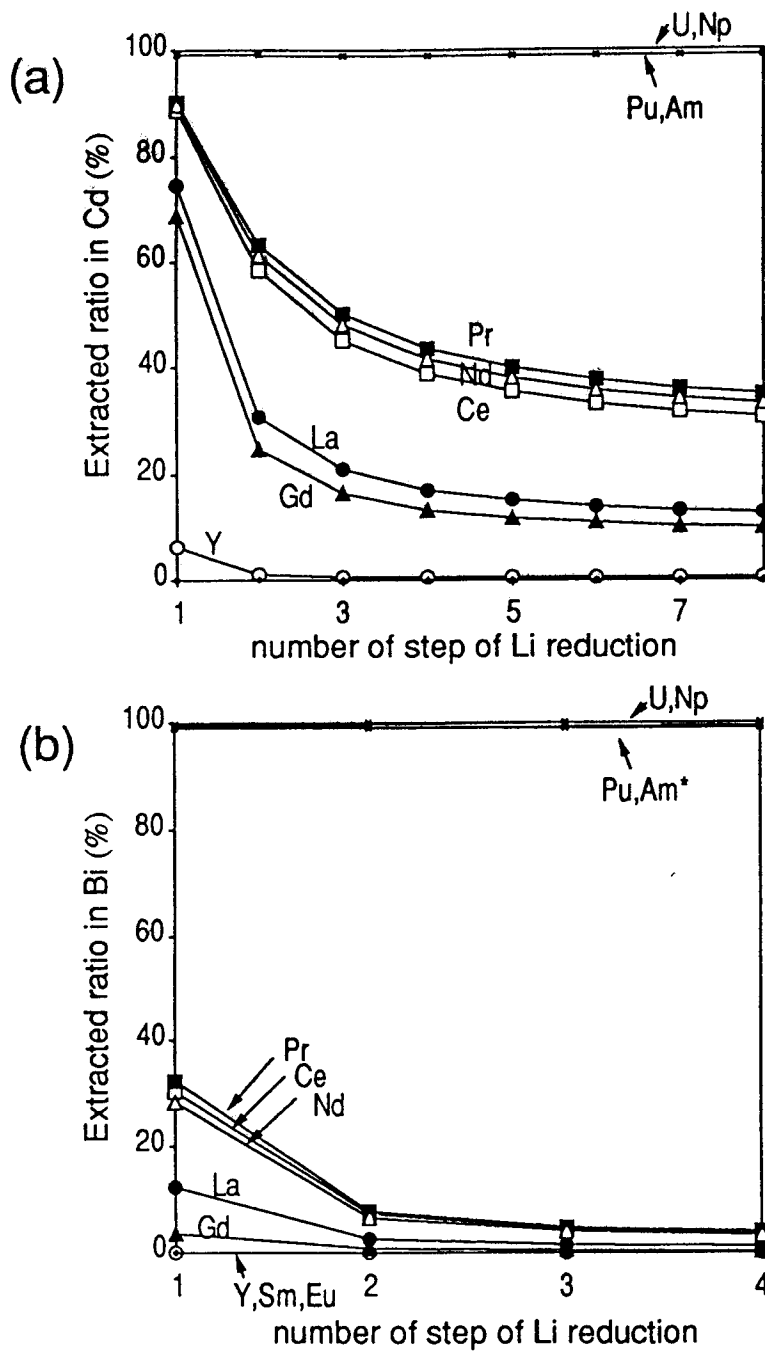


Fig. 5 Extracted ratio of actinides and lanthanides in multistep Li reduction at 500 °C under the condition of 99% of Am and Np is extracted. (*using estimated value)
 (a) in LiCl-KCl / liquid Cd system
 (b) in LiCl-KCl / liquid Bi system

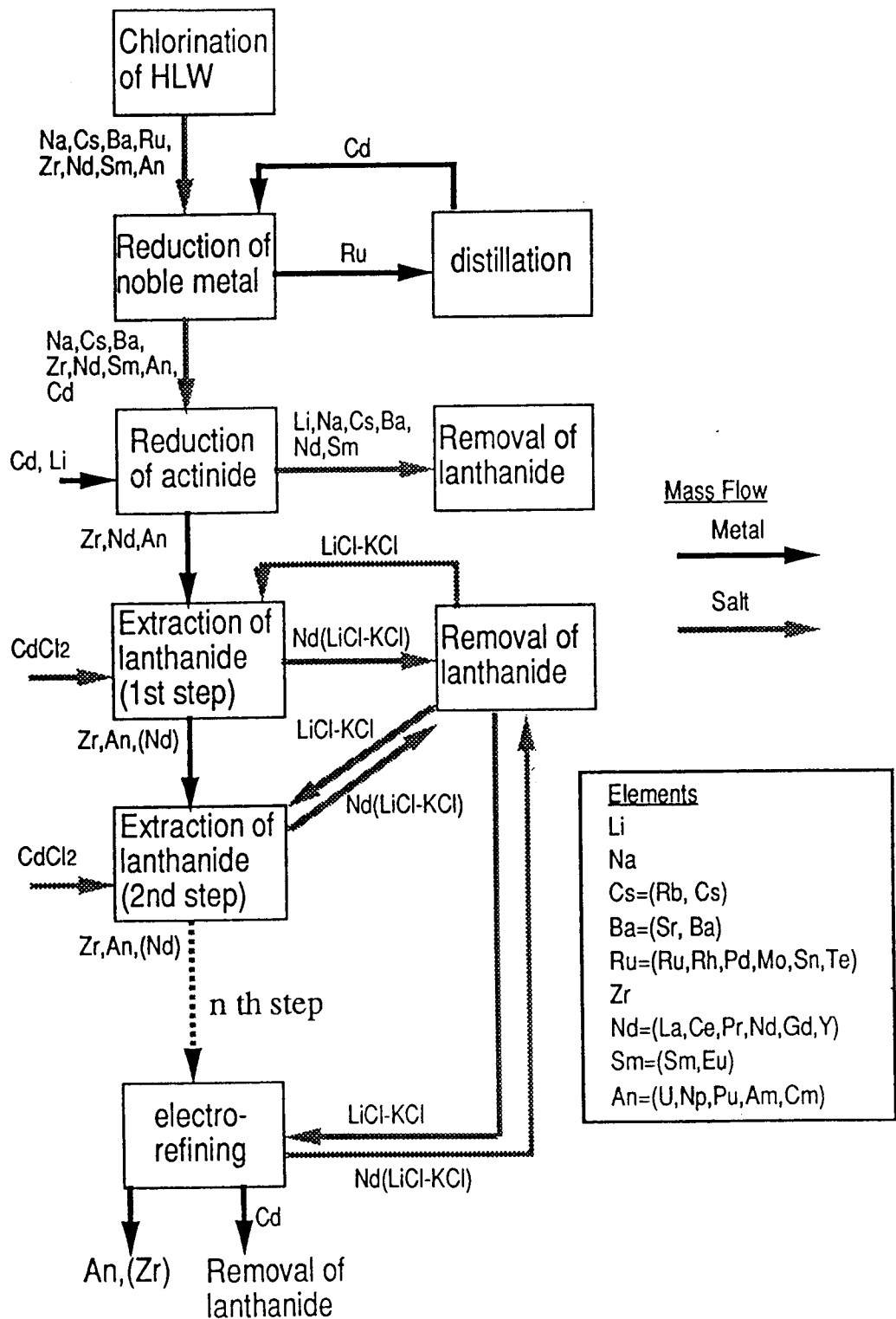


Fig. 6 Process flow of pyrometallurgical partitioning using liquid cadmium as a solvent.

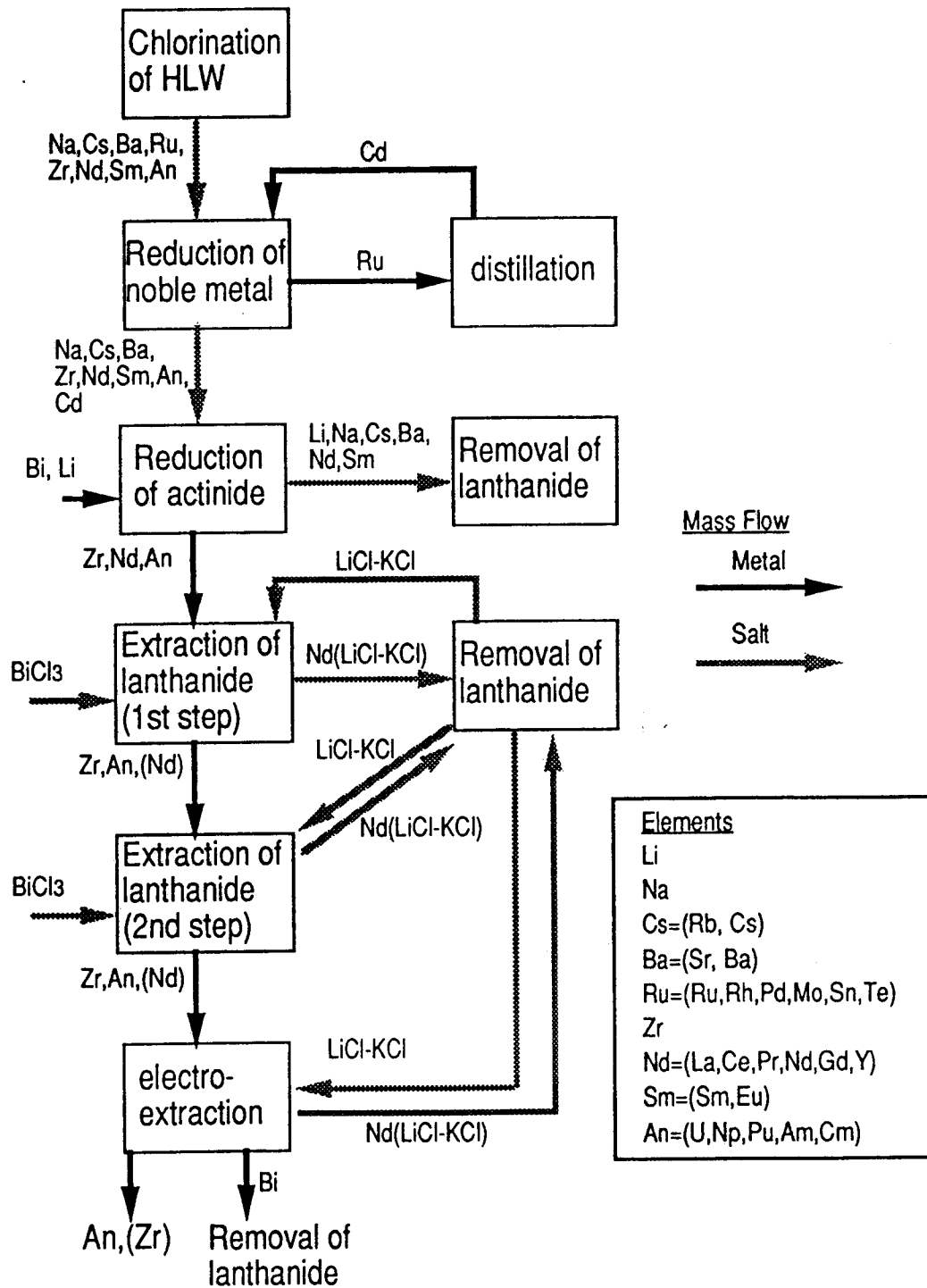


Fig. 7 Process flow of pyrometallurgical partitioning using liquid bismuth as a solvent.

INVESTIGATING THE SOLVENT EXTRACTION OF TECHNETIUM(VII) FROM ALKALINE
SODIUM NITRATE SOLUTION BY CROWN ETHERS

Bruce A. Moyer, Peter V. Bonnesen, John H. Burns, Lætitia H. Delmau, Tamara J.
Haverlock, Derek J. Presley, Richard A. Sachleben, and Frederick V. Sloop

Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
P. O. Box 2008, 4500S, MS-6119
Oak Ridge, Tennessee 37831-6119 U.S.A.

ABSTRACT

Schemes under development for treatment and long-term disposal of radioactive defense wastes in the United States include steps for the removal of key fission products before vitrification of the waste. A need to remove the long-lived radionuclide technetium has been identified, but prior technology has been less than satisfactory. An analysis of anion-exchange principles in combination with the chemistry of crown ethers has led us to propose a new process for separating technetium from tank waste. The basis of selectivity in this system is similar to that of classical anion exchange, but the process can be readily reversed with a water strip. Candidate extraction solvents have been identified, and a process cycle has been tested.

INTRODUCTION

If options for transmutation of radionuclides are to be comprehensively evaluated in the United States, long-term risk factors demand consideration of the vast quantities of accumulated waste from past weapons production. At the Hanford site alone, approximately 2.4×10^5 m³ of highly radioactive wastes stored in 177 underground tanks await treatment [1]. Current agreements dictate disposal by vitrification and long-term storage. Treatment of the waste prior to vitrification likely will involve separation of certain fission products including ⁹⁰Sr, ¹³⁷Cs, and ⁹⁹Tc, and thus methods for achieving these separations are being investigated actively. Among the radionuclides of interest, ⁹⁹Tc poses a long-term risk because of its environmental mobility and long half life of 2.1×10^5 y. In addition, its volatility as Tc₂O₇ poses problems in off-gas treatment during vitrification. Because of these long- and short-term issues, we have been investigating the separation chemistry applicable to the removal of technetium from alkaline media. At the outset of this work, it was necessary to consider the fundamental nature of technetium chemistry together with the principles that give rise to high selectivity for technetium in a background of concentrated salts. These principles may be applied through the chemistry of crown ethers, and a process has now been proposed for technetium solvent extraction employing crown ethers. The approach employed in carrying out this work relies on a "synergism" between basic and applied research. Accordingly, the applied research identifies certain problems to solve and exploits known chemistry, while the basic research establishes applicable underlying principles of behavior. In this paper, we outline the problem regarding separation of technetium from highly alkaline media, propose a basic chemical strategy based on the use of crown ethers, and present selected supporting experimental data.

THE PROBLEM

Waste solutions of concern initially include the supernatant liquid in the tanks. Later, solutions resulting from washing tank solids, comprising salt cake and hydrolytic precipitates, with water will be considered. Thus, any method for treating the supernatant solutions should ideally be able to handle streams from these washes also. The bulk of the waste is simply sodium nitrate and water. Hydroxide, converted partially to carbonate, gives the high alkalinity of the solutions. Other constituents in high concentration include aluminate, nitrite, phosphate, and sulfate. Some of the tanks contain chelating agents and their degradation products up to a few weight percent. At this writing, characterization data remain far from complete, but it is already clear that a wide variation in composition will be encountered in processing. In particular, data concerning the technetium content of the wastes has been lacking, partly because of the difficulty in measuring trace levels of a pure beta emitter. The total tank inventory of technetium at Hanford has been estimated at 1.8 metric tons and is thought to exist primarily in the supernatant solutions rather than in the sludge [1]. The levels of technetium in these solutions will then be of the order of 10^{-4} M on average.

Owing to its high selectivity and good mass-transfer properties, solvent extraction offers a potentially attractive vehicle for technetium removal from tank waste. The high ionic strength of the feed promotes good phase separation and minimizes (by "salting out") the solubility of organic solvent components in the aqueous phase. In addition, traces of solvent which may escape into the raffinate pose little difficulty for the high-temperature processes to follow.

A number of solvent-extraction systems have been demonstrated to remove technetium from aqueous solutions. Specifically applicable to alkaline solutions are pure solvents such as cyclohexanone and anion-exchange reagents such as quaternary amines. Pure solvents were shown to weakly extract sodium pertechnetate from alkaline solutions [2]. These included simple monofunctional ketones, alcohols, trialkylphosphates, nitriles, nitro compounds, and nitrogen bases. The extractions were promoted by high dielectric constant and high molar concentration of the polar group. Within a given family of solvents, the extraction ability decreases as the number of carbon atoms in the solvent molecule increases. Thus, to obtain usable distribution coefficients, the low molecular-weight compounds in a series must be employed. But as the number of carbon atoms in the solvent molecule decreases, the solubility in water increases, the volatility increases, and the ability to extract other electrolytes increases. Despite these disadvantages, it has been proposed to remove technetium from alkaline, high-salt solutions by methyl ethyl ketone [3] or by cyclohexanone [4]. The latter was in fact considered a strong candidate for removal of technetium from Hanford waste, but formation of emulsions on stripping was considered a disadvantage [4]. Both of these ketones possess low flash points, which would present safety concerns and regulatory burdens associated with production of "mixed wastes," defined in the United States as containing a hazardous substance (in this case, the two solvents possess the ignitability characteristic under U.S. regulations) and radionuclides.

Extraction of technetium by anion-exchange solvent extraction may be accomplished from both acid and alkaline solutions [2]. A number of organic salts having bulky cations have been employed for this purpose, but the most common reagents are the long-chain quaternary ammonium salts. Such anion exchangers have been shown to be capable of removing pertechnetate from alkaline solutions containing high concentrations of sodium nitrate [5]. To strip the resulting solvent, one must either replace the pertechnetate with an anion more strongly held by the solvent or to change the form of the technetium. Both options require the addition of chemicals to the system and potentially add to the overall waste volume. The former option can be accomplished by contact with strong nitric or perchloric acid solutions [6]. The latter may possibly be accomplished by reduction [5].

In view of these points, a new process for removal of technetium from highly alkaline media is desirable. The process would ideally involve chemicals which have low aqueous solubility, low volatility, low toxicity, minimal regulatory burdens, and good stability. Further, the process should require the addition of no new chemicals to the waste stream. Rapid throughput dictates that the process also have good kinetics and fast phase disengagement; this must be regarded as essential for efficient use, and minimum inventory, of expensive extractants. High selectivity will be needed to improve the performance of post-processing steps for the isolation of a concentrated technetium stream, especially if transmutation is considered an end-option.

CHEMICAL PRINCIPLES

From available reduction potentials [7], the pertechnetate ion, TcO_4^- , is the most stable form of technetium in aerobic, noncomplexing environments from pH 0 to 14. In the absence of complexants, Tc(IV) is the only other important oxidation state in solution, but it readily oxidizes to TcO_4^- ion in the presence of air and radiolytic conditions [7]. Organic complexants are not known to interact with the TcO_4^- ion in aqueous solution, but lower oxidation states of technetium form a variety of complexes [8,9]. However, formation of these complexes still generally requires reducing conditions. Thus, the applicable state of technetium in the tank wastes is reasonably expected to be the TcO_4^- ion. As a cautionary note, in view of the lack of direct analytical data concerning the exact form of technetium in the Hanford tank wastes, the possibility of other forms of technetium cannot be ruled out, especially since some of the wastes contain high concentrations of complexants. Keeping this possibility in mind for consideration as data becomes available, we nevertheless presume at this stage that the major separation problem

Table 1. Ion Size and Hydration Data for Representative Anions

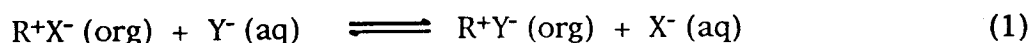
Anion	Ionic Radius (nm) ^a	Thermochemical Radius (nm) ^b	$-\Delta G_h(M^+)^c$ kJ mol ⁻¹	d_{M-O}^d (nm)
F ⁻	0.130	0.126	472	
OH ⁻	0.137	0.133	439	
Cl ⁻	0.181	0.172	347	
NO ₂ ⁻		0.192	339	0.125
Br ⁻	0.196	0.188	321	
NO ₃ ⁻		0.179	306	0.125
I ⁻	0.220	0.210	283	
MnO ₄ ⁻		0.229	245	0.159
ClO ₄ ⁻		0.240	214	0.144
TcO ₄ ⁻		(0.241 est)		0.171
ReO ₄ ⁻		(0.244 est)		0.174
IO ₄ ⁻		0.249		0.179
CO ₃ ²⁻		0.178	1479	
SO ₄ ²⁻		0.258	1090	
PO ₄ ³⁻		0.238	2754	

^aEffective ionic radii from crystallographic data [11]. ^bDetermined from lattice energies; these values are applicable to thermodynamic calculations for nonspherical anions [12,13]. Values for TcO_4^- and ReO_4^- anions were estimated by adding 0.70 (difference between the thermochemical radius and d_{M-O} for MnO_4^-) to d_{M-O} . ^cFree energies of hydration taken from the tabulation in ref. [14]. ^dMean bond distances between central atom M and the oxygen atoms in selected oxyanions [15,16].

of interest involves removing trace levels of TcO_4^- anion from high concentrations of other anions, including OH^- , NO_3^- , NO_2^- , CO_3^{2-} , SO_4^{2-} , $\text{Al}(\text{OH})_4^-$, and PO_4^{3-} . A method that achieves this end without adjusting the waste in some manner must obviously possess extreme selectivity for the TcO_4^- anion.

In Table 1 are listed the ionic radii of various anions together with selected M-O bond distances $d_{\text{M-O}}$ and free energies of hydration $\Delta G_{\text{h}}(\text{M}^+)$. Since the concept of anion size loses some definition in comparing oxyanions of different geometries, thermochemical radii derived from lattice energies are also included in the table. One may see that the strength of anion hydration decreases (i.e., the free energy of hydration becomes less negative) as anion size increases. Unfortunately, thermochemical radii and $\Delta G_{\text{h}}(\text{M}^+)$ values are not available for TcO_4^- , but from M-O bond distances, it may be estimated that this anion (and its closely related analog ReO_4^-) is effectively larger and less strongly hydrated than the abundant anions OH^- , CO_3^{2-} , NO_2^- , NO_3^- , SO_4^{2-} , and PO_4^{3-} .

