SESSION 4

Chairman: Dr. L.H. BAETSLÉ (Belgium)

MOLTEN SALT ELECTROREFINING TO SEPARATE TRANSURANIUM ELEMENTS FROM RARE EARTH ELEMENTS

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ABSTRACT

CRIEPI has proposed a pyrometallurgical process to separate actinides from high level radioactive waste (HLW) and solvent scrubbing waste. In the concept, HLW is converted to chlorides, and the molten chlorides are reduced into liquid cadmium and/or bismuth by the addition of lithium metal as reductant. Then, the actinides are purified by electrorefining. Since rare earth elements (RE), which are chemically similar to actinides, are existing an order of magnitude more than actinides in the HLW, a key issue in the pyrometallurgical process is the efficient separation of the actinides from RE.

This study shows the separation between actinides and RE by the electrorefining with two stages. The first stage was carried out to transport actinides to the molten salt electrolyte and the Ta cathode from Cd anode. After removing the actinides was removed from Cd, the anode was changed to Li_2Sb for the following electrorefining, in which actinides were reduced on the Ta cathode from molten salt. The chemical composition in the system was adjusted according to the ratio of actinides to RE (Y, La, Ce, Nd and Gd) with HLW, except U and Pr. In the result, U and Np were easy to separate from RE, and Pu and Am showed small separation factor from RE, because the concentration of Pu in molten salt and Cd is quite low (log $X_{Pu} < -4$) and the redox potential was similar to RE. The current efficiency in this experiment was less than 30 %, since the deposition of actinides, especially U, dropped from the cathode. In the second stage, as the concentration of actinides in the salt, the separation of actinides from RE became more difficult. The final ratio of actinides to RE on the cathode was more than unity through this experiment.

INTRODUCTION

Central Research Institute of Electric Power Industry (CRIEPI) in Japan has proposed a concept to separate actinides from HLW by a pyrometallurgical process and then to transmute them to short-lived nuclides in a metallic fuel FBR [1]. The pyrometallurgical process has been predicted to reduce the total amount of radioactive waste and has been suggested to favor compact facilities as compared with the aqueous processes such as solvent extraction, ion exchange etc., in spite of a relatively low purity of actinides elements in a final product. The pyrometallurgical partitioning process of HLW from PUREX process is shown in Fig. 1. The pyrometallurgical process consists of (1) denitration to form oxides, (2) chlorination of oxides to form chlorides, (3) reductive extraction of actinides from molten chlorides into liquid cadmium (Cd) or bismuth [2-6] and (4) electrorefining of actinides from fission product [7,8].

Since the amount of rare earth elements (RE) are in order of magnitude more than that of actinides in HLW, a key issue in the pyrometallurgical process is the efficient separation of actinides (U, Np, Pu, Am and Cm) from RE. In this study, separation of actinides from RE was carried out by the electrorefining in following two stages. In the first stage was transported actinides from Cd anode to the Ta cathode through the molten salt electrolyte. In the second stage, the anode was replaced by Li_2Sb, and actinides in the molten salt were reduced on the Ta cathode.

EXPERIMENT

The electrorefining apparatus was equipped in the furnace well of glove box where circulating argon gas was purified by DRYTRAIN and NITRAIN. During the experiments, oxygen and water content were both