Anion-exchange principles as applied to solvent extraction or resin ion exchange have long been known to predict selectivity for large, poorly hydrated anions [10]. Consider the anion-exchange reaction below:



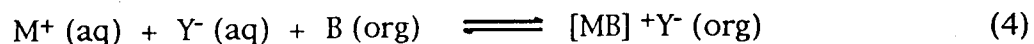
Here R^+ is a lipophilic cation which is paired with exchangeable anion X^- in the organic phase. In the most general terms, the hydration of the anion usually predominates in controlling the free energy of anion exchange. Hydration free energy varies inversely with ionic radius through the Born equation, and thus, it may be expected that anion exchange in eq. 1 will be favored when Y^- is larger than X^- . One study of relevance to the present problem showed that anion exchange involving tetraheptylammonium salts in benzene follows the order $\text{ReO}_4^- > \text{ClO}_4^- > \text{Br}^- > \text{NO}_3^- > \text{Cl}^-$ [17]. From the results of that study, it may be concluded that one must employ bulky cations and solvents of relatively low dielectric constant. Thus, it should be possible to separate TcO_4^- from smaller anions by anion exchange (eq. 1). The question arises as to the severity of the competition from nitrate, which is more concentrated in the waste by a factor of at least 10^4 . As pointed out above, data show that the requisite selectivity is attainable, giving acceptable distribution coefficients from concentrated nitrate media [5,6].

In view of the desirable selectivity characteristic of anion exchange, an improved process would result by replacing the quaternary ammonium cation by another bulky cation that can be reversibly decomposed. Crown ethers offer an ideal vehicle for the reversible formation of lipophilic salts having a bulky cation. By analogy to eq. 1, one may write an anion-exchange reaction in which the cation R^+ is replaced by the complex $[\text{MB}]^+$ resulting from inclusion of a metal cation M^+ by the neutral crown ether B:



It follows that such a reaction favors large, poorly hydrated anions such as TcO_4^- .

Formation of the organic-phase salts $[\text{MB}]^+\text{X}^-$ and $[\text{MB}]^+\text{Y}^-$ starting with only crown ether in the organic phase may be written as ion-pair extractions:

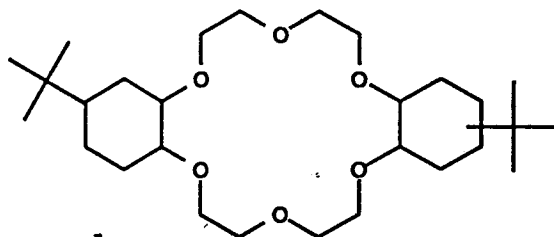


It may be noted that eq. 2 is simply the resultant reaction upon subtracting eq. 3 from eq. 4. If eqs. 3 and 4 lie far to the right, then the resultant chemistry may best be given by eq. 2. In considering the tank-waste problem, let X^- , Y^- , and M^+ respectively be the ion of interest TcO_4^- , the major competitor anion NO_3^- , and an abundant cation Na^+ (or K^+).

Although ion-pair extraction differs in its equilibrium properties from anion exchange, the selectivity for large, poorly hydrated anions is retained provided the cationic complex $[MB]^+$ is sufficiently bulky. This may be shown by examining the equilibrium constants $K_{X,Y}$, $K_{ex,MBX}$, and $K_{ex,MBY}$ corresponding to eqs. 2, 3, and 4. Since $K_{X,Y} > 1$ for Y^- larger than X^- and $K_{X,Y} = K_{ex,MBY}/K_{ex,MBX}$, then $K_{ex,MBY} > K_{ex,MBX}$ for Y^- larger than X^- . That is, the efficiency of ion-pair extraction increases with increasing anion size.

The effect of anion size on ion-pair extraction has been reported by a few workers and qualitatively agrees with the above expectations. The efficiency of extraction of the alkali metals $Li^+ - Cs^+$ by the crown ether dicyclohexano-18-crown-6 (presumably mixed isomers) in dichloroethane was found to follow the order $ClO_4^- > I^- > NO_3^- > Br^- > OH^- > Cl^- > F^-$ [18]. This order may at once be recognized as resembling the order of anion selectivity by use of lipophilic tertiary alkyl ammonium salts $ClO_4^- > NO_3^- > Cl^- > F^-$ [19]. By comparison with Table 1, it may also be seen that the extraction of alkali metal salts by the crown ether indeed increases with both increasing anion size and decreasing strength of hydration.

Not surprisingly, the extraction of TcO_4^- anion from aqueous electrolyte solutions has been reported for several crown ethers. Dicyclohexano-18-crown-6 (DCH18C6) was shown to extract TcO_4^- from nitric acid into trichlorobenzene [20]; the postulated organic species was $[K(DCH18C6)]TcO_4$. The related crown ether dibenzo-18-crown-6 extracts TcO_4^- from sulfuric acid into 1,2-dichloroethane [21]. In the SREX process for the extraction of Sr^{2+} from nitric acid [22], the crown ether 4,4'(5')-di(*tert*-butylcyclohexano)-18-crown-6



4,4',5'-di(*t*-butylcyclohexano)-18-crown-6
DtBuCH18C6

Figure 1. Preferred crown ether for technetium extraction. Commercial material consists of a mixture of isomers.

(Fig. 1) in 1-octanol also extracts TcO_4^- . Crown ethers have been employed in the analysis of Tc in radioactive effluents by solvent extraction [23]. On the alkaline side, several crown ethers were found to extract TcO_4^- from sodium hydroxide into benzene, nitrobenzene, and several halogenated diluents [24]; the organic-phase species was thought to be $[Na(DCH18C6)]TcO_4$.

Many crystal structures of alkali metal complexes of the form $[MB]^+X^-$ have been reported, and the encirclement of metal cations by crown ethers of sufficient size has been demonstrated repeatedly. A complex related to the present work has the formula $[Na(\text{benzo-15-crown-5})]ReO_4$ [25]. In the crystal structure, the sodium cation occupies a nearly planar cavity formed by the five oxygen atoms of the

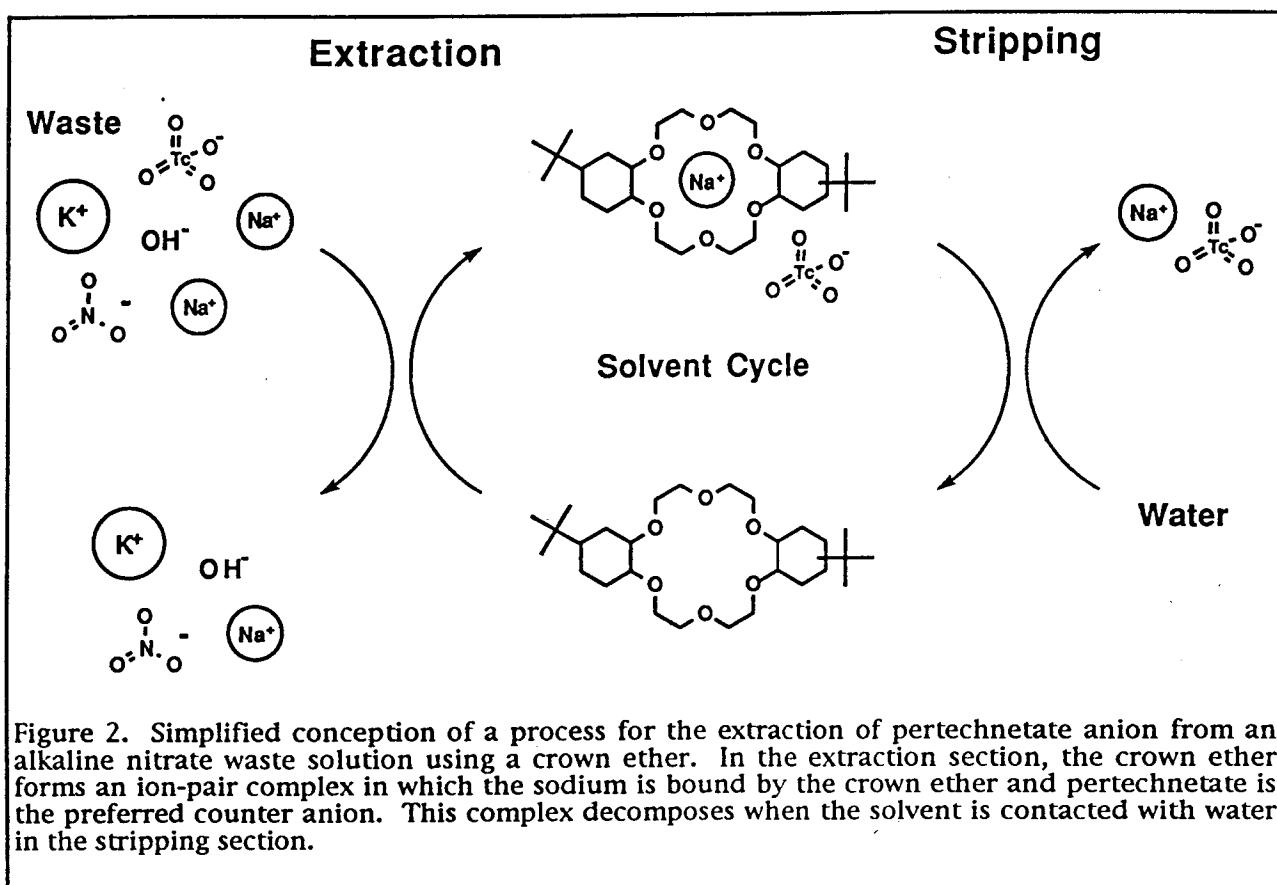


Figure 2. Simplified conception of a process for the extraction of pertechnetate anion from an alkaline nitrate waste solution using a crown ether. In the extraction section, the crown ether forms an ion-pair complex in which the sodium is bound by the crown ether and pertechnetate is the preferred counter anion. This complex decomposes when the solvent is contacted with water in the stripping section.

crown ether. Each sodium cation is coordinated to two perrhenate anions at the apical positions, forming a pentagonal bipyramid of oxygen atoms. The perrhenate anions each bridge two sodium cations so as to form linear chains. The crown ether presents hydrocarbon groups to the environment and thereby renders the entire complex lipophilic.

Mass-action properties of the equilibrium given by eq. 3 make crown ethers especially adaptable to economical extraction of TcO_4^- . It may be seen that the driving force of ion-pair extractions, such as eqs. 3 and 4, increases with increasing concentration of cations M^+ in the aqueous solution. Thus, concentrated salt solutions, as found in tank waste, are optimum for such a process. To reverse the extraction, the solvent containing the extracted $NaTcO_4$ needs only to be contacted with water, releasing the $NaTcO_4$. Figure 2 depicts in simplified terms the extraction and stripping process envisioned.

EXTRACTION RESULTS

To test the concepts presented above, a series of experiments have been carried out to determine the most effective crown ether and solvent system for removal of technetium from tank waste [26]. Initial systematic studies of extraction behavior were carried out with the diluent 1-octanol, though evaluation of the diluent effect

(see below) has subsequently indicated better diluents for practical use. Among the available crown ethers, DCH18C6 gave the strongest extraction of NaTcO_4 from alkaline nitrate media. Solutions of DCH18C6 in 1-octanol extracted Tc rapidly, reaching equilibrium in a few minutes of dispersing the two phases. However, DCH18C6 probably does not have the needed lipophilicity to minimize its own distribution to the aqueous phase; because of the expense of the crown ether, such losses dominate process economics. Thus, DtBuCH18C6 (Fig. 1) currently offers the best properties for development of a process. The *t*-butyl groups provide the requisite lipophilicity but involve some trade-offs: increased cost of the crown ether, increased isomeric complexity owing to the random substitution at the 4' or 5' positions of the cyclohexane ring, and a slightly lower Tc distribution coefficient.

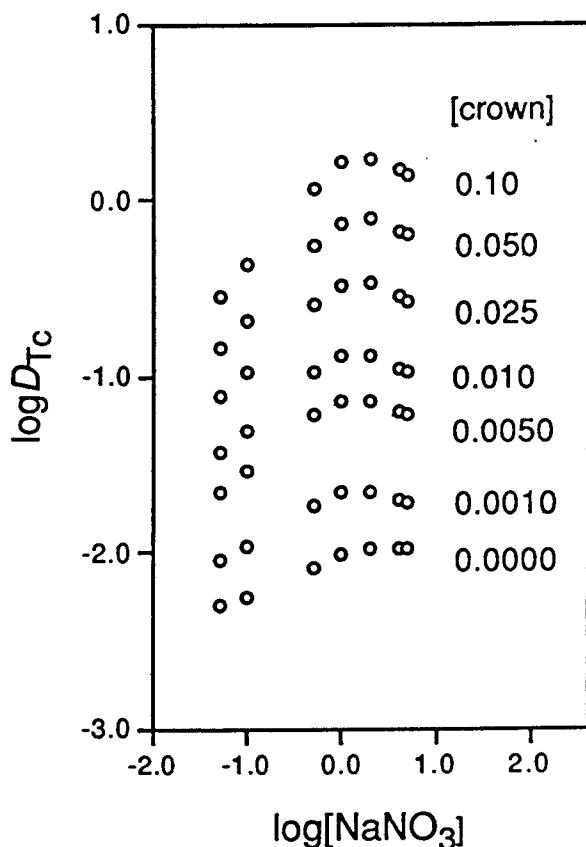


Figure 3. Extraction of pertechnetate by *cis-syn-cis*-dicyclohexano-18-crown-6 in 1-octanol at 25 °C as a function of the initial aqueous-phase concentration of NaNO_3 . The pure isomer of DCH18C6 was used so as to obtain best reproducibility. The initial Tc concentration was 3.47×10^{-5} M, and the phase ratio was 1:1.

Figure 3 shows the extraction of trace pertechnetate from sodium nitrate solutions by 1-octanol solutions of the *cis-syn-cis* isomer of DCH18C6. It may be seen that the Tc distribution coefficient D_{Tc} ($[\text{Tc}]_{\text{org}}/[\text{Tc}]_{\text{aq}}$) increases as the sodium nitrate concentration increases up to approximately 1 M. This trend qualitatively follows expectations based

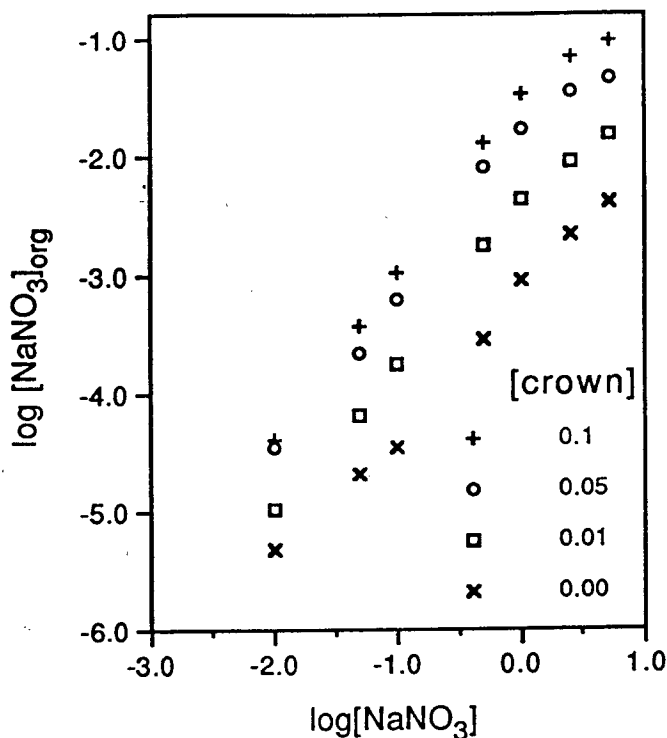


Figure 4. Extraction of sodium nitrate by *cis-syn-cis-dicyclohexano-18-crown-6* in 1-octanol at 25 °C as a function of the initial aqueous-phase concentration of NaNO₃. The phase ratio was 1:1.

description of the equilibria in the system is complicated and remains under investigation. Among the complications being elucidated is the non-negligible extraction of sodium nitrate, hydroxide, and pertechnetate by 1-octanol alone, as can be seen in Figs. 3 and 4. In addition, the diluent has sufficient polarity ($\epsilon > 10$) to partially dissociate the ion pairs in the organic phase. It also contains significant concentrations of water.

The strength of pertechnetate extraction from alkaline sodium nitrate by crown ethers depends markedly on the type of diluent employed (25). Polar diluents perform particularly well, but many of them have unwanted properties such as high loss to the aqueous phase, toxicity, environmental restrictions, and volatility.

Table 2. Pertechnetate Extraction and Stripping Employing the Crown Ether 4,4'(5')-di(*t*-butylcyclohexano)-18-crown-6^a.

Simulant	% Tc Extracted ^d	% Tc Stripped ^d
Simple ^b	89.46 ± 0.07	97.67 ± 0.03
DSSF-7 ^c	97.20 ± 0.08	95.90 ± 1.10

^aThe solvent consisted of the crown ether at 0.01 M concentration in a 1:1 v:v mixture of 4-(1-butylpentyl)pyridine in Isopar[®] M.

^bSimple simulant is 0.1 M NaOH, 5.0 M NaNO₃.

^cDSSF-7 approximates Hanford tank 101-AW Double-Shell Slurry Feed.

^dAfter two contacts at a 1:1 phase ratio at 25 °C; deionized water was used for stripping.

on eq. 3. However, the curves exhibit maxima as the controlling equilibria apparently shift to a situation in which further addition of sodium nitrate impairs the extraction of pertechnetate. Such could be the case if the crown ether becomes significantly loaded with competing sodium nitrate (eq. 4), whereupon the extractant effectively becomes [Na(DtBuCH18C6)]TcO₄ and the equilibrium effectively becomes anion exchange (eq. 2).

Indeed, the crown ether extracts significant levels of sodium nitrate, as shown in Fig. 4. The sodium distribution coefficient D_{Na} also increases with increasing sodium nitrate concentration, reaching a maximum at approximately 1 M NaNO₃. At that point, the concentration of sodium in the solvent approaches the crown ether concentration. Although the data in Figs. 3 and 4 provide qualitative confirmation of the expectations put forth in the preceding section, the actual

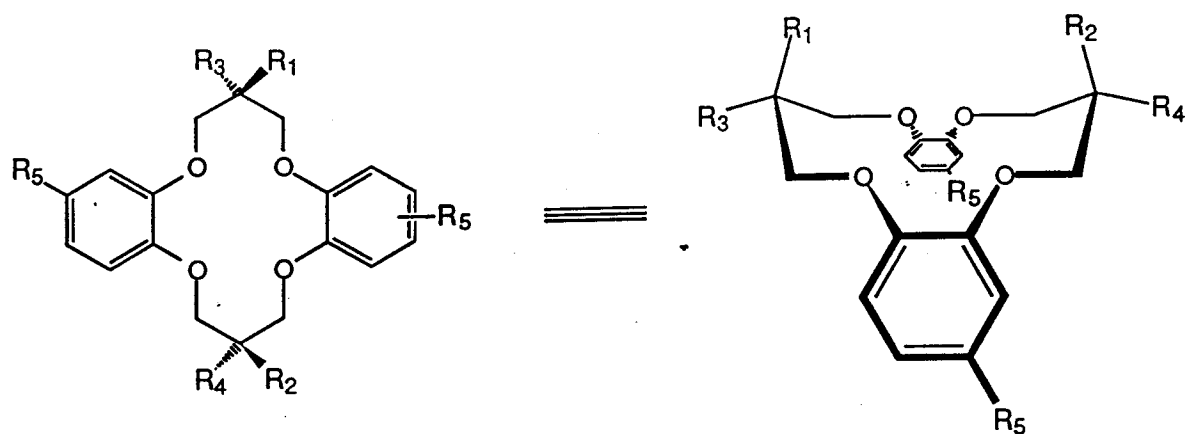
Table 3. Waste Simulants Used in This Study.

Species	Concentration (M)	
	Simple Simulant ^a	DSSF-7 simulant ^b
Na ⁺	5.10	6.999
K ⁺	not present	0.945
Cs ⁺	not present	7.0 x 10 ⁻⁵
Al ³⁺	not present	0.721
OH ⁻ (total)	0.1	4.634
OH ⁻ (free)	0.1	1.750
NO ₂ ⁻	not present	1.512
NO ₃ ⁻	5.00	3.521
Cl ⁻	not present	0.102
SO ₄ ²⁻	not present	0.008
CO ₃ ²⁻	not present	0.147
PO ₄ ³⁻	not present	0.014
⁹⁹ TcO ₄ ⁻	6.0 x 10 ⁻⁵	6.0 x 10 ⁻⁵

^aSimple simulant is 0.1 M NaOH, 5.0 M NaNO₃.
^bDSSF-7 approximates Hanford tank 101-AW Double-Shell Slurry Feed.

Moreover, distribution coefficients tend to be so strong that stripping with water can no longer be carried out. In fact, the maximum in the dependence of D_{Tc} on the aqueous sodium nitrate concentration appears to shift to the left with the strongest diluents such as nitrobenzene. Good properties were, however, found with modified alkane diluents. Effective modifiers include 4-substituted pyridines, ketones, and tributyl phosphate (TBP). Data for a pyridine modifier are given in Table 2. Table 3 defines the aqueous phases employed, including a simple simulant together with a more complex tank-waste simulant. As shown in Table 2, pertechnetate can be readily removed from such media and then stripped from the solvent with water.

Based on the commercially available crown ether DtBuCH18C6, solvent systems such as the one shown in Table 2 appear to be suitable for process development. However, improvements could yet have significant impact on process economics. It may be noted that only a small fraction of the total capacity of the crown ether is used, and thus owing to the expense of the crown ether, strong incentive exists to reduce the crown-ether concentration. A possible avenue toward this end lies in more effective binding and encapsulation of the sodium cation. To explore this possibility, the series of crown ethers shown in Figure 5 is being synthesized and studied. The series is built upon the rigid framework of dibenzo-14-crown-4, which provides the base from which 3-dimensional coordination of the cation can be supplied by the upright sidearms. The best performance found at this writing has



R ₅ = H				R ₅ = <i>t</i> -Octyl			
R ₁	R ₂	R ₃	R ₄	R ₁	R ₂	R ₃	R ₄
1	H	H	H	11	H	H	H
2	OH	H	H	12	OH	H	H
3	OAc	H	H	13	OAc	H	H
4	OCH ₃	H	H	14	OCH ₃	H	H
5	OCH ₂ COCH ₃	H	H	15	OCH ₂ COCH ₃	H	H
6	OH	OH	H	16	OH	OH	H
7	OAc	OAc	H	17	OAc	OAc	H
8	OCH ₃	OCH ₃	H	18	OCH ₃	OCH ₃	H
9	OCH ₂ COCH ₃	OCH ₂ COCH ₃	H	19	OCH ₂ COCH ₃	OCH ₂ COCH ₃	H
10	OH	OH	CH ₃	20	OH	OH	CH ₃

Figure 5. New crown ethers for extraction of alkali metal salts. The compounds are built upon dibenzo-14-crown-4. Alkyl substituents on the benzo rings supply lipophilicity.

been obtained with the *cis*-bis(oxyacetone) compound, which gives approximately the same Tc distribution coefficient as DtBuCH18C6.

X-ray crystal structures show that the dibenzo-14-crown-4 compounds complex sodium ion. As shown in the example in Fig. 6, the *cis*-bis(diol) derivative binds Na⁺ ion with its six available donor atoms. As expected, the dibenzo-14-crown-4 ether provides the base of four ether oxygens, and the hydroxy sidearms coordinate the cation on opposite sides. The perrhenate anion coordinates to the sodium cation in monodentate fashion. Only one of two unique crown ether molecules is shown. The other holds a sodium cation in a similar manner, and this cation receives coordination from a second oxygen atom of the perrhenate anion shown. Thus, the anion bridges two crown-ether-sodium complexes. A second perrhenate anion (not shown) is not coordinated to any sodium cation but rather interacts with one of the hydroxy ligands by hydrogen bonding. Details of the structure will be published in full elsewhere. As for the structure of the complex in solution, the crystal structure provides no definite information, but rather only possibilities. Experiments are in progress to gain information on solution stoichiometry and structure by extraction, NMR, and other methods.

CONCLUSIONS

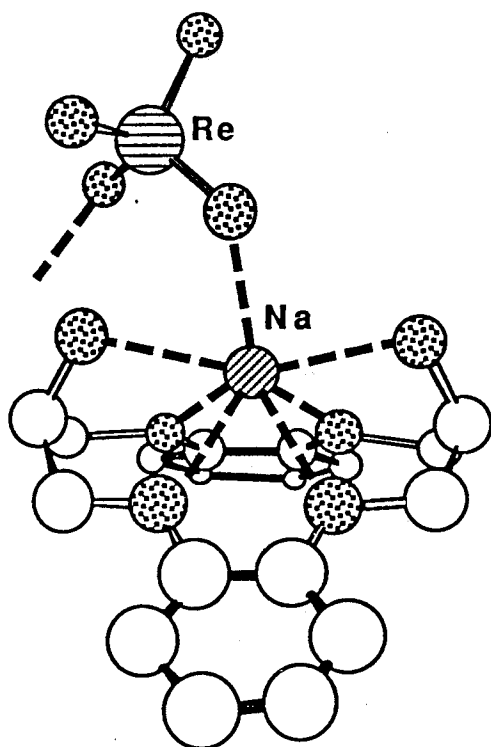


Figure 6. Portion of the crystal structure of $[\text{Na}(\text{cis-sym-dibenzo-14-crown-4-diol})]\text{ReO}_4$. Hydrogen atoms have been omitted for clarity.

Anion-exchange principles as applied to solvent extraction or resin ion exchange have long been known to predict selectivity for large, poorly hydrated anions. Although typical anion-exchange extractants function effectively in the separation of pertechnetate anion from highly alkaline media, stripping presents difficulties because a means to reverse the anion-exchange process is inherently lacking. By contrast, crown ethers offer an ideal vehicle for the reversible formation of lipophilic salts having a bulky cation. In this case, the bulky cation forms via the inclusion of a metal cation by the crown ether, resulting in the co-extraction of the metal cation and an aqueous anion for charge neutrality. One may view the extracted anions as exchangeable with other aqueous anions, a process again expected to favor large, poorly hydrated anions such as pertechnetate. Thus, the resulting selectivity in the overall extraction of a metal salt by a crown ether is determined largely by the effective binding of the metal cation by the crown ether and the hydrophobicity of the anion. Such an extraction is driven by high concentrations of alkali metal cations and is

reversed by contacting the loaded solvent with water or solutions containing low concentrations of extractable metal salts.

Experiments have shown that solvents containing crown ethers indeed reversibly extract pertechnetate anion from aqueous solutions containing alkali metal salts, including a simulant of Hanford tank waste. Dependencies of the technetium distribution ratios on the concentrations of system components have been determined for *cis-syn-cis*-dicyclohexano-18-crown-6 in 1-octanol. Qualitatively, the dependencies agree with the expected ion-pair extraction. A number of commercially available crown ethers have been examined and compared with several novel crown ethers based on the dibenzo-14-crown-4 framework. Structural properties of a sodium perchlorate complex with *cis-sym*-dibenzo-14-crown-4-diol have been characterized by X-ray crystallography, showing the encapsulation of the sodium cation by the six oxygen atoms of the crown ether.

ACKNOWLEDGMENTS

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NEPTUNIUM AND TECHNETIUM CONTROL IN REPROCESSING

Sachio FUJINE, Gunzo UCHIYAMA, Mitsuru MAEDA
Japan Atomic Energy Research Institute(JAERI)

Abstract

A concept of the modified Purex reprocessing incorporated with partitioning is proposed for the purpose of enhancing the efficiency of long-lived nuclides control in the future. Not only long-lived actinides but also long-lived fission products are taken into account in the process concept. The process is expected to reduce the long-term toxicity and the volume of radioactive waste as well as the radioactivity released to the environment as low as reasonably achievable. Separation of the extractable Np-237 and Tc-99 has been demonstrated by the modified Purex extraction process using salt-free reagents of butyraldehyde. A new experimental equipment, which has been installed in a $\alpha \gamma$ cell, is going to be introduced for the feasibility study of the modified Purex process; PARC process.

INTRODUCTION

Plutonium recycle without the integration of long-lived nuclides is the ideal concept of the nuclear power supply system in the future. The centralized large scale reprocessing facility for LWR fuels in the future is expected to reprocess the advanced fuels which contain more actinides and fission products than the present fuel¹⁾. Plutonium recovery rate must be kept at the high level and must be improved further in the future. The increase of Am and Cm content in the spent fuels leads to the increase of heat generation and neutron discharge in high level liquid waste (HLW) of reprocessing. The extractable long-lived Np-237 (The half-life is 2.14×10^6 years.) and Tc-99 (The half-life is 2.11×10^5 years.) require much effort to purify the U and Pu products in the solvent extraction cycles.

The reprocessing in the future should have the advantages of reducing the long-term toxicity of radioactive waste, reducing the volume of the waste, and also reducing the radioactivity released to the environment as low as reasonably achievable. Attention must be paid not only to the long-lived actinides but also to the long-lived fission products, because the volatile long-lived C-14 (The half-life is 5.73×10^3 years.) and I-129 (The half-life is 1.57×10^7 years.) are easy to be released to the environment from normal operation of the reprocessing plant. Those long-lived fission products are assessed to have the relatively bigger effect on the collective dose rather than the minor long-lived actinides²⁾. From those points of view, we made a concept of advanced reprocessing incorporated with partitioning; PARC process. Long-lived nuclides are separated and isolated in the process.

CONCEPT OF ADVANCED REPROCESSING

A modified Purex process incorporated with partitioning may be illustrated as the block flow diagram shown in Fig.1. Plutonium and uranium are decontaminated in a single extraction cycle. Plutonium recovery rate is enhanced by optimizing the operation condition, although the decontamination factor of Pu may be slightly lower than the standard 3 extraction cycle process. The recovered Pu may contain a part of U and Np. Long-lived nuclides such as C-14, I-129, Tc-99 and Np-237 are controlled in the reprocessing. Undissolved residue which contains approximately 30% Tc is not mixed in HLW. Am and Cm, which have leaked out to the raffinate, are assumed to be recovered from the raffinate. As the long-lived actinides, Np-237, Pu-239, Pu-240, Am-241, Am-243 and Cm-244 must be considered. Half-life on Np-237 is 2.14×10^6 years. Half-lives of the other actinides are 2.41×10^4 years for Pu-239, 6.58×10^3 years for Pu-240, 7.95×10^3 years for Am-243. Half-life of Am-241 is not long, but, it decays to long-lived Np-237 by half-life of 458 years. Long-lived Am-243 decays by half-life of 7.95×10^3 years to long-lived Pu-239. Cm-244 decays to long-lived Pu-240 by half-life of 17.6 years.

An assessment of the collective dose due to the radioactivity released both to the atmosphere and to the ocean from a reprocessing plant shows that C-14, I-129, Pu-239 and Pu-240 among the above mentioned long-lived nuclides take a big part of the dose²⁾. The effect of Np-237 and Tc-99 on the collective dose is assessed to be relatively small. However, those nuclides are extractable to the extractant TBP. Much effort is required to remove Np-237 and Tc-99 from the U and Pu products in the extraction process of reprocessing. The extraction process is forced to be complicated to remove and confine those dispersed elements. A high efficient technology of controlling Np and Tc must have a big advantage of simplifying the purification processes and reducing the waste volume contaminated with those long-lived nuclides. Separation of those nuclides in reprocessing helps reducing the burden of partitioning those nuclides from HLW. Those nuclides have high potential as the hazardous elements because they have the chemical property of fast dispersion in the environment if the confining barrier is eroded. Np and Tc are expected to be separated in the purified condition in the modified reprocessing

Our concern on the long-lived nuclide control in reprocessing is summarized as follows,

- Remove C-14 and I-129 from the off-gas
- Enhance Pu recovery rate
- Separate the extractable Np and Tc
- Recover the inextractable TRU elements: Am and Cm.

SEPARATION PROCESS OF Np, Tc, Pu AND U USING BUTYRALDEHYDES AS SALT-FREE REDUCTANTS

Valency control technique takes the important role to control the elements behaviour in the extraction process. Valency changes depending on electric potential of the liquid. Reducing reagents are effective to control the electric potential homogeneously of the solution in a large scale contactor. Those reagents must be decomposable to gas and water, namely, salt-free. Otherwise, the volume of α contaminated waste will be increased. Butyraldehyde is one of the salt-free reagents. Butyraldehyde has isomers. The redox potentials of normal- and iso-butyraldehydes in 3M HNO₃ at 25°C are app.0.72 and 0.66 V versus saturated calomel electrode, respectively. The potential of n-butyraldehyde is much higher than the standard redox potential of the U(VI)-U(IV) system, a little higher than that of the Pu(IV)-Pu(III) system, and lower than that of the Np(VI)-Np(V) system. The potential of iso-butyraldehyde is a little lower than that of the Pu(IV)-Pu(III) system.

Normal-butylaldehyde reduces hexa-valent Np selectively. Iso-butylaldehyde reduces hexa-valent Np and tetra-valent Pu as well. Normal-butylaldehyde has much higher selectivity and a much lower reaction rate than iso-butylaldehyde. The results of the kinetics study(Fig.2) show that n-butylaldehyde reduces Np(VI) to Np(V) in the Purex solution but does not reduce Pu(IV) and U(VI), and iso-butylaldehyde reduces Np(VI) and Pu(IV) but does not reduce U(VI)⁹.

Inter-element separation of U, Pu and Np is possible by using normal- and iso- butylaldehyde properly. Feasibility study of a new process has been conducted to separate Np, Pu and U, selectively. Stripping Np from the solvent before the U/Pu partition step is considered to be favorable to prevent Np from diffusing into the downstreams. A proposed process, shown in Fig.3, consists mainly of three steps: a codecontamination(coextraction) step, a Np separation step using n-butylaldehyde, and a U/Pu partition step using iso-butylaldehyde as a Pu(IV) reductant. Hexa-valent Np(VI) ions, which is extracted by 30%TBP/n-dodecane solvent together with Pu(IV) and U(VI), are reduced and back-extracted from the solvent. Leakage of Np to the raffinate is prevented by the inserted oxidation step to the codecontamination step. Ammonium vanadate were employed in the experiment. The effectiveness of the separation process is demonstrated in the chemical flow sheet study using miniature mixer-settlers. In the Np separation step, app. 99.98% of the Np, which is extracted by 30%TBP/n-dodecane solvent along with U(VI) in the coextraction step, is reduced by n-butylaldehyde and separated from the uranium stream. In the U/Pu partition step, over 99% of the plutonium is reduced by iso-butylaldehyde and separated from the uranium stream. Pu(IV) is effectively reduced by iso-butylaldehyde without hydrazine as nitrous acid decomposing reagent. Figure 4 shows one of the result of flow sheet experiment.

Technetium can be separated along with neptunium by n-butylaldehyde. Experimental study is under way to optimize the operation condition to separate both Tc and Np in a proposed process.

STUDY ON MINOR ACTINIDES RECOVERY

Oxidation step was needed to increase the recovery rate of Np from the raffinate of codecontamination step. Salt free reagent is preferable, although non-salt free reagent, ammonium vanadate, was used in the experiment of Np recovery process. We will study salt-free methods to oxidize minor actinides in the raffinate to the higher valent states which are extractable to TBP. The calculation result(Fig.5) under a simple condition shows much higher electric potential is needed to change the tri-valent Am to the higher valency states than that is needed to change penta-valent Np to the extractable hexa-valent state. Unfavorable reactions caused by the high electric potential must be avoided.

NEW EXPERIMENTAL FACILITY

A bench scale experimental equipments for dissolution, off-gas treatment, extraction and liquid waste recycling process has been installed in $\alpha \gamma$ cell of BECKY facility in NUCEF(Nuclear Fuel Cycle Safety Engineering Research Facility)⁴⁾. High burnup spent fuel specimens(Max.3kg/year) will be transferred to the cell after chopped at the outside of the facility. Main flow sheet is shown in Fig.6. Acid test is undergoing. Uranium test is scheduled to start in the spring of 1995. Study on reprocessing consists of five subjects:(1)Kinetics of continuous dissolution of spent fuel and collection of basic data on the solubility of spent fuel, (2)The simplified reprocessing incorporated with partitioning, (3)Demonstration on the confinement of radioactive nuclides in reprocessing process, (4)Development of process simulation code system, (5)Iodine and carbon-14 confinement technology by dry process.

The outcomes of those research will be applied to the development of an advanced reprocessing incorporated with partitioning(PUREX-integrated partitioning system). Study on the volatile I-129 and C-14 is to understand their behaviour in the dissolution and to develop a dry technology to reduce those long-lived nuclides as low as reasonably achievable. Some new adsorbents are scheduled to be tested on the efficiency of removing iodine and carbon oxide. A simulation code system ARECS, as shown in Fig.7, is under development to understand the behaviour of long-lived nuclides in the dissolution, off-gas treatment and extraction steps of a reprocessing process for LWR⁵⁾, aiming at the improvement of the efficiency of the long-lived nuclides control. The simulation codes will be verified and improved through analyzing the data obtained from the experiment in $\alpha \gamma$ cell.

As a goal of the process concept of the advanced reprocessing incorporated with partitioning, we have made a block flow diagram of PARC process, as shown in Fig.8, taking into account of the past study⁶⁾. The combined work of the experimental study and analysis by the simulation code is expected to show the way to the goal of PARC process through modifying the present Purex process.

CLOSING REMARK

In the history of the development of reprocessing technology, much effort has been made on reducing the radioactivity released to the environment. The new effort of reducing the volume and long-term toxicity of the radioactive waste by controlling long-lived nuclides is expected to lead us to a new standard of the confinement of radioactivity. We think that the concept of the modified Purex reprocessing incorporated with partitioning is the practical way to achieve the new standard in the future.

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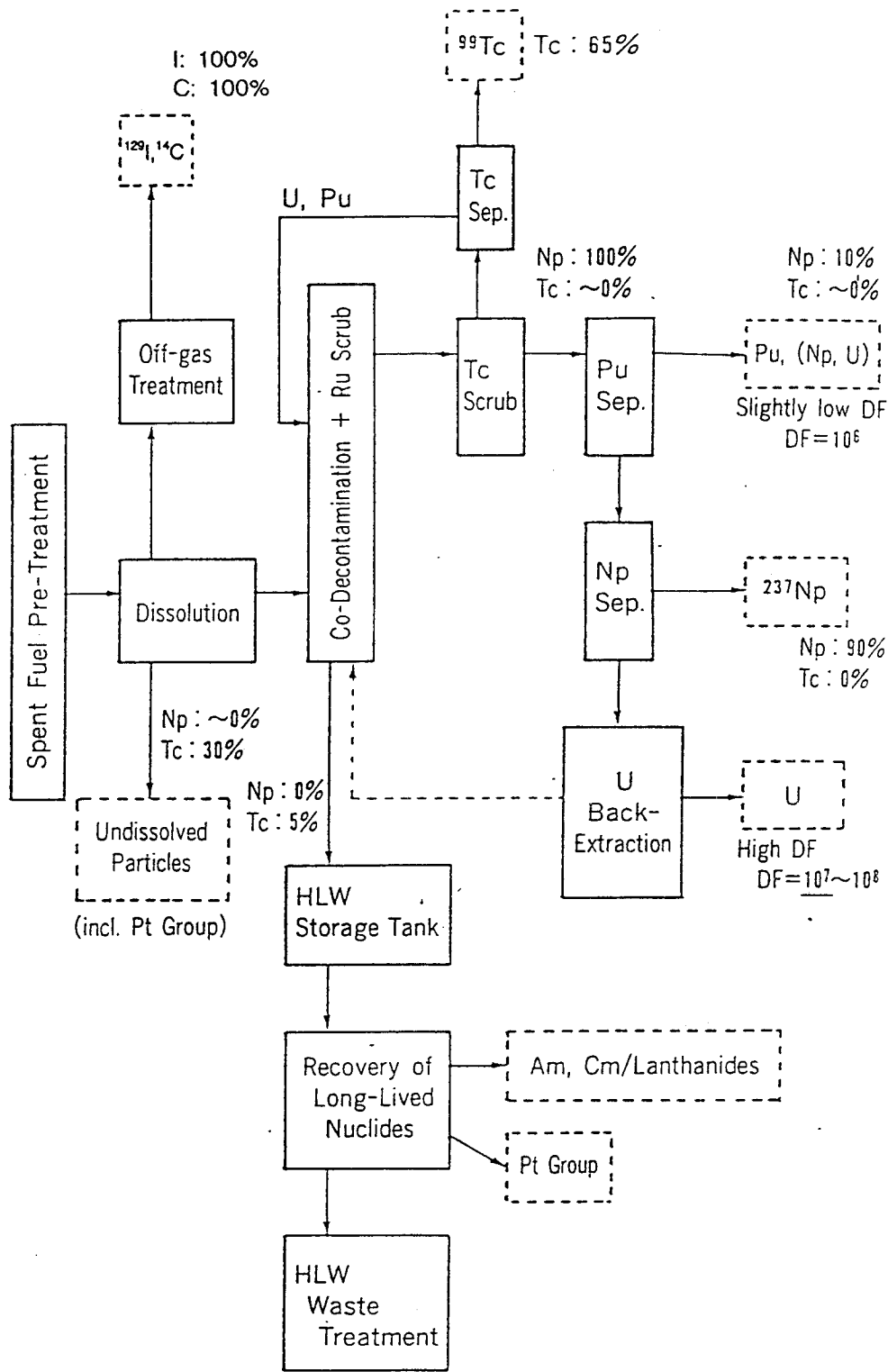


Fig.1 A conceptual block flow diagram of the advanced reprocessing incorporated with partitioning.

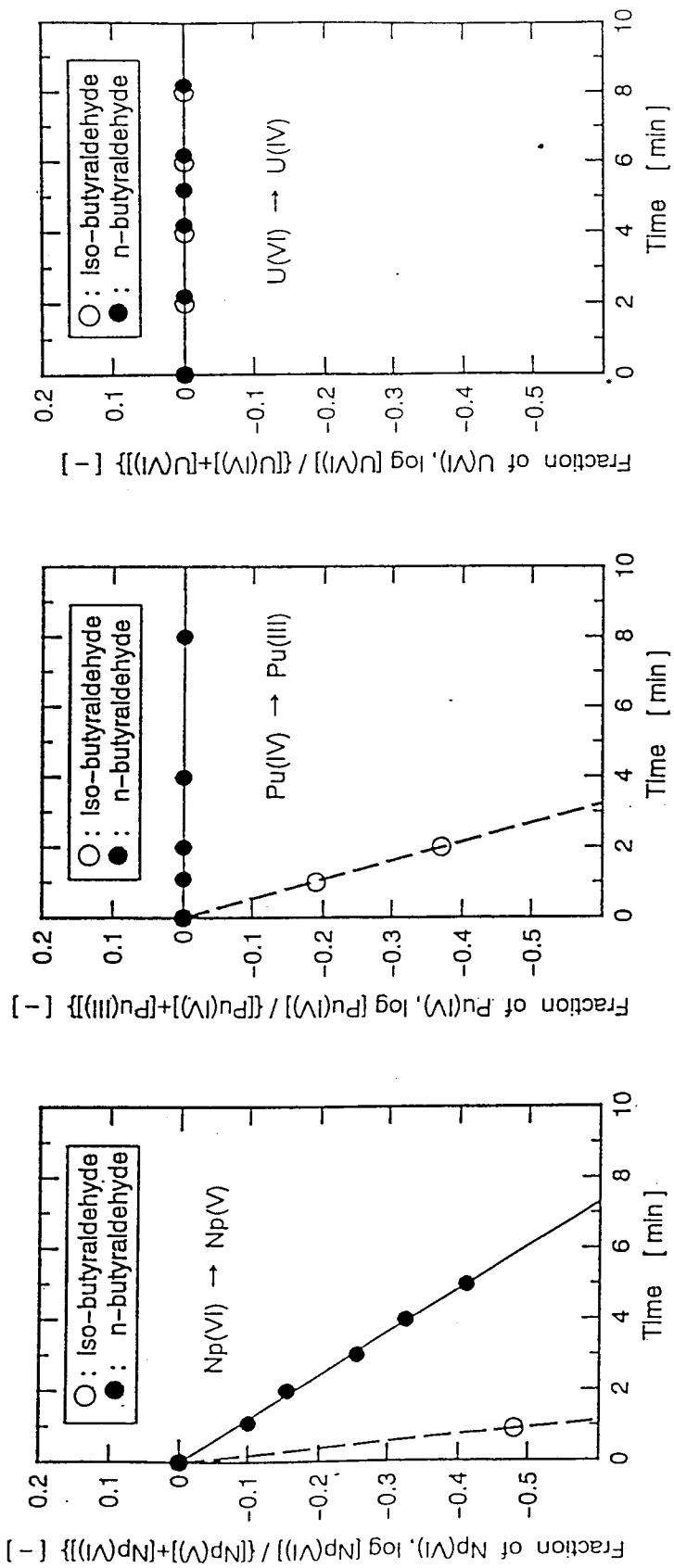


Fig.2 A result of kinetics study; Time dependency of fractions of Np(VI), Pu(V) and U(VI) under the reduction reaction by normal- and iso-butyraldehydes, Np(VI):0.13g/l, Pu(VI):5.5g/l, U(VI):20g/l, H⁺:3M, Temperature:293K.

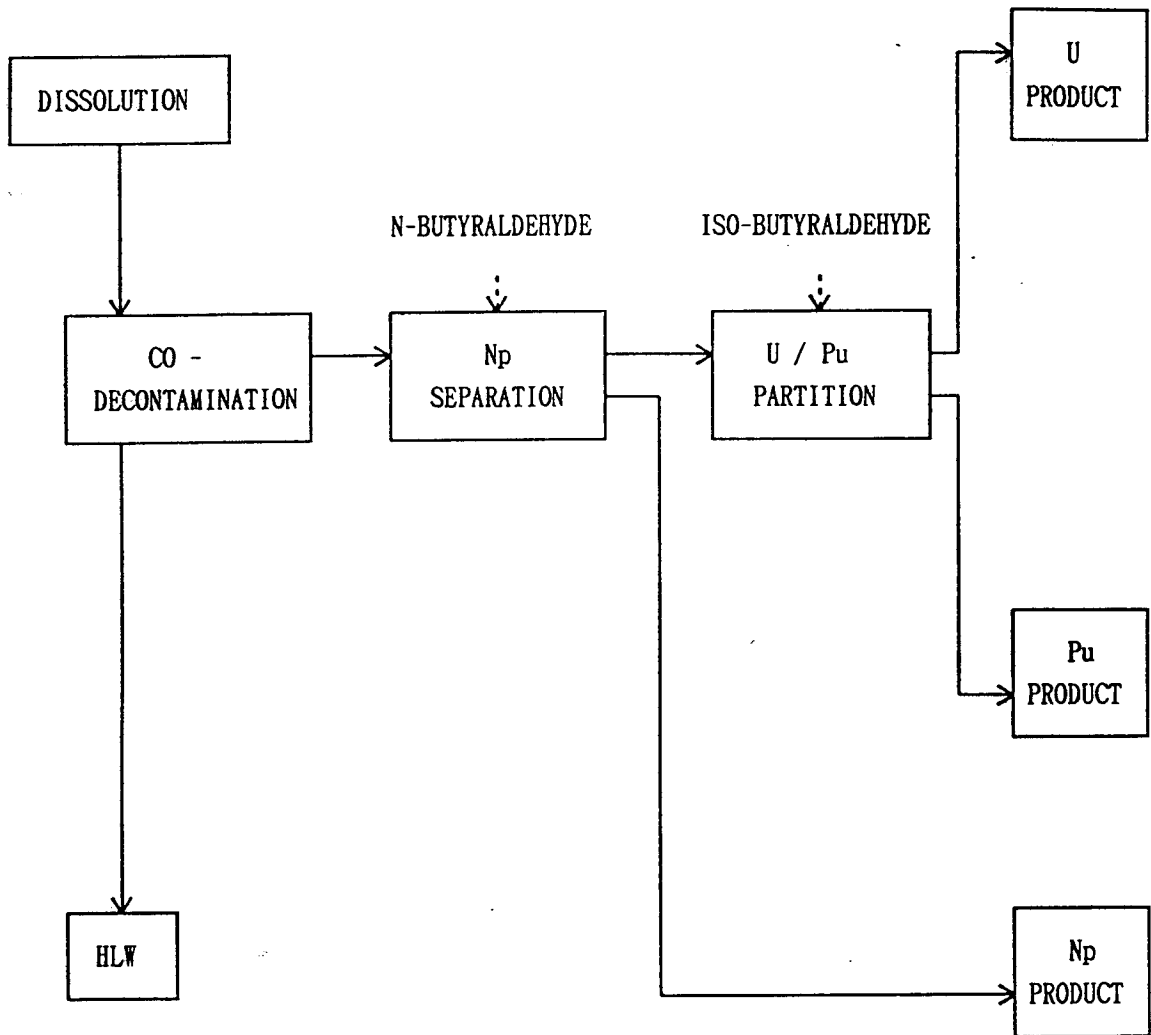


Fig. 3 A proposed flow sheet for Np, Pu and U separation by using normal- and iso-butyraldehydes in the first extraction cycle of reprocessing.

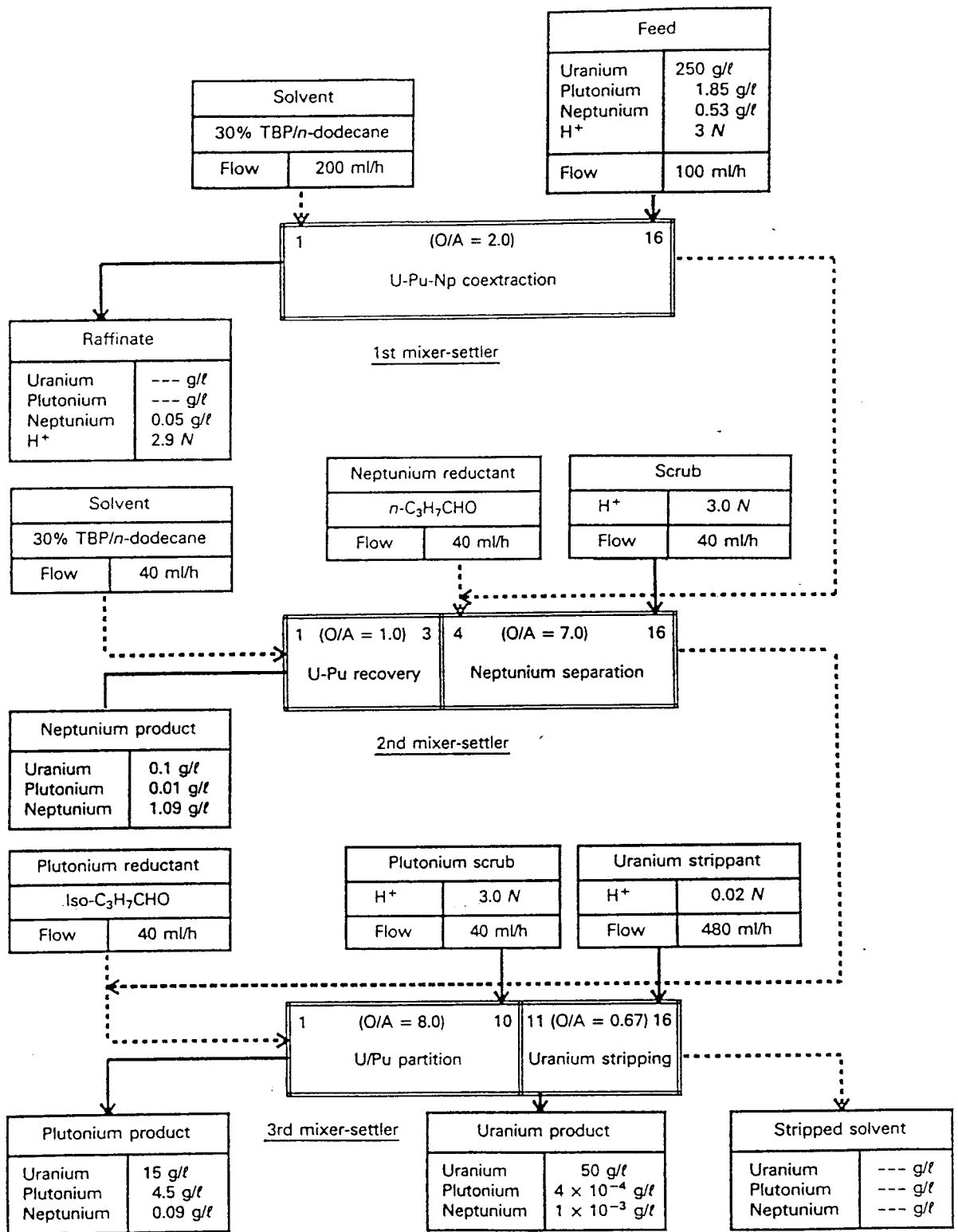


Fig.4 A result of chemical flow sheet study; Concentrations of H⁺, Np, Pu and U in solutions in a flow sheet trial.

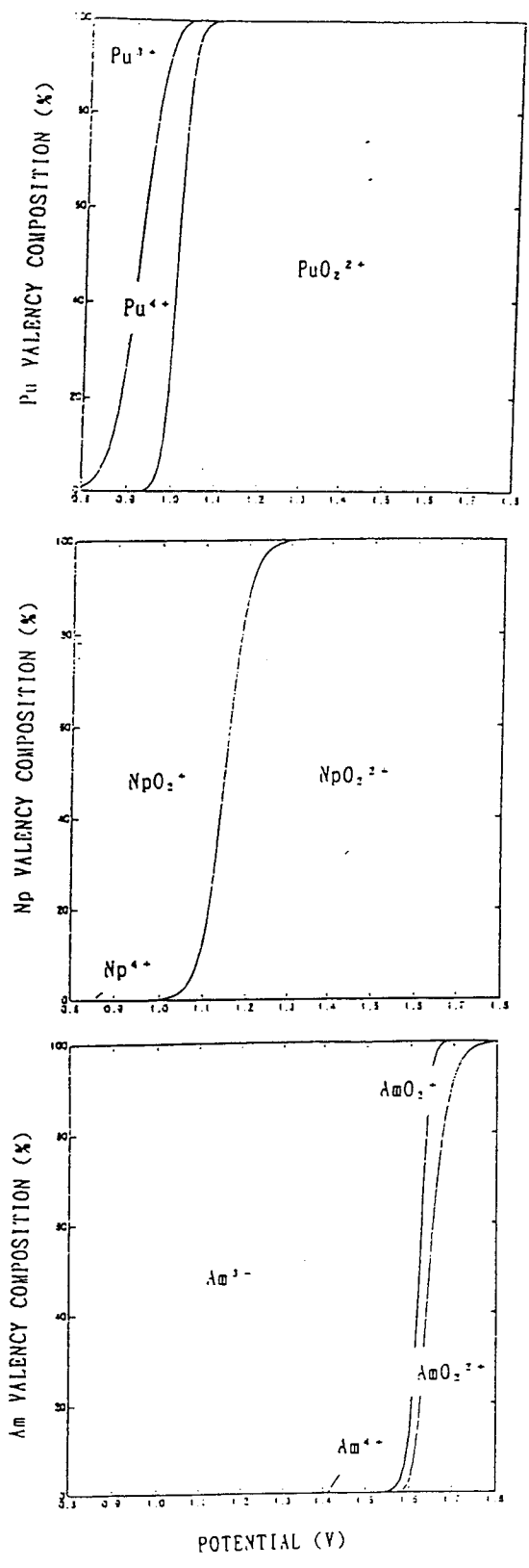
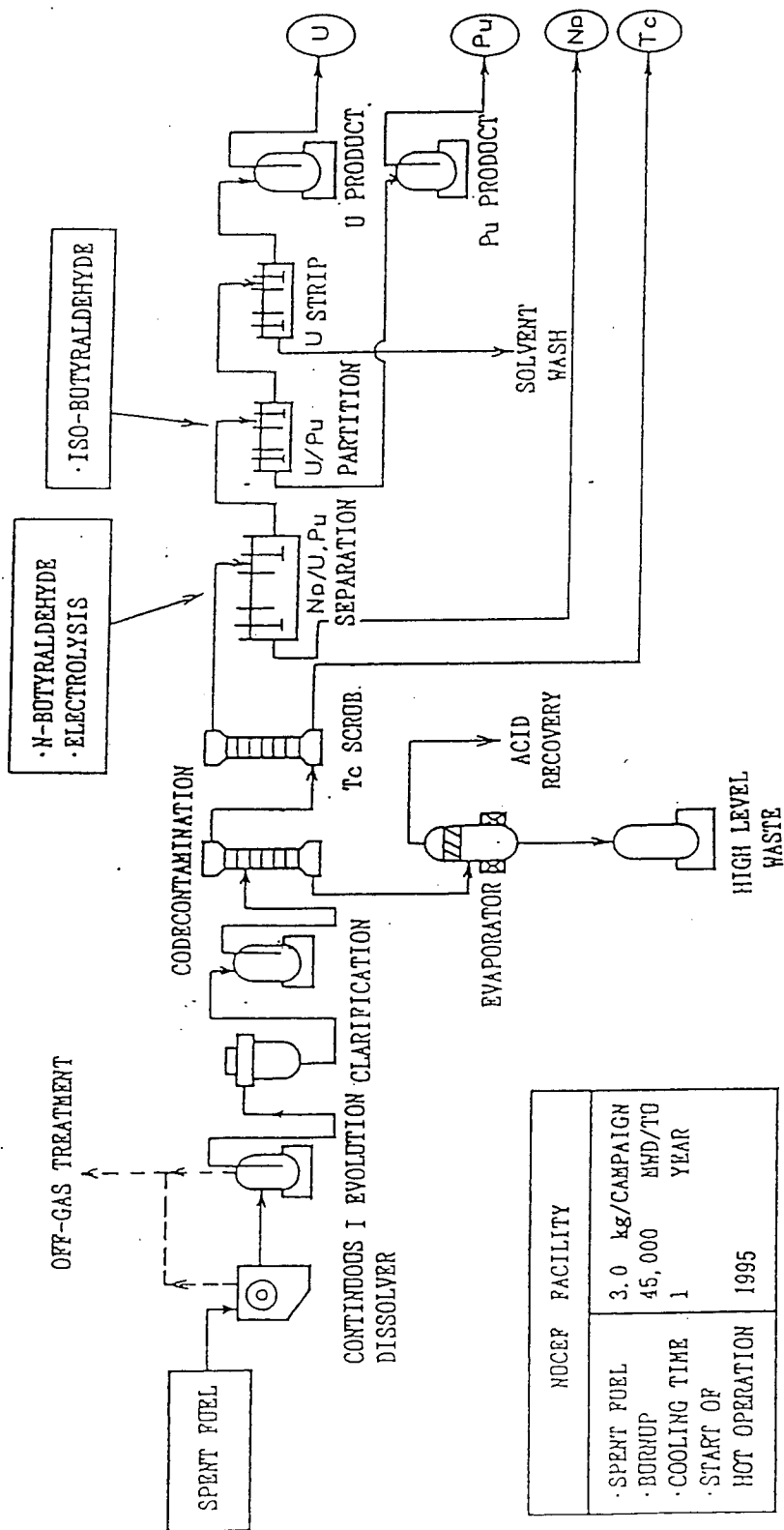


Fig.5 A calculation result of valency composition of actinides



NUCEF FACILITY	
· SPENT FUEL	3.0 kg/CAMPAIGN
· BURNUP	45,000 MWD/TO
· COOLING TIME	1 YEAR
· START OF HOT OPERATION	1995

Fig.6 Main flow sheet of the new bench scale experimental equipment installed in a 7 cell of BECKY facility in NUCEF.

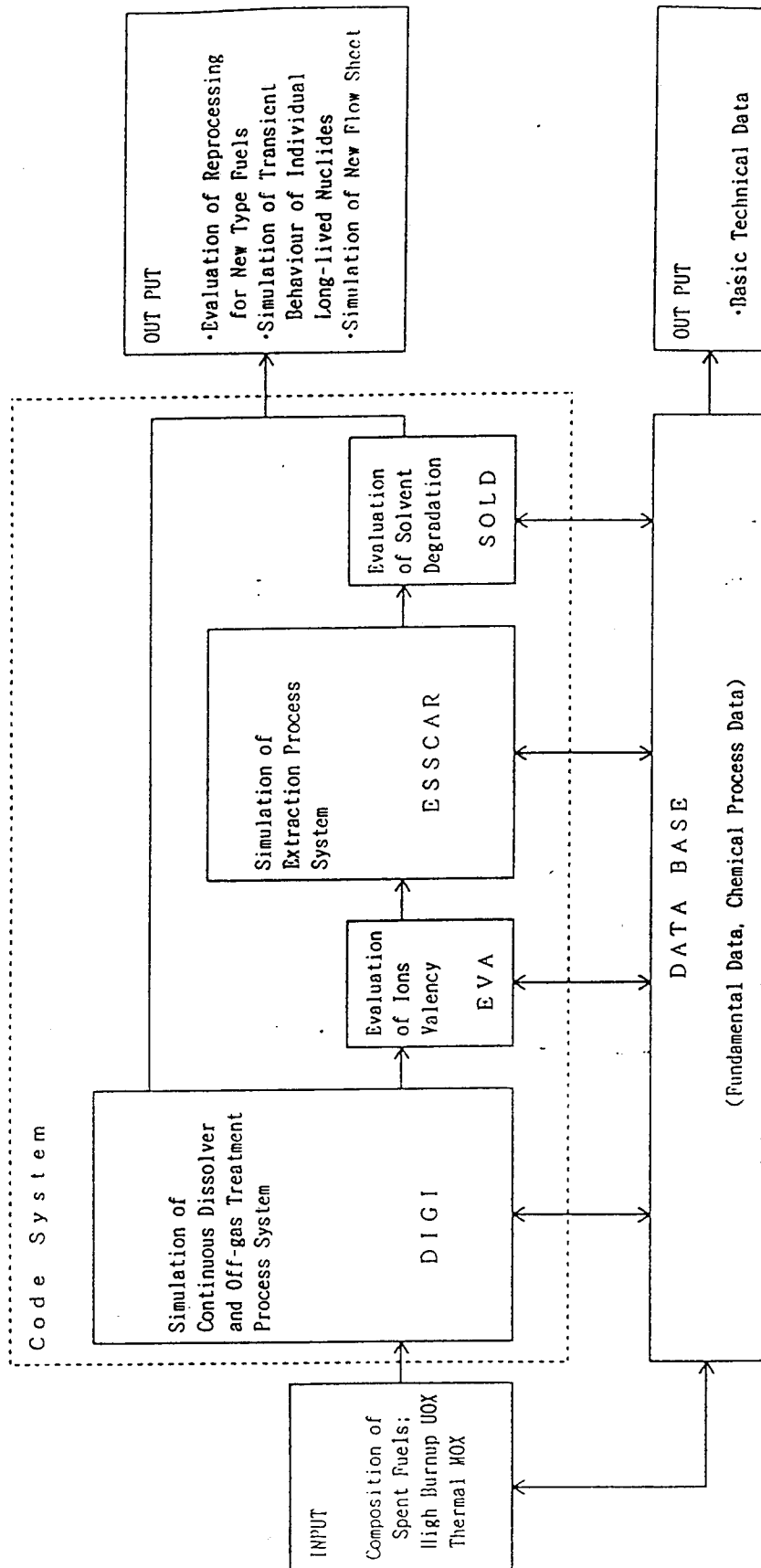


Fig.7 Simulation code system ARECS under development.

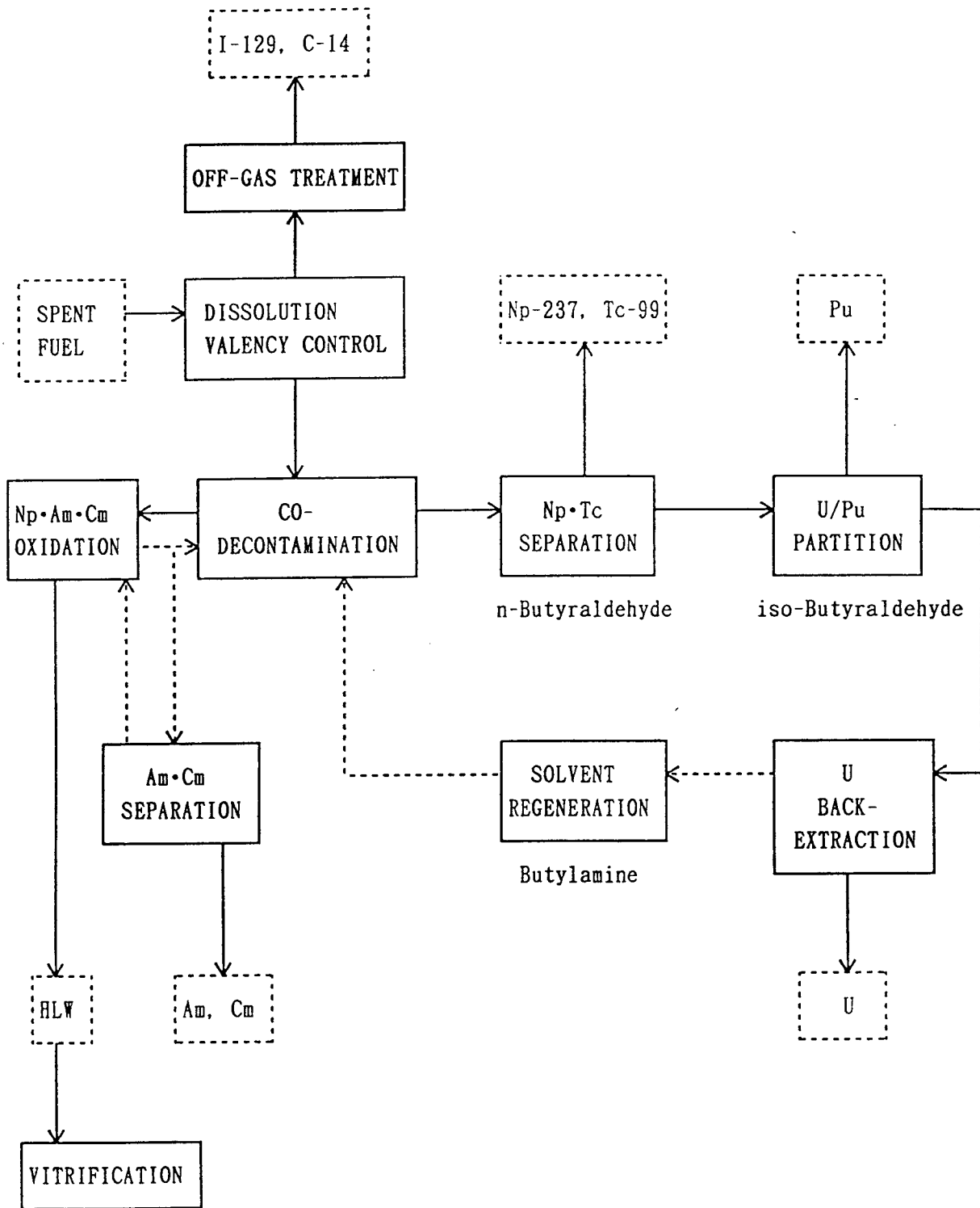


Fig. 8 Block flow diagram of a process concept of the advanced reprocessing incorporated with partitioning; PARC process.

The progress of TRUEX process improvement in PNC
- The applicability of "Salt-free" reagents-

Hiroyasu Hirano, Kazunori Nomura, Yoshikazu Koma, Shinichi Nemoto,
Masaki Ozawa and Akio Togashi

Reprocessing Technology Development Division
Power Reactor and Nuclear Fuel Development Corporation (PNC)
Tokai-mura, Ibaraki-ken, Japan

ABSTRACT

PNC has been promoting actinides partitioning studies as a part of advanced reprocessing system development efforts since 1990.¹⁾ Concurrently, the general TRUEX process was studied as a reference partitioning tool. In the counter-current flow-sheet tests using mixer-settler, some portion of U, Pu and Ru used to remain in the solvent by conventional stripping methods. Therefore a new "Salt-free" solvent-washing methods were studied to remove these nuclides and Zr from TRUEX solvent. Hydrazine oxalate was tested for U. Hydrazine oxalate, hydrazine carbonate and TMAH (tetramethylammonium hydroxide) were tested for Ru and Zr. The stripping behavior of Pu by hydrazine oxalate was studied through the counter-current test. It was concluded that various "Salt-free" reagents will be effective, if these are used in combination manner, for reducing these nuclides retention in the solvent.

INTRODUCTION

Partitioning of actinides in the High Level Liquid Waste (HLLW) is one of the key technology to achieve advanced reprocessing system in which recovered minor actinides will be recycled to reactor with U and Pu. This system is named "Actinide Recycle System". Such an innovative reprocessing may contribute to increase the fuel utilization efficiency and to decrease potential radioactive hazard of vitrified HLLW.

PNC has been studying the applicability of the TRUEX process²⁾ as a method for removal of actinides in the HLLW from the PUREX process. The batch-wise basic tests and the counter-current tests using the real highly active raffinate (HAR) derived from the PUREX process of FBR spent fuel have been carried out.

In these tests, the extraction behavior of actinides, lanthanides and some fission products became almost clear; Actinides and lanthanides were extracted quantitatively from HAR in the extraction bank and a high α -decontamination factor, $>ca.10^3$, was obtained.³⁾ Trivalent actinides and lanthanides were co-recovered from the loaded solvent in the stripping bank using dilute nitric acid. On the other hand, some portion of U, Pu and Ru were difficult to remove from the solvent by conventional stripping methods. In former counter-current test^{3),4)}, dilute nitric acid, HAN (Hydroxylamine nitrate), oxalic acid and sodium carbonate were tested as stripping reagents. Sodium carbonate seems to be highly effective at least in reducing amount of Pu as well as Ru in the solvent.^{3),4)}

Sodium carbonate has been employed as the solvent-washing reagent in PUREX process. From a view of a secondary waste generation, sodium-based reagents should be avoided. Therefore "salt-free" solvent-washing reagents, which were able to be decomposed to gaseous material by an electrochemical process, etc., were adopted to PUREX process⁵⁾ and were tested in the TRUEX process.

EXPERIMENTAL

Two kinds of tests were carried out. The objective element of the first test was U, and the second ones were Ru and Zr which were also troublesome fission products in PUREX and TRUEX processes. These two tests were carried out in a batch-wise method. The other kind of tests was the counter-current test using real HLLW aiming to evaluate an effect of salt free reagent on Pu and Ru stripping.

In U test, hydrazine oxalate was tested and compared with sodium carbonate, and a mixture solvent was composed 0.2M CMPO-1.0M TBP in n-dodecane. The test was performed at a room temperature(R.T.) and the organic/aqueous ratio (O/A ratio) was 1.

In Ru and Zr test, hydrazine oxalate, hydrazine carbonate and TMAH were tested. The reference alkali reagent was sodium carbonate. The solvent composed 0.2M CMPO-1.0M TBP in n-dodecane was irradiated up to 10^7 R by γ - ^{60}Co . The test was performed at R.T. and the O/A ratio was 1.

In the counter-current test using mixer-settler at the chemical processing facility (CPF), hydrazine oxalate was tested as stripping reagent for Pu. Feed solution was a real HAR derived from FBR-PUREX reprocessing tests. This solution contained much amount of corrosion products, Fe,Cr,Ni, corresponded to the concentration in the real HLLW from LWR reprocessing plant. (Refer to figure 1) The amount of total metals in the feed solution was about 5 times higher than in normal FBR-HAR. The flow-sheet of this test was shown in figure 2. The mixed solvent was 0.2M CMPO-1.4M TBP in n-dodecane. The concentration of TBP was a little higher than the former tests^{3),4)} attempting to avoid a third phase split. The extraction/scrubbing bank employed 32 stages and the stripping bank employed 19 stages. The dual-scrubbing method offering two scrubbing solutions was employed for improved Ru decontamination in the same manner as former tests.³⁾ The stripping bank was divided in two parts, the former was the trivalent actinides and lanthanides stripping part using dilute nitric acid and the latter was the Pu and U stripping part using hydrazine oxalate.

RESULT and DISCUSSION

The distribution ratio of U vs. reagent concentration was shown in figure 3. When the reagent concentration was lower than 0.1M, hydrazine oxalate showed less efficient than sodium carbonate. However, the distribution ratio of U using hydrazine oxalate, ca.0.1, was enough low to reduce U retention in the solvent. When the reagent concentration exceeded 0.1M, which were much excess to U concentration in the solvent, hydrazine oxalate indicated a good efficiency of U stripping as well as sodium carbonate. This indication was considered from the results that almost U was formed a water-soluble complex with oxalate ion or carbonate ion and then removed from the solvent.

The stripping efficiencies of Ru and Zr using another salt-free reagents were tested. Figure 4 shows the stripping ratio vs. reagents concentration in the case of pre-irradiated TRUEX solvent. TMAH showed a higher efficiency. Ru was stripped quantitatively when the reagent concentration was higher than 0.1M. In the case of reagent concentration exceeded 0.2M, the stripping ratio by sodium carbonate and hydrazine carbonate also became sufficient (>90%). But, hydrazine oxalate was not effective to strip Ru. As reported in the former paper ³⁾, the efficiency of Ru stripping was affected by the pH-value of aqueous phase and the significant Ru stripping can be obtained in higher pH value conditions. Figure 5 showed the stripping ratio of Zr vs. reagents concentration in the case of pre-irradiated solvent. The strip tendency of Zr was essentially similar to Ru; the higher Zr stripping was obtained in the higher complexing reagent concentration, about more than 10 times the Zr concentration. In the results showed, hydrazine oxalate was more efficient for Zr than for Ru. A similar result was experienced in the PUREX process ⁵⁾. It was considered that the complex formation with oxalate ion contributed to be stripped Zr from the solvent. In the most case of Ru and Zr stripping test, the interfacial cruds formation was observed. While the behaviors of cruds formation and decomposition have not become clear yet, the control of cruds is one of the problems to solve for the application of salt-free reagent.

The material balance of main elements in the counter-current test was shown in Table 1. Trivalent actinides (Am, Cm), lanthanides (Eu) and Pu were extracted quantitatively from the HAR to the solvent. Fission products (Cs) were not extracted and then retained in the raffinate stream. Some portion of Ru was extracted to the solvent. In the strip bank used dilute nitric acid, some portion of trivalent actinides and lanthanides were stripped from the solvent. However, a major portion of these was leaked to the later strip bank used hydrazine oxalate. Both of Pu and Ru were not stripped by dilute nitric acid. Because of the large amount of metal leakage, a precipitation formed in the stripping bank used hydrazine oxalate. The amount of elements in the precipitation was not measured, thus the stripped portion by hydrazine oxalate in Table 1 was estimated from the balance of the other fraction.

Pu was completely removed from the spent solvent. However, Ru was not stripped sufficiently and almost of the extracted Ru was still remained in the spent solvent. The precipitation formation was observed in the stripping bank used hydrazine oxalate. However, hydrazine oxalate was proved to be effective reagent for Pu stripping. On the other hand, hydrazine oxalate was not sufficient for Ru stripping, and it was the same result that obtained in the batch-wise test.

After the operation of counter-current test used the HAR corresponding to the LWR-HLLW, the third phase splitting was observed in the half part of extraction/scrubbing bank, and then the third phase seemed to form during the operation. However, the extraction behaviors of main elements in the extraction bank were not significantly different from the former tests used the normal FBR-HAR^{3),4)}, in which the third phase was not observed. Though the third phase was not recognized to affect seriously for extraction in this test, avoiding the third phase formation might be important to obtain selective actinide fractionation according to their valency.

Considering the results mentioned above, the next counter-current test using the improved flow-sheet will be carried out in near future. In this test, three kinds of salt-free reagent will be tested; the first is HAN in dilute nitric acid for Pu stripping, the second is hydrazine oxalate for mainly U and Pu stripping and the third is hydrazine carbonate for Ru stripping.

CONCLUSIONS

Some salt-free reagents, which were used in the PUREX process, were tested for nuclei stripping from the TRUEX solvent in the batch-wise tests and the counter-current test used the FBR-HAR. Hydrazine oxalate was proved to be reagent sufficient for U and Pu stripping from the TRUEX solvent. Hydrazine carbonate and TMAH were sufficient for Ru and Zr stripping from the pre-irradiated TRUEX solvent. The efficiency of salt-free reagents was not much inferior to sodium carbonate. It means that conventional sodium-based reagent is able to be replaced by the salt-free reagent from a view of nuclei removal from the TRUEX solvent.

The optimization of the flow-sheet condition aiming complete "Salt-free" TRUEX process is in progress.

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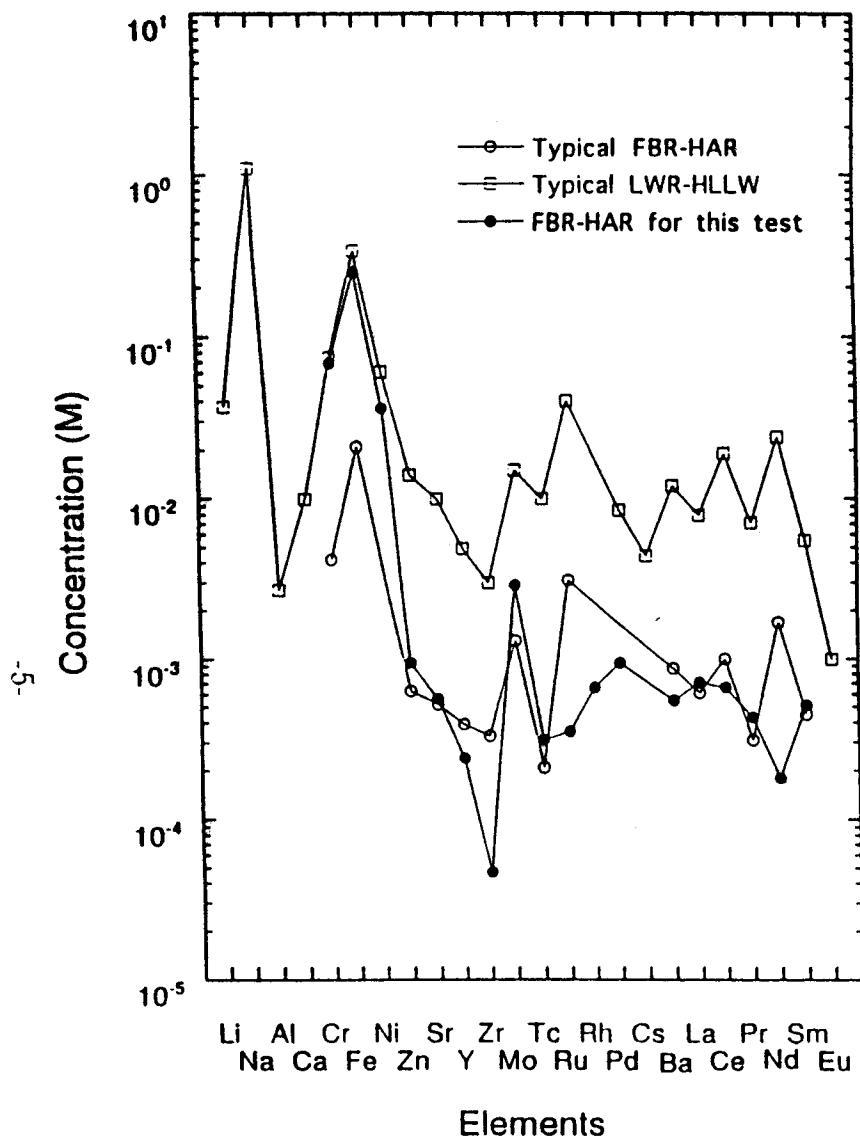


Figure 1 The composition of solution used for the counter-current test

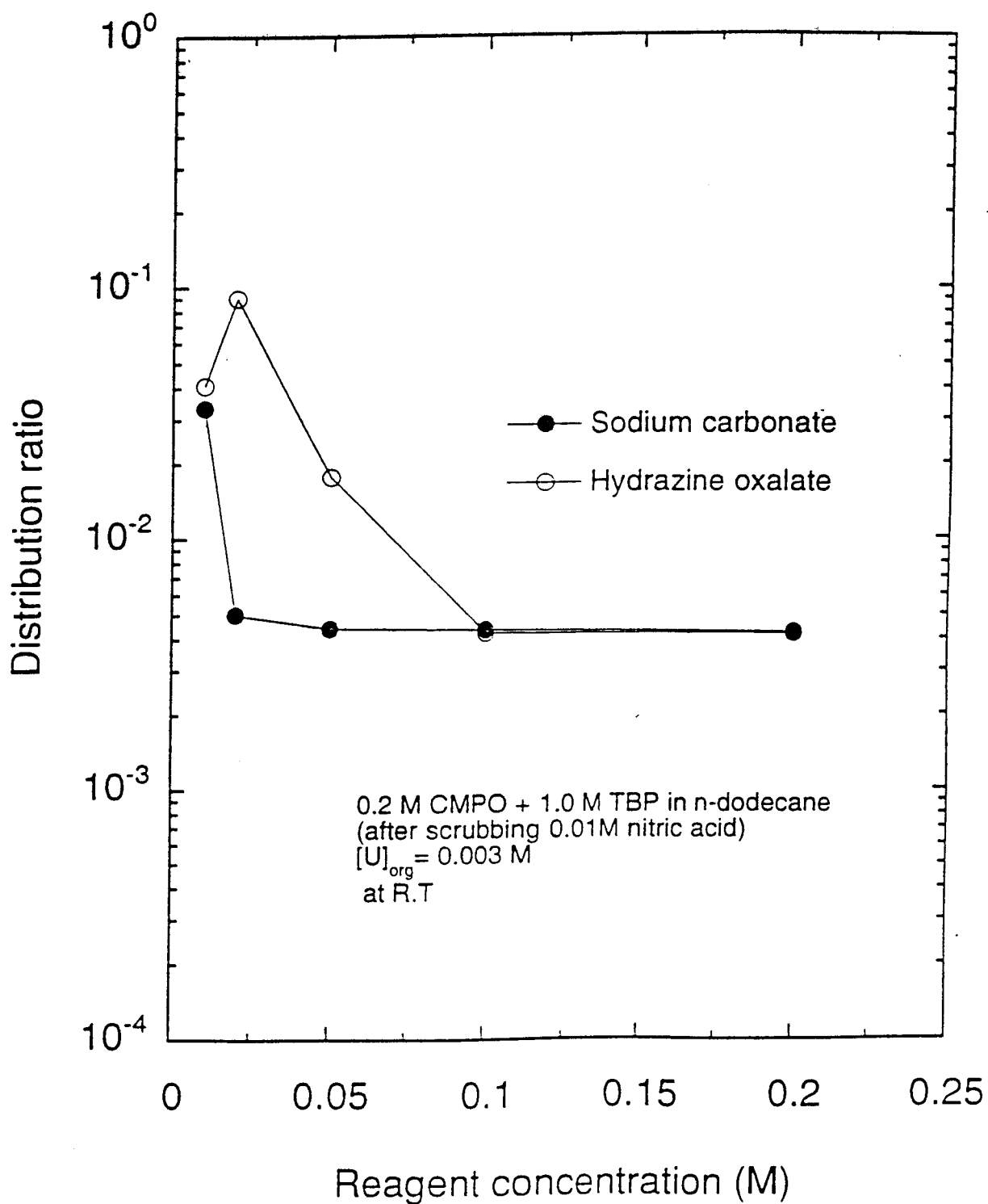


Figure 3 The dependency of U distribution ratio on reagent concentration

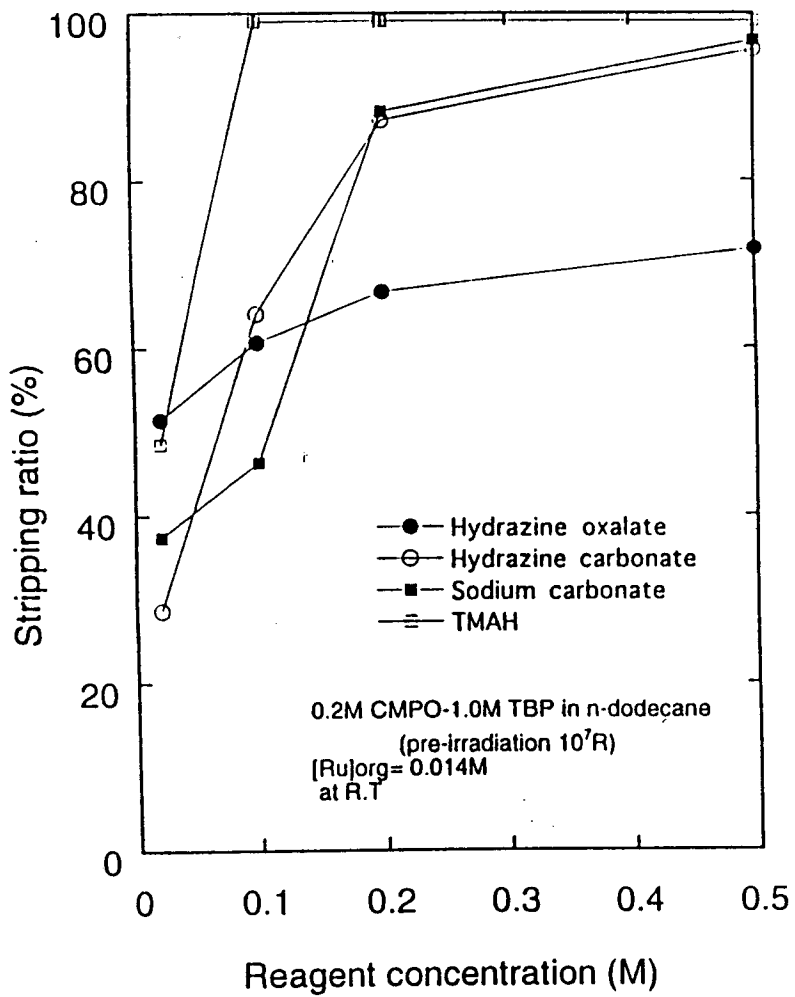


Figure 4 The dependency of Ru stripping ratio on reagent concentration

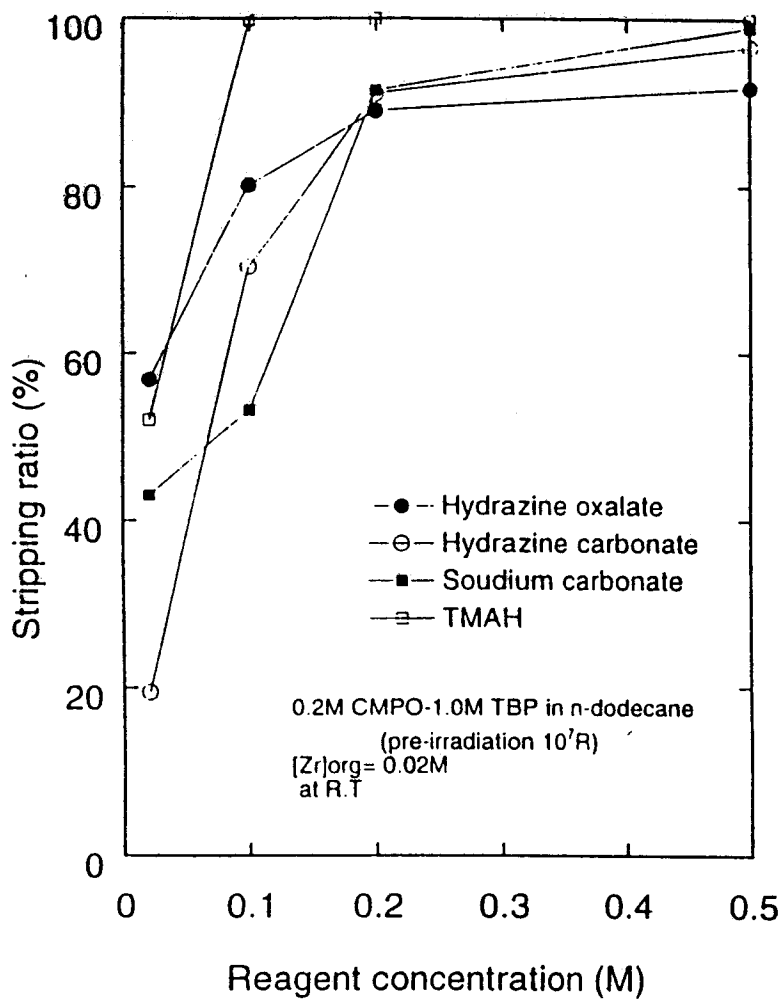


Figure 5 The dependency of Zr stripping ratio on reagent concentration

Table 1 The material balance for the main elements in the counter-current test

Elements	Strip(1)		Strip(2)	
	Raffinate	Diluted nitric acid	Hydrazine oxalate	Spent solvent
Cs	ca. 100%	-	-	-
Eu	-	ca. 5%	95%*	-
Am**	-	ca. 3%	97%*	-
Cm	-	ca. 4%	96%*	-
Pu	-	-	100%*	-
Ru	-	-	0~4%	~5%

Amount of feed = 100%

- : Not detected

* Calculated value : (100% - (Raffinate + Strip(1) + Spent solvent)

** Am-241 + Pu-238

PARTITIONING AND TRANSMUTATION OF ACTINIDES AND FISSION PRODUCTS CONSIDERATION OF MEDIUM AND LOW LEVEL WASTE STREAMS

**R K WEBSTER
FOR AEA TECHNOLOGY, HARWELL UK**

ABSTRACT

The partition-transmutation process has been proposed for the treatment of radioactive waste. A complete scheme requires:

- inclusion of all radionuclides which might have radiological impact after disposal;
- consideration of all significant waste streams.

The first point requires extension of the range of nuclides, for example to cover chlorine-36 and radium-226. This point has been covered in a previous paper and will not be discussed further.

On the second point, most schemes concentrate on the treatment of highly active waste liquor only. However, a complete scheme requires consideration of all subsidiary waste streams: solid, aqueous, organic, and gaseous. For example, up to 2% of plutonium could be present in these streams.

It is necessary to consider all waste streams from the fuel cycle, covering fuel fabrication, enrichment and reprocessing. The components of a conceptual process will be outlined, including:

- conversion of organic waste to inorganic aqueous waste by catalysed electrochemical treatment in nitric acid;
- dissolution of insoluble plutonium oxide by a similar electrochemical process;
- separation of the required radionuclides from aqueous streams by selective electrochemical ion exchange.

1. INTRODUCTION

This paper will concentrate on the removal of minor actinides (Np, Am, Cm) and on the improved recovery of U and Pu, in both cases from secondary waste streams. The proposed processes can be regarded as either (i) a potential input into schemes to increase the recovery of actinides from waste streams for destruction by transmutation, or (ii) as a step in the longer term for increasing the quantity of energy which could be obtained from a given inventory of uranium by recovery and recycle of the actinides.

A few comments will be made on long-lived fission products, as appropriate.

2. INVENTORY

Table 1 shows the volumes and activities of conditioned wastes expected to arise in the UK up to the year 2030, in order to illustrate the problem. The total volume of about one million cubic metres is divided between:

- HLW: High Level Waste; in Japan this will consist of the high level liquid waste from reprocessing, or the vitrified waste product.
- ILW: Intermediate Level Waste; in the UK this includes other wastes where the alpha activity exceeds 4 GBq/te, or the beta-gamma activity exceeds 12 GBq/te.
- LLW: Low Level Waste; wastes below these limits, but in the UK with a cut-off of 0.4 Bq/g.

Table 1

Volumes and Activities of Conditioned Wastes from All Sources to 2030

Waste type	Volume m ³	Activity	
		TBq alpha	TBq beta/gamma
HLW	3,800	7,900,000	660,000,000
ILW	260,000	67,000	43,000,000
LLW	730,000	100	590

Table 2 provides the corresponding percentage comparison. It highlights the need for attention to ILW which represents about 26% of the total waste volume, and contains nearly 1% of the alpha activity.

As with the fission products, the alpha radioactivity of the total inventory is dominated by short-lived species. In the current UK inventory to 2030, nearly 80% of the alpha activity is accounted for by curium-244 which decays with a half-life of 18 years to its long-lived daughter plutonium-240. Americium-241 is another major contributor, with a half-life of about 460 years. However, from a processing viewpoint, the actinide mass is also important and most of this is associated with the longer-lived components.

Table 2

Percentage Comparison of Volumes and Activities of UK Conditioned Wastes from All Sources to 2030

Waste type	Volume %	Activity	
		% alpha	% beta/gamma
HLW	0.38	99.2	93.9
ILW	26.20	0.8	6.1
LLW	73.40	0.001	0.0001

3. SOURCES OF ALPHA CONTAMINATED ILW

The following comments identify potential sources of waste. Not all will occur, depending on the flow-sheet and the plant design.

(a) Reactors, fuel transport, fuel storage

The inventory from routine operations will be primarily beta-gamma activity from activated corrosion products. The issues raised by damaged fuel and accidents, as at Chernobyl, are not covered by this note.

(b) Fuel reprocessing: head-end section

In the head-end section of the plant, irradiated fuel assemblies or pins are sheared, and the fuel dissolved in nitric acid.

Wastes will include:

- fuel hulls;
- centrifuge cake (PuO₂ fuel residues; insoluble fission product alloys);
- HEPA filters;
- off-gas scrubber liquors;
- shear pack decontamination liquor.

(c) Separation plant: Cycle-1

The main outputs are:

- U and Pu product steams;
- HA waste stream;

- solvent scrub liquors;
- solvent for recycle.

The solvent is normally washed with sodium carbonate and dilute nitric acid to remove degradation products; this generates:

- solvent wash raffinate (SWR), a sodium nitrate stream,

and if the SWR is concentrated by evaporation:

- off-gas scrubber liquors;
- HEPA filters.

Eventually solvent will need to be replaced, leaving

- waste solvent.

(d) HA waste stream

HA waste will normally pass to buffer storage, evaporation, storage, and vitrification.

Wastes will arise as:

- off-gas scrubber liquors;
- HEPA filters;
- plant washings.

The recovery of actinides from the HA waste stream itself is the subject of other papers, and is not discussed in this note.

(e) Separation plant: cycles 2 and 3

These are the medium and low active stages, and will vary with the flowsheet. The terms medium and low active refer to fission product activity: the uranium, and plutonium throughputs will be as in Cycle-1. Similar alpha contaminated wastes will arise as in sections 3(c) and 3(d) above. The medium and low active aqueous waste streams are noted as secondary wastes, but in practice they might be concentrated by evaporation and recycled to the HA waste stream.

Plutonium and uranium product streams may be washed by the solvent diluent to remove traces of tributyl phosphate (or other) extractant, yielding:

- diluent wastes.

(f) Pu and U product evaporators

In each case:

- off-gas scrubber liquors, if not recycled;
- HEPA filters.

(g) Plutonium finishing

Plutonium oxide will be obtained by precipitation as the oxalate or as ammonium plutonyl carbonate for calcination, or directly by thermal denitration. Wastes will include those from off-gas control:

- off-gas scrubber liquors;
- HEPA filters,

and plant clean-out wastes

- wash liquors;
- possibly tissues.

(h) Uranium finishing

Finishing will be by precipitation as ammonium diuranate or as ammonium uranyl carbonate, for calcination, or by thermal denitration. Wastes will be similar to those from section 3(g).

(i) Uranium enrichment

Very briefly, UO_2 is converted to UF_6 for enrichment by reactions typically with hydrogen fluoride to form UF_4 , and then fluorine to yield UF_6 . Following enrichment, UF_6 is converted to UF_4 by reaction with hydrogen, and then to UO_2 by reaction with steam, or by the ammonium diuranate or ammonium uranyl carbonate routes.

This area is not discussed in detail as it is assumed that uranium recovery is not a prime objective. However, uranium contaminated wastes may arise from off-gas and plant clean-up operations, and as calcium or magnesium fluoride slag if uranium metal is required. The routes for neptunium and technetium in the reprocessing flowsheet should also be assessed.

(j) Mixed oxide fuel fabrication

UO_2 and PuO_2 will be mixed, ground, made into pellets, sintered, ground to size if appropriate, followed by assembly in fuel pins. Wastes may include:

- PuO_2 dust;
- grindings;
- contaminated tissues from cleaning operations;

- hypalon gloves;
- polyethylene;
- PVC bags, where bagless transfer is not feasible;
- off-gas scrub liquors where appropriate;
- HEPA filters.

(k) Uranium oxide fuel fabrication

UO₂ fuel fabrication may yield a comparable range of wastes to those from mixed oxide fuel fabrication. The alpha contamination will be much lower, but the waste volume may be higher.

(l) Actinide oxide fuel fabrication

This is not a current problem, but will need consideration when actinide recycle projects are implemented.

(m) Maintenance, refurbishing and decommissioning operations

- waste liquors from plant wash-out and decontamination operations for all previous stages.

4. SUMMARY OF POTENTIAL ALPHA CONTAMINATED SECONDARY WASTES

Section 3 attempts to identify potential sources of alpha active waste from the fuel cycle. Not all will occur: some will be eliminated by changes to the flowsheet, recycle, or by new technology. However, for the purpose of this note the secondary wastes can be grouped into three main classes.

(a) Organic wastes

- waste solvent (eg. tributyl phosphate/dodecane);
- diluent wastes (eg. dodecane);
- tissues;
- hypalon;
- PVC;

- polyethylene;
- HEPA filters;
- complexing agents used in decontamination operations.

(b) Solid wastes

- fuel hulls;
- undissolved PuO₂ rich residues;
- Pu-Pd type alloys in insoluble fission products;
- slags, eg. calcium fluoride (if uranium metal is required);
- PuO₂ or MOx waste:
 - from fuel production;
 - as sub-standard fuel or intermediaries.

(c) Liquid wastes

- MA, LA waste streams;
- solvent wash raffinates (SWR);
- off-gas scrubber liquors;
- plant washings;
- decontamination liquors.

Of these, the solvent wash raffinates will have high sodium nitrate concentrations, unless an alternative washing reagent can be developed.

5. TREATMENT OF ORGANIC WASTES

(a) Key requirements

The key requirements are:

- (i) to destroy organic materials totally in order to minimise any risk of interference with subsequent actinide recovery processes.
- (ii) to generate an aqueous waste stream from which actinide recovery is reasonably feasible; again, this needs avoidance of organic complexants; and where possible it implies a

need to avoid the introduction of large concentrations of inorganic salts, and of inorganic ions that might interfere with separations, for example carbonate, fluoride and sulphate ions.

- (iii) to avoid the generation of solid materials from which actinide recovery could be difficult.

While incineration type processes will meet the first requirement, they do not generate an aqueous product, and incinerator ash can be very difficult to process. 'Acid digestion' introduces large quantities of sulphate ions. Treatment with hydrogen peroxide avoids many of the difficulties, but may not give complete destruction of the organic components.

The process that meets the requirements most closely appears to be electrolytic oxidation in nitric acid using a catalyst.

(b) Summary of Silver (II) process

In the silver (II) process, organic materials are destroyed in an electrochemical cell. The cell is similar to those used in chlorine manufacture. It is divided into anode and cathode compartments by a membrane which allows the flow of ions which carry the current, but prevents gross mixing of the contents of the two compartments. Silver (I) is oxidised to silver (II) at the anode. Silver (II) is a very powerful oxidising agent, and reacts with water to form oxidising and reactive radical species. These species react with organic materials fed to the anode compartment, and oxidise them to carbon dioxide, some carbon monoxide, water, and inorganic acids from any hetero atoms such as nitrogen, phosphorus or sulphur present in the organic wastes. The silver (I) is reoxidised at the anode, so there is no net consumption of silver in the process.

(c) Application to organic waste arisings

The silver (II) process can destroy all the organic materials listed in 4(a), with the exception of some HEPA filters and PVC; however, these two exceptions would be decontaminated.

Some of these organic materials contain inorganic fillers. For example, hypalon can yield 30% by weight of ash after incineration: mainly alumina, silica and titania, with smaller quantities of Ca, Fe, Mg, Na and Zn. If these fillers were to dissolve, they would set further targets for the aqueous treatment process. In practice, it is more likely that they will have been incorporated into the plastics as fine ceramic grade pigments, etc. These remain as undissolved fine particles, and can be removed by cross-flow filtration.

6. TREATMENT OF SOLID WASTES

(a) Key requirements

The key requirements are to dissolve PuO₂ rich residues, and plutonium from other contaminated wastes, and to generate an aqueous stream, preferably in nitric acid.

(b) Treatment

Any plutonium contamination of the organic wastes listed in section 4(a) will have been dissolved by the silver (II) process. A similar silver (II) scheme can be applied to plutonium rich residues and scrap from mixed oxide fuel fabrication but probably with a different operating regime.

The silver (II) process can be used to decontaminate hulls. The separation of plutonium from Pu-Pd alloys or from slags is unlikely. However, the slags will be from uranium processing, where the quantities of other actinides should be small.

If the quantities of plutonium in Pu-Pd and similar alloys are significant, an alternative electrochemical process may be feasible as a separate small scale batch operation. This requirement is unlikely for thermal reactor fuel, but may need consideration for high burn-up fast reactor fuel.

7. TREATMENT OF AQUEOUS WASTES

(a) Key requirements

The key requirements are:

- (i) to separate actinides from all other ionic components, preferably in a nitric acid solution.
- (ii) to suit operation on:
 - solutions containing significant quantities of phosphate;
 - aluminium solutions containing silicon and titanium ions if these are dissolved instead of being removed by filtration;
 - the liquid wastes arising directly, as listed in 4(c); these will contain significant quantities of sodium ions; complexing agents in decontamination liquors are assumed to have been destroyed.
- (iii) if feasible, to offer options for the removal of key anions, for example pertechnetate and iodide, to support improved management of long-lived fission products.
- (iv) to avoid or minimise the generation of secondary wastes for recycle.

(b) Summary of the electrochemical ion exchange process

Of the various processes available, electrochemical ion exchange is a very promising, selective and flexible technique. The following section gives a brief description of the process.

Electrochemical ion exchange (EIX) is an advanced ion exchange process. An electrical driving force is used to enhance both the adsorption and elution reactions: the process is controlled by the direction of electric current flow.

The EIX electrode is made by coating a thick layer of ion exchange resin onto a mesh electrode using a suitable binder. The ion exchanger can be organic or inorganic, although the

latter is normally favoured for nuclear applications. An expanded mesh counter electrode is mounted close to the surface of the ion exchanger which is exposed to the waste stream.

For cation removal the EIX electrode is the cathode, and the counter electrode is the anode. Cations are absorbed from the waste solution, and replaced by hydrogen ions generated at the anode. Thus the EIX system can be used to treat very large volumes of dilute effluent in this way. Modified schemes are used for concentrated or high salt content streams.

When absorption on the ion exchanger is close to capacity, the EIX electrode is regenerated by discharging the ions into usually one column volume of liquid. This is achieved by reversing the cell polarity, when the separated cations are driven off from the ion exchanger back into solution in a selected eluant, often water. The pH of the eluant can be adjusted to prevent precipitation of metal hydroxides.

In trial systems, over 2000 absorption/elution cycles have been performed without loss in system performance.

(c) Application to liquid waste streams

EIX appears to match all the requirements listed in 7(a):

- the ion exchange units are recycled many times (several thousand) so the quantity of the main process waste is small, and it has been decontaminated before discharge;
- in principle, actinide elements might be separated as a group (U, Np, Pu, Am, Cm), or as separate streams;
- anion separation is feasible to generate key fission product streams (eg. TcO_4^- , I have already been separated in trials);
- separation can be made from main components such as high concentrations of sodium or phosphate;
- anion and cation EIX units can be operated in parallel within a single module;
- units for different separations can be operated in series.

8. CONCEPTUAL PROCESS FOR TREATMENT OF MEDIUM AND LOW LEVEL SECONDARY WASTE STREAMS

(a) Outline of conceptual process

The treatment of all secondary waste streams from the fuel cycle to recover actinides is a very complex problem. Ideally, it should be planned in parallel with a reconsideration of the reprocessing and fabrication processes in order to optimise the complete system. However, based on waste streams from current reprocessing and fabrication practice, a conceptual scheme might be developed as follows:

- organic waste pre-treatment to suit the silver (II) process;

- destruction of organic materials by the silver (II) process;
- treatment of plutonium rich residues or scrap by a silver (II) process;
- separation of any particulate fillers remaining from organic waste by cross-flow filtration;
- an optional initial actinide separation by solvent extraction from the silver (II) cell is feasible; any waste solvent remaining in the cell after separation would then be destroyed by reactivating the silver (II) process;
- any essential aqueous waste pre-treatment;
- separation of actinides by EIX.

(b) Status

Nearly all of the key steps have been performed in isolation, but they have not yet been integrated into a single process.

There are many operational uncertainties that need consideration. For example:

- will uranium be separated?

This could have a very significant effect on throughput requirements;

- will the aim be to have one common plant, or a set of smaller plants for each fuel cycle facility or waste stream?

This will affect the duty expected of any single unit both on throughput and on separation targets. However, note that both the silver (II) and the EIX processes are modular in concept. Throughput is increased by adding more cells to operate in parallel.

(c) Other points

While the main aim of this note has been to focus on actinide recycle, the process should be adaptable for the removal of key fission product species, including technetium-99 as the pertechnetate anion, and iodine-129 as the iodide anion.

If required for the pre-treatment of aqueous waste, other electrochemical processes might be introduced for the adjustment of nitric acid concentration and for the destruction of ammonium and oxalate species.

A further electrochemical scheme might be feasible to enable the recovery of actinides (mainly Pu) from the insoluble fission product metal alloy particles from the dissolver. This may merit consideration for high burn-up fast reactor fuel.

This note is based on wastes from current reprocessing and fabrication practices. If partition-

transmutation is introduced by extraction of actinides from the highly active aqueous waste stream and fabrication of fuel elements containing minor actinides, there will be many new waste streams that will need consideration. However, in principle they should be amenable to treatment by the conceptual scheme outlined in this note.

SOME IMPLICATIONS OF PARTITIONING PROCESSES FOR HIGH LEVEL WASTE

R.P. Bush, A.L. Mills and M.L. Stearn
AEA Technology, Harwell, UK

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.

* PTA - partitioning and transmutation of actinides

It has been assumed that in the co-processing stages the loss of U and Pu to the high level aqueous raffinate is U 0.005g/l^{-1} , Pu 0.001g/l^{-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 Process^{(b)(c)} (CMPO)					
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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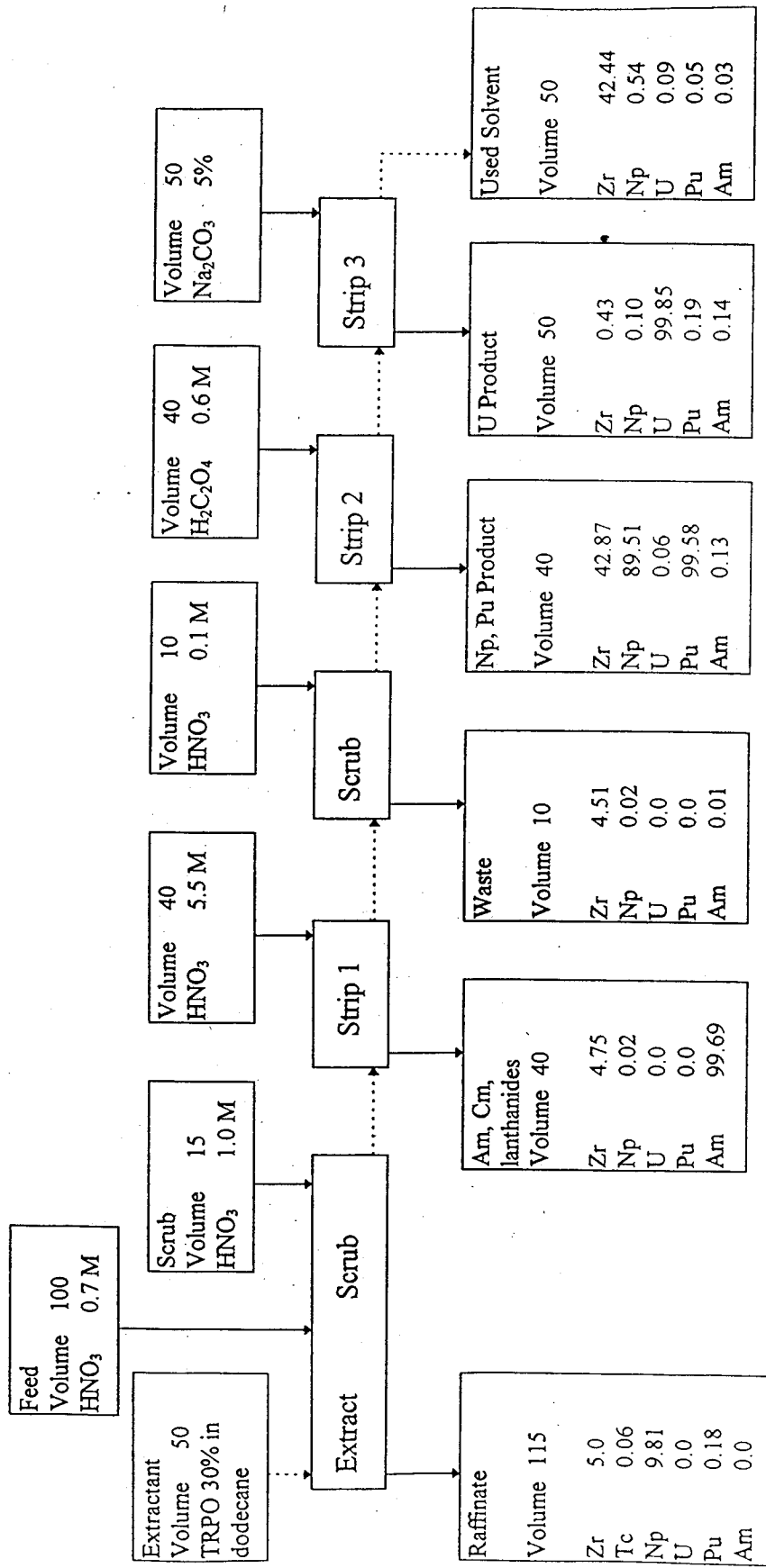


Figure 1 TRPO Process Flowsheet

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

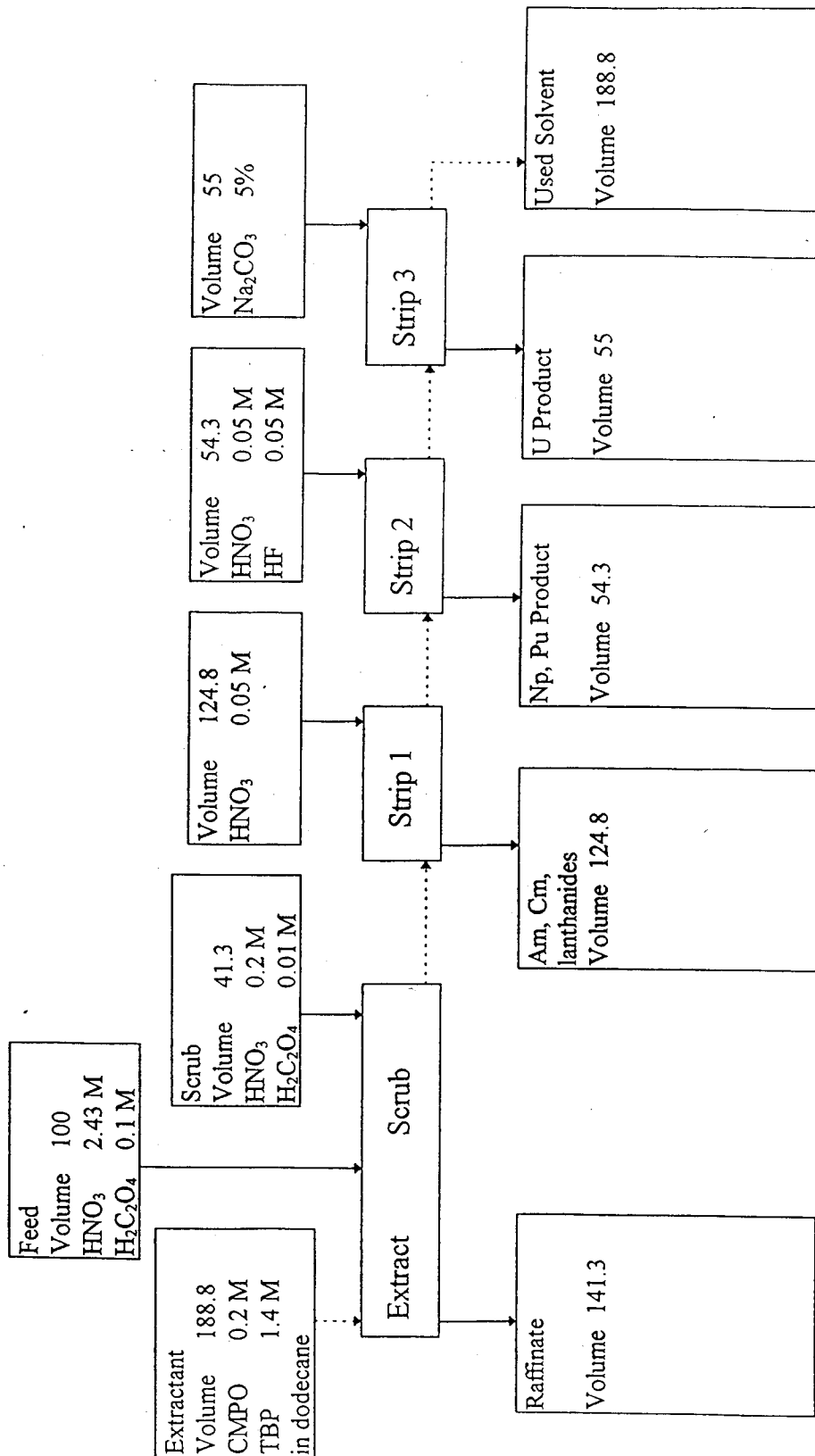


Figure 2 Truex (CMPO) Process Flowsheet

Note. Volumes are normalised to 100 units feed.

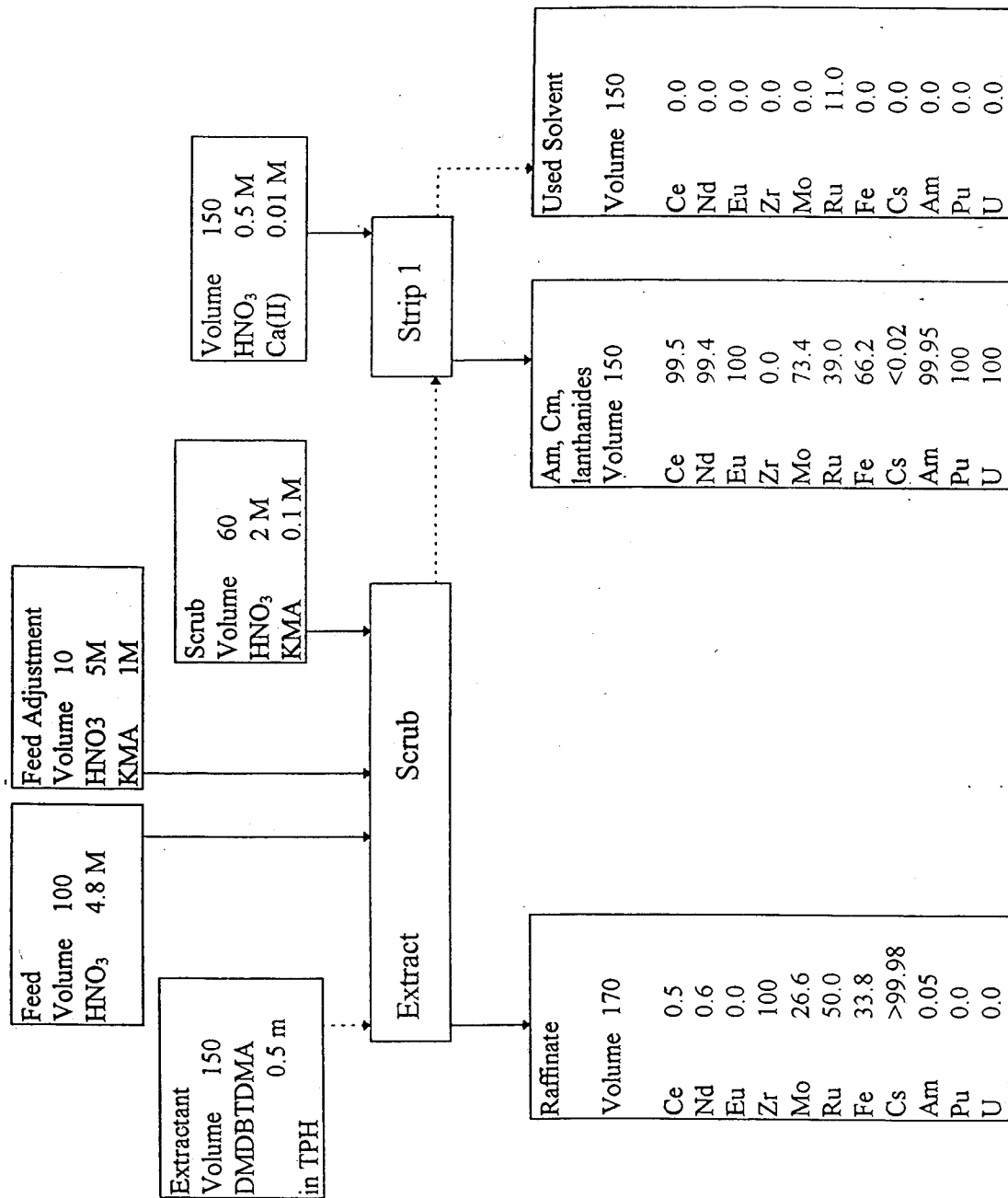


Figure 3 Diamex Process Flowsheet

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

THEORETICALLY AND EXPERIMENTALLY DERIVED CRITERIA FOR PARTITIONING AND TRANSMUTATION OF RADIONUCLIDES IN EXISTING REACTORS

J.-P. Glatz, J.-F. Babelot, G. Nicolaou, L. Koch,
European Commission, Joint Research Centre,
Institute for Transuranium Elements,
Postfach 2340, D-76125 Karlsruhe

Abstract

In international co-operation partitioning schemes have been experimentally compared and minor actinides containing targets and fuels have been developed for transmutation purposes. In order to set targets values to what extent radioactive nuclides have to be partitioned and what should be the specification of fuels and targets for the transmutation, the most likely strategies of recycling minor actinides and technetium from existing reactors have been compared to the direct disposal concept of spent PWR fuels.

For a given reduction of the radiotoxicity by a factor of hundred, the research needs and the impact on the existing fuel cycle have been evaluated:

- basic data needed to design fuels
- simulation experiments to assess the radiation behaviour
- planning and execution of radiation experiments
- assessing the additional radiation doses of the new fuels
- decontamination factors for lanthanides
- separation yields in partitioning required for the given radiotoxicity reduction

The resulting target values for partitioning and specification for targets and fuels have been achieved to a large extent by experimental data.

Scope of Partitioning

The transmutation of a radiotoxic nuclide cannot be carried to such a sufficiently high yield in a single irradiation, that the radiotoxicity is significantly (e.g. by a factor of 100) reduced. This is because the structure material of the target degrades as well during irradiation. Hence a recycling of the remaining radiotoxic nuclides becomes necessary. In case of a homogeneous, self generated recycling [1], the same partitioning process can be applied as used for the "first" separation from the waste.

Presently, there is no common agreement on the ranking of the radiotoxic nuclides, which pose a hazard, when eventually migrating out from a geophysical repository. In the following therefore the radionuclides are regarded as equally dangerous and all are partitioned and transmuted to such a degree, that the definitely discharge mass to a repository is 1 % of that discharged with the directly disposed spent fuel after having generated the same amount of energy [1]. Under this constraint, the needed decontamination factors (DF) have been calculated (table 1). They refer to the self generated minor actinides (MA) and ^{99}Tc recycling in a 1000 MWe FBR under equilibrium conditions [1].

Tab.1 Target decontamination factors for partitioning strategies

	Tc	Np	Pu	Am	Cm
TU recycle in LWR	350	110	230	530	1900
TU recycle in FR	310	64	1060	630	2300

In order to achieve for the MA, especially for Am and Cm (An) the DF values given in table 1, lanthanides (Ln) will have to be carried over to the product. The neutron poisoning in a FBR reactor is not the hinting factor for the Ln concentration but rather the fuel irradiation behaviour itself. Neither in metal alloys nor in mixed oxides, Ln's form solid solutions but segregate in separate phases, with the tendency to grow under thermal treatment. Because of their chemical nature, Am and Cm tend to concentrate in these phases leading to an unacceptable non-uniform heat distribution in the fuel matrix under irradiation. Therefore in case of a heterogeneous fuel concept, with Am + Cm concentrations of up to 20 % a Ln/An separation of about 100 would be needed, which with present extraction techniques is difficult to reach observing an overall decontamination for An as specified in table 1. The situation is more favourable in the case of the homogeneous selfgenerated concept, where the fuel composition under equilibrium conditions is: $(\text{U}_{0.8}\text{Pu}_{0.186}\text{Am}_{0.007}\text{Cm}_{0.006}\text{Np}_{0.001})\text{O}_{2-x}$ [1]. Assuming a Ln concentration of about 1 % being acceptable for the two fuel types, a Ln/An separation of 10 should be achieved with the proposed partitioning process schemes.

Irradiation Experiments

An important contribution to the experimental programmes related to the research on transmutation consists of the irradiation of candidate fuels in a reactor or a burner. These fuels are by definition new fuels, with a given fraction of one or more radionuclides to be transmuted. The properties of these fuels have first to be determined, both for the selection of the appropriate candidate fuels, and for the safety analysis to be prepared prior to any irradiation experiment.

Most of the basic data concerning the new fuels, although related to the behaviour under irradiation, can be measured out-of-pile in laboratories equipped for the handling of radionuclide materials. However the radiation creep, the swelling, the densification and the fission gas release can only be studied by irradiation experiments or through computer simulation.

The Institute of Transuranium Elements (ITU) has no nuclear reactor and therefore runs irradiation experiments in the frame of external collaborations or contracts. The METAPHIX programme, conducted in collaboration with CRIEPI (Japan) and CEA (France) concerns the irradiation in the PHENIX reactor of metallic fuel samples containing minor actinides and rare earths [2]. The irradiation of targets for transmutation of minor actinides and fission products in accordance with the heterogeneous recycling route is the subject of the EFTTRA collaboration presented in a separate paper at this meeting [3].

The ITU is also participating with KFK (Germany) and CEA (France) in the irradiation of fuels containing minor actinides in accordance with the homogeneous recycling route. Two experiments are in preparation, namely ACTINEAU planned for 1996 in the OSIRIS reactor and SUPERFACT 2. The ACTINEAU experiment will contain 1 MOX pin with 2 % Am, to be fabricated by ITU, SUPERFACT 2 is a follow-up of the SUPERFACT 1 experiment [4], and concerns the irradiation of (U,Pu)O₂ pins containing 2 % of minor actinides (Am, Np); the start of this irradiation is planned for the end of 1995 in the PHENIX reactor. ITU is in charge of the fabrication of the Am containing pins. Finally, the irradiation of Np containing fuels in the HFR Petten (TRABANT experiment, planned for 1995) and at a later stage in SUPERPHENIX, is foreseen in the CAPRA programme.

Dosimetry Aspects of MA-Containing Fuels

The inclusion of MA, and particularly americium and curium, in a fuel for subsequent transmutation, will increase the radiation dose levels of these fuels. Knowledge of these dose levels would allow measures to be conceived for the handling of such material. Radiation dose levels have been calculated at fabrication and discharge for the MA-containing fuels irradiated during the SUPERFACT 1 program. In order to assess the accuracy of these predictions, the calculated radiation doses are compared to measured ones. Verification of such predictions are essential since future industrial scale fabrication of MA fuels will be planned on computer predictions.

Under the SUPERFACT 1 program, a series of oxide fuels containing ²³⁷Np and ²⁴¹Am at low and high concentrations were prepared at ITU and irradiated in the fast reactor PHENIX [5]. The gamma dose rates of the pins were measured during fabrication using portable ionisation instrumentation. After discharge (cooling 57 months), the gamma and neutron dose rates were measured using a passive neutron-gamma interrogation unit developed for the characterisation of spent fuel inside a hot cell at ITU [6]. The isotopic evolution of the fuels during irradiation and cooling has been studied using the computer code KORIGEN [7] with the cross-sections adjusted to those for the PHENIX reactor. The neutron and gamma dose rates were calculated using the computer program PUDOL [8]. The dosimetry calculations are performed on the basis of the fuel composition, physical properties, cladding and self-shielding in the fuel and cladding. Furthermore, it allows the use of a range of shielding materials for radiation protection purposes.

The high radiation doses from the americium containing mixtures is confirmed through the measurements at fabrication [9]. The presence of 2% and 20% ^{241}Am in the fuel results in an increase of the gamma dose by 7 and 40 times respectively over the dose from a standard fast reactor fuel. However, the resulting soft gamma ray spectrum from the presence of americium can be easily shielded by 1-2 mm Pb. The use of freshly purified plutonium does not demand for further shielding, due to its soft spectrum, while the buildup of ^{208}Tl is avoided. The dose rates of these fuels were calculated, for comparison purposes, on the basis of the isotopic composition obtained by chemical analyses. The level of agreement is within 30%, which is an acceptable accuracy for radiation protection purposes.

At discharge, the gamma and neutron dose rates were calculated on the basis of the fuel isotopic composition predicted by KORIGEN [10]. Although a considerable amount of curium is produced during the irradiation, the gamma dose dominates the total dose from the fuel. If the gamma dose due to soft part of the gamma spectrum is excluded, then the gamma dose is determined by the final burn-up achieved by the fuel during irradiation, i.e. by the content in fission products with an effective gamma energy of 0.7 MeV. From the gamma dose point of view, the problems encountered during unloading would not differ much from those with a present day commercial fuel of the same burn-up. The neutron dose at 1 m however, is up to 20 times higher, for the fuels with ^{241}Am at charge, than a standard fuel. A shielding of 100 mm Pb and 200 mm polyethylene would be required for the handling at 1 m of a single such pin during unloading. The necessity for remote handling, particularly in the case of assemblies, is evident. The gamma dose dominates further the total dose from the fuels with cooling time due to the decay of ^{242}Cm and ^{244}Cm .

In order to verify the predictions on spent fuel, the measured and calculated dose rates of the MA fuels after irradiation and 57 months cooling were compared. The dose rates were calculated on the basis of the isotopic composition predicted by KORIGEN. An agreement within 50% is observed between the measured and calculated values. The discrepancy can be attributed to different sources: the reproducibility of the experimental set-up in the calculations; the fuel compositions predicted obtained from KORIGEN predictions. The reliability of KORIGEN, for the source term nuclides, has been checked through the comparison of its predictions with chemical analyses [10]. The agreement is within 25% for the actinides and 50% for the fission products. This agreement, although sufficient for dose rate calculations indicates limitations in its basic nuclear data libraries. The latter should be considered when neutron physics calculations are performed.

The high radiation dose levels encountered during the fabrication of MA fuel requires the construction of a special hot cell laboratory for the handling of large amounts of these elements.

Partitioning

The feasibility of transmutation strongly depends on an effective partitioning process. Apart from a few studies on pyrochemical reprocessing [11,12], liquid-liquid extraction processes are mainly considered to fulfil this task. At ITU a study has been carried out to compare the partitioning capabilities of three organic molecules, e.g. trialkyl (C6-C8) phosphine oxide (TRPO), n-octyl(phenyl)-N,N-diisobutyl carbamoylmethylphosphine oxide (CMPO) and diisodecyl phosphoric acid (DIDPA). Similar process schemes were applied and tested out for the three different extractants [13].

Genuine HLW from LWR reactor fuel (ca. 30,000 Mwd/t U) was treated in a continuous countercurrent mode by means of centrifugal extractors, installed in a hot cell facility. The decontamination factors obtained for the most relevant isotopes are given in table 2.

Tab. 2 Decontamination factors(DF) determined for the different extractants

isotope	Concentration in the feed (g/l)	DF TRPO	DF CMPO	DF DIDPA
⁹⁹ Tc	0.14	> 1760	> 180	-
¹⁴⁴ Nd	0.47	> 22000	> 30000	> 4000
²³⁷ Np	0.05	12.4 (> 4100*)	> 30000	>5
²³⁸ U	0.86	> 5400	> 100000	>20000
²³⁹ Pu	0.02	> 760	> 4000	> 150
²⁴³ Am	0.06	> 900	> 15000	> 10000
²⁴⁴ Cm	0.007	> 600	> 1500	> 1500

* HNO₃ concentration in the feed increased from 0.7 to 1.35 M

Except for Tc, CMPO gives the highest decontamination factors. The rather low values for Cm are estimated lower limits, due to a low initial concentration of this element in the feed. The analytical detection limit and the back-ground in the hot cell facility are the limiting factors for the DF value calculated for Cm. With higher concentrations in the feed, to be expected for the above mentioned reference case of a self generated MA and ⁹⁹Tc recycle in a 1000 MWe FBR under equilibrium conditions [1], higher DF values would certainly be observed as in the case of Nd for the 3 extractants. It is known, that Ln and An have a very similar behaviour in these 3 extraction processes. The low values determined for Np in the DIDPA and the TRPO (at low HNO₃ concentration) is due to the slow kinetics of the NpO₂⁺ reduction to the oxidation state IV required for the extraction of this element.

However with a view to the fabrication of new targets not only a good extraction with high decontamination factors is necessary but also a high recovery rate from extraction process with small overall losses is of great importance in any P&T strategy. For the present comparative study, the distribution of the actinides on the process streams is given in table 3

Tab. 3 Relative distribution (in %) for the main actinide isotopes

process	process stream	²³⁷ Np	²³⁸ U	²³⁹ Pu	²⁴³ Am
TRPO		9.81(0.0*)	0.0	0.2	0.0
CMPO	raffinate	0.0	0.0	0.0	0.0
DIDPA		15.8	0.0	0.5	0.0
TRPO		0.0	0.0	0.0	99.7
CMPO	stripping 1	7.7	0.1	12.3	7.2
DIDPA		0.0	0.0	0.3	97.9
TRPO		89.5	0.1	99.6	0.1
CMPO	stripping 2	2.2	0.4	3.5	6.7
DIDPA		72.6	0.7	91.1	2.1
TRPO		0.1	99.9	0.2	0.1
CMPO	stripping 3	2.6	98.8	1.3	4.9
DIDPA		-	-	-	-
TRPO		0.5(0.1*)	0.1	0.1	0.0
CMPO	used organic	0.1	0.6	0.0	0.3
DIDPA		11.6	99.3	8.1	0.0

* HNO₃ concentration in the feed increased from 0.7 to 1.35 M

These results show, that for the chosen operation conditions TRPO has the best back-extraction properties. Although for CMPO the organic phase is almost actinide free after stripping, only low amounts of Pu and Am are recovered in the respective stripping solutions, due to an accumulation of these elements in the corresponding extractor stages.

As mentioned above the organic molecules commonly used for partitioning of actinides generally have almost identical extraction properties for An and Ln; thus the An/Ln separation is one of the most challenging tasks in any partitioning and transmutation project. The high neutron capture cross sections of Ln but mainly their tendency to form separate phases upon re-fabrication are the reasons for the absolute necessity for the Ln/An separation.

In extraction processes schemes three main routes can be envisaged to achieve the required separation factors mentioned above.

- use of an additional chromatographic process
- use of an additional extractant with the known capability of separating Ln from An by means of complexing agents
- use of complexing agents in an existing process without changing the primary extractant.

Separation of Ln and An by high performance liquid chromatography (HPLC) on ion exchange columns using α -hydroxy isobutyric acid in a pH gradient for elution gives a complete Ln/An separation. The feasibility to separate gram amounts of those elements under real conditions was demonstrated at ITU [14]. The drawback of this technique is the batch operation mode as a follow-up of the extraction process, generally conducted continuously either in a mixer settler, column or centrifugal extractor equipment.

A classical example for the use of a second extractant would be the TALSPEAK [15] process where Ln are extracted by di(2-ethylhexyl)phosphoric acid (HDEHP) after complexation of Am and Cm by diethylenetriaminepentaacetic acid (DTPA). An alternative could be the reversed TALSPEAK [16] process with a selective stripping of Am and Cm by DTPA after extraction with HDEHP. Ln/An separation factors around 10 could be achieved in a single extraction stage. A continuous experiment carried out at CEA (CEN Fontenay aux Roses, France) on real HLW using 6 extraction stages and 4 back-extraction stages in a mixer settler device, gave an Am/Cm product containing less than 1 % of Ln; separation factors of 150 for Eu and more than 1000 for Ce were attained [17].

Finally the use of complexing agents in an additional back-extraction step included in an established process would possibly offer the most appropriate solution. Because DIDPA has a chemical structure very similar to HDEHP the process based on this extractant seems to be the most suitable to fulfil this purpose. First test with DTPA gave very promising results [18]. A single stage extraction gave a separation factor of 10 between Am and Nd. It could be calculated, that this value will considerably improve in a continuous multistage process. In this case 99.99 % of Am and Cm would be recovered with a total Ln contamination of about 10 %. Similar results were obtained with diamides and SCN⁻ as a complexing agent [19]. In a single extraction step an Am/Eu separation of 9 was obtained.

Tests are presently running at ITU to evaluate the possibility to include a similar stripping step in the TRPO process, which revealed the most promising results in the back-extraction part.

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THE ROLE OF SYNROC IN HLW MANAGEMENT SYSTEMS
BASED ON PARTITIONING/TRANSMUTATION STRATEGIES

A. JOSTSONS, E.R. VANCE and D.J. MERCER
Advanced Materials Program, ANSTO, Private Mail Bag 1, Menai, N.S.W., 2234, Australia

ABSTRACT

The total destruction of long-lived fission products and alpha emitters in HLW is unlikely to be practicable on an industrial scale. The use of Synroc for conditioning of the major heat emitters and Cm²⁴⁴ is examined in the context of UOX and UOX plus MOX reprocessing. Synroc can immobilise in 100 kg the above wastes from reprocessing of 1 tonne of 5 year old PWR fuel. Together, with borosilicate glass, after partitioning and recycle of Np and Am, the total conditioned waste could be reduced to about 150 kg/tHM versus current achievements of 300 kg/tHM.

1. INTRODUCTION

The goal of partitioning and transmutation (P/T) strategies is the reduction of waste radiotoxicity through separation of various waste components followed by incineration in reactors and/or accelerators. The current focus of these strategies is the reduction of the amount of long-lived fission products and alpha emitters in the wastes from spent fuel reprocessing. Total destruction of these long-lived radionuclides is not feasible. Hence, geological disposal of wastes will be required even though current studies⁽¹⁾ have demonstrated the possibility for significant reductions in the potential radiotoxicity of wastes through improved recovery and recycle of Pu and through separation and transmutation in reactors of minor actinides such as Np and Am.

Curium²⁴⁴ with a half life of 18 years does not influence the long term radiotoxicity except through its daughters. However, Cm²⁴⁴ complicates fuel fabrication⁽²⁾ because it is a neutron emitter and hence it is unlikely to be recycled. As noted by Baestle⁽²⁾, an efficient rare earth/Am/Cm separation must be available before Am can be incorporated in fuel pins for transmutation in reactors.

The radionuclides to be taken into account for residual toxicity⁽¹⁾ are those with the greatest solubility and mobility in the disposal medium, i.e. I¹²⁹, Tc⁹⁹, Cs¹³⁵ and Se⁷⁹.

More than 90% of thermal energy in HLW 30 years after reprocessing is due to Cs¹³⁷ and Sr⁹⁰. The separation of Cs¹³⁷ and Sr⁹⁰ followed by conditioning in stable matrices (e.g., borosilicate glass or Synroc) and storage for about 150 years has been advocated by Northrup et al.⁽³⁾ as means to reduce the size of geological repositories for HLW disposal. Lefevre et al.⁽¹⁾ have extended this concept by proposing that Cm²⁴⁴ as well as Cs¹³⁷ and Sr⁹⁰ could be conditioned in a crystalline matrix such as Synroc, to enable safe storage for some centuries until the essential completion of radioactive decay of the heat-generating radionuclides prior to disposal. The concept can be extended further to include some of the long-lived fission products such as Tc⁹⁹ and Se⁷⁹, in the crystalline matrix, if they are separated from other wastes. This would represent an intermediate strategy in which transmutation would be employed on Np and Am to reduce the impact on residual radioactivity of wastes from advanced reprocessing, with the separated waste streams directed to Synroc and to borosilicate glass.

2. SYNROC

Synroc-C, a formulation developed for the immobilisation of HLW from the reprocessing of commercial LWR spent fuel, consists mainly of zirconolite, CaZrTi₂O₇, barium hollandite Ba(Al,Ti)₂Ti₆O₁₆, perovskite CaTiO₃ and excess titanium oxides. A combination of the first three phases has the capacity to accept, in solid solution, most of the elements present in HLW. Under the redox conditions chosen for Synroc fabrication, a number of waste elements such as Ru, Rh, Pd, and Tc, are reduced to the metallic state and form alloys that are microencapsulated within the titanate phases. Hollandite is the host for Cs, Ba, and Rb, perovskite is the major host for Sr, and zirconolite and perovskite are the hosts for rare earths and actinides. The partitioning of radwaste species between the various phases in Synroc has been described^(4,5) extensively.

The use of the Ti₂O₃-TiO₂ buffering system provided by the reaction between excess TiO₂ of the formulation and titanium metal powder added (at the 2 wt% level) to calcined Synroc powder before hot-pressing is an important aspect of Synroc chemistry. An excess of reduced rutile provides Synroc with the capability to maintain the desired phase assemblage (by changes in the abundance of the phases) even if unexpected fluctuations in the HLW stream composition occur. This process flexibility is evidenced by the ability to use the same Synroc precursor composition for waste loadings in the range 0-30% without deleterious effects on the chemical durability.

The Synroc microstructure, Fig. 1, is fine grained ($\leq 1\mu\text{m}$), with the metallic particles of about 10 nm in size encapsulated by the titanate phases. It is best fabricated by sub-solidus hot-pressing at 24 MPa and 1170°C.

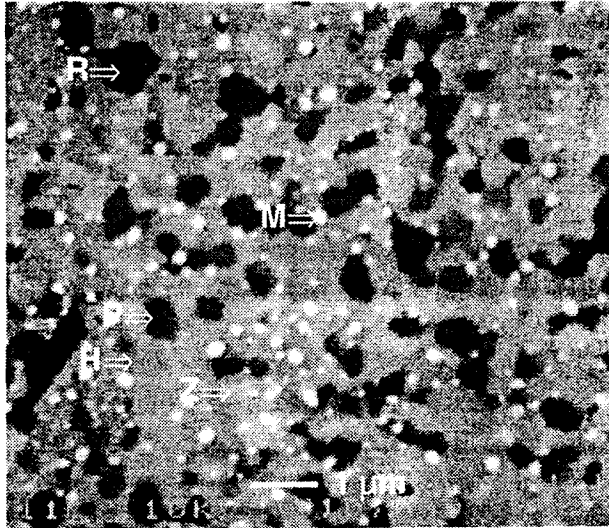


Fig. 1 Microstructure of Synroc-C showing a multiphase ceramic with grain size less than 1µm. The small bright areas show the reduced metallic components microencapsulated within the titanate matrix.

The key physical properties of Synroc are listed in Table 1. The higher density and thermal conductivity compared with borosilicate glass wastefoms permits higher waste loadings per unit volume, particularly in cases where the heat-generating solidified waste is intended to be stored for extended periods in engineered facilities prior to geological disposal. Allowable heat loadings are further enhanced by the relatively high melting point.

Table 1. Physical Properties of Synroc

Density	4.48 g/cm ³
Young's Modulus (25°C)	200 MPa
Thermal Conductivity (0-500°C)	2.5 W/m K
Thermal Expansion (75-1000°C)	10x10 ⁻⁶ K ⁻¹
Melting Point (incongruent)	~1350°C
Fracture Toughness	2MPa.m ^{-1/2}
Poisson's Ratio	0.3
Compressive Strength	700-800 MPa

The data base on the aqueous chemical durability is extensive^(4,6). Protection is afforded by hydrated films of TiO₂ which form on Synroc and the leach rate decreases rapidly with time even with frequent replacement of leachant. At long dissolution times, the normalised leach rate of Cs at 70°C is less than 1x10⁻⁴g/m².d and for the actinide elements is less than 1x10⁻⁵g/m².d. Matzke⁽⁷⁾ has shown that the dissolution rate of Synroc at 150°C is less than 0.15 nm per day. Consequently, Synroc can be considered to be an important barrier to the return of radioactive waste elements to the biosphere.

The key parameters for Synroc processing are effectively dictated by the need for a dense fine grained product, i.e. $\geq 98\%$ of theoretical density, and control of redox potential at all key stages of the process to eliminate the possible losses of volatile species whilst maintaining chemical control to ensure appropriate partitioning of radwaste species into targeted phases. The redox potential is controlled during calcination of the Synroc precursor and HLW solutions at 700°C by a counter-current flow of 3.5% H_2/N_2 reducing gas that prevents the formation and subsequent loss of volatile species such as Cs, Tc and Ru. The calcine is blended with $2 \text{ wt}\%$ titanium powder to control the redox potential during hot-pressing in stainless steel bellows containers, normally containing 35 kg of Synroc. The use of the innovative bellows containers, that are eventually stacked in standard waste canisters for storage, transport and disposal, avoids unnecessary generation of process wastes. The technology for handling and processing of Synroc in bellows of 300 and 400 mm diameter has been demonstrated. A standard glass canister is capable of accepting $400\text{-}440 \text{ kg}$ of Synroc.

The bellows containers also facilitate heat transfer from Synroc to the waste canister. The metallic top and bottom plates provide a short heat conduction path to the canister and hence high waste loadings are possible for wastes to be stored for extended periods in engineered facilities prior to disposal. Direct methods of quality control are possible through sampling of Synroc in the bellows on a statistical basis.

The principal source of radiation damage in Synroc is expected to arise from α -decay from the incorporated actinides. Studies of natural zirconolite show that it becomes fully amorphous after experiencing about 10^{19} α -decays per gram^(4,8) from the decay of uranium and thorium impurities. Despite the crystalline to amorphous transition, there is no evidence of geochemical alteration under conditions expected in geological repositories. The nature of damage in natural zirconolite is consistent with the results of accelerated damage tests on synthetic zirconolite. The most realistic damage acceleration is achieved by incorporation into Synroc of short-lived, α -emitting actinides, e.g. Pu^{238} or Cm^{244} , with half-lives of 87.8 and 18.1 years respectively. In this way damage corresponding to 10^5 yr in a geological repository can be accumulated in about 2 years but dose rate effects must be considered as defect annealing during irradiation is not simulated adequately.

The most extensive measurements of α -decay damage in Synroc-C have been performed by Marples and colleagues^(9,10) in a collaborative study between AEA, Harwell and ANSTO. Their studies were based on Synroc-C incorporating up to $10.4 \text{ wt}\%$ Pu^{238} or $4 \text{ wt}\%$ Cm^{244} . The macroscopic swelling of Synroc containing $4 \text{ wt}\%$ Cm^{244} as a function of dose⁽¹⁹⁾ is shown in Fig. 2. The swelling saturates at about $4 \text{ vol}\%$ which is less than the value of about $6 \text{ vol}\%$ observed^(9,10) in $5 \text{ wt}\%$ Pu^{238} doped Synrocs where the ambient temperature during specimen storage may have been lower. A 30% reduction in the rate of swelling with α -decay dose in $0.97 \text{ wt}\%$ Cm^{244} doped Synroc-C has been observed by Muraoka et al.⁽¹¹⁾ at 200°C compared to ambient temperatures. Clinard et al.⁽¹²⁾ found that the rate of swelling decreased by 60% at 300°C compared to 70°C and that at 600°C the zirconolite remained crystalline at high α -decay doses and the swelling was limited to $0.4 \text{ vol}\%$. The α -decay dose has no significant effect on the leach rate of Cm^{244} from Synroc.

3. WASTE CHARACTERISTICS

Fission products and minor actinides constitute about 35 kg in a ton of uranium oxide fuel enriched at 3.5% in U^{235} , irradiated to a burn-up of $33,000 \text{ MWd/t}$ in a PWR. The decay heat and quantities of selected fission products and Cm^{244} per ton of fuel irradiated and reprocessed 5 years after discharge from a reactor are shown in Table 2 (references 4 and 5). This Table shows the increasing importance of Cm^{244} in MOX fuels irradiated in thermal reactors and the resultant need for co-reprocessing of UOX and MOX fuels in a ratio of 4 to 1 in current reprocessing plants⁽⁶⁾. The quantity of Cm in MOX fuel glass, even with the above dilution, exceeds the specifications by a factor of two⁽⁶⁾.

4. PARTITIONED WASTE LOADING IN SYNROC-C

The waste loading in Synroc-C is determined either by the heat output of radionuclides or by chemical solubility limits. Table 2 suggests that decay heat will determine the waste loading if 5 yr old fuel is reprocessed and wastes are to be conditioned immediately thereafter. For Synroc bellows of internal diameter 0.35m the maximum heat loading just after conditioning is about 2000 watts per 100 kg Synroc⁽¹⁶⁾. This corresponds⁽¹⁶⁾ to a centre line temperature of about 650°C and a radial temperature gradient of about 120°C across the Synroc bellows in an air cooled store.

The fission products and Cm shown in Table 2 do not exceed solubility limits in the desired phases of Synroc-C for UOX and 4/5 UOX+1/5 MOX fuels considered. Storage of HLW from MOX fuel for 10 years before conditioning would enable 100 kg of Synroc to contain all of the nuclides listed in Table 2.

The rare earth oxides are included in the stream to Synroc on the assumption that Am can be selectively extracted from the RE/Am/Cm stream and that there are no benefits in additional partitioning of Cm from the RE's.

Table 2 Heat output and quantities of selected fission products and Cm²⁴⁴ per tonne of fuel from partitioning at a burn-up of 33000 MWd/t, reprocessed 5 years after discharge from a reactor as a function of cooling time.

	Watts/tHM					
	g/tHM	5yr	10yr	30yr	100yr	300yr
Cs ₂ O	2,700	980	540	250	51	0.5
SrO	900	480	425	238	42	0.4
Tc oxide	800	-	-	-	-	-
RE's oxides	10,000	200	50	8	-	-
Cm ²⁴⁴ -UOX	30	73	62	30	2	0.1
Cm ²⁴⁴ -MOX	550	1,350	1,136	550	38	2.0
Σ Decay Heat-UOX		1,733	1,077	526	95	1.0
Σ Decay Heat-MOX		3,010	2,151	1,046	131	3.0
Σ Decay Heat-4/5-UOX+1/5 MOX		1,990	1,295	630	102	1.5

Technecium-99 is distributed amongst various streams from conventional reprocessing. The entire amount is shown for incorporation in Synroc because it will reside in the metallic alloy phases and hence would not be readily mobilised in a repository environment. Metallic technecium is not very soluble in groundwaters and furthermore, the metallic phase in Synroc is protected by more resistate ceramic phases. The other advantage of routing Tc⁹⁹ to Synroc is to prevent loss of Tc by volatilisation that occurs in the oxidising environment of vitrification. Similarly, Ru and Se, if partitioned could be directed to Synroc as both would reside in the metallic phase.

These considerations show that 100 kg of Synroc can be used to condition the major heat generating radionuclides from reprocessing of 1 ton of 5 year old fuel from a PWR. In essence, half of the wastes from reprocessing have been directed to Synroc in the above strategy. In the absence of a heat load and Cm^{244} , the remaining radionuclides from the reprocessing of 1t of fuel could be conditioned in say 50 kg of borosilicate glass (i.e. a 1/6 of current glass waste produced per 1 ton of reprocessed PWR fuel).

The α -decay dose to Synroc containing 0.134 wt% Cm^{244} , as a function of time is shown in Table 3 for the case of MOX reprocessing in dilution with UOX on a 1/5 MOX plus 4/5 UOX basis.

Table 3 α -decay damage dose (α -decay events/g) in Synroc containing 0.134 wt% Cm^{244} as a function of storage time (year).

10 yrs	30 yrs	60 yrs	100 yrs	300 yrs
1.06×10^{18}	2.26×10^{18}	2.97×10^{18}	3.23×10^{18}	3.30×10^{18}

The effects of α -decay damage can be minimised by maintaining Synroc at or above 500°C for the first 60 years in the air cooled store. This could be achieved by a transition from forced air cooling in the first 30 yrs to convection cooling. If the α -decay damage is fully annealed out for the first 60 years, then only 3×10^{17} α -decays/g would be experienced to 300 years. Fig. 2 shows that such a low α -decay dose, even at temperatures near ambient, would result in less than 0.5 vol% swelling of Synroc.

Cm^{244} decays to Pu^{240} which is also an α emitter, with a half life of about 6500 years. The α -decay dose from Pu^{240} decay will result in swelling, after disposal, of about 4 vol% but the dose will be much below that attained in accelerated damage tests shown in Fig. 2. Similar considerations apply to the other daughters.

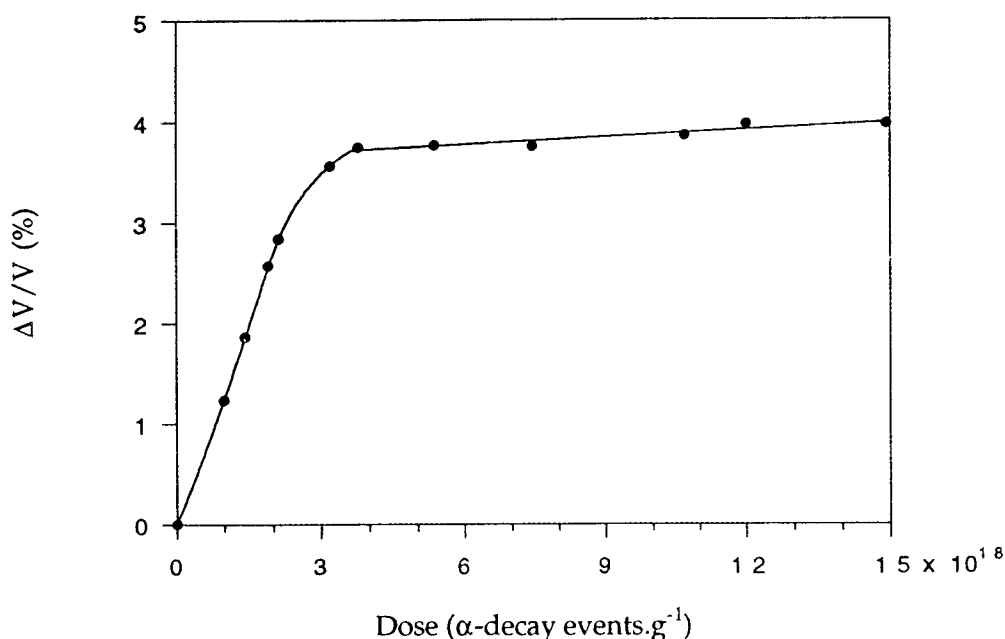


Fig. 2 Swelling of Synroc containing 4 wt% Cm^{244} as a function of damage dose. (From Hough and Marples⁽¹⁰⁾).

5. DISCUSSION

Partitioning permits the use of Synroc for conditioning of the main heat generating radionuclides present in liquid HLW from reprocessing in parallel with the established borosilicate wastefrom for the remaining HLW elements. Since the waste loading in Synroc is limited by decay heat, it is convenient to simplify the partitioning by routing Cm and the RE's to Synroc. Additionally, Tc⁹⁹ and Se⁷⁹ can be incorporated in Synroc to provide a more stable matrix and to avoid complications from volatilisation of Tc⁹⁹ in the oxidising atmosphere of vitrification.

There is a simple elegance in using partitioned Cs and Sr with Cm²⁴⁴ to minimise the effects of α -decay processes on the wastefrom durability. The radiogenic heat ensures that most of the α -decay damage for Cm²⁴⁴ is self-annealed.

The parallel use of Synroc and borosilicate glass for conditioning of HLW results in a significant saving in the weight of total conditioned HLW. For 1 ton of original PWR fuel the total weight of conditioned HLW is expected to be about 150 kg, even when MOX is co-reprocessed with UOX.

The evolution of decay heat in Synroc, Table 2, suggests that it could be disposed in a deep geological repository after about 100 year storage without much effect on repository heat loadings. The glass waste could be sent to a geological repository immediately after conditioning. The strategy outlined in this study will provide savings from both intermediate storage and repository viewpoints.

The strategy outlined in this paper is simplistic by necessity because there are many uncertainties surrounding the feasibility of partitioning on an industrial scale with attendant uncertainties of the likely cross-contamination of the various streams from partitioning. Similarly, we have not addressed reprocessing of high burnup fuel, multiple recycle processes and effects of the use of fast breeder reactors. Nevertheless, the results are encouraging and the use of more than one waste form should continue to be examined in future evaluations of the P/T strategies.

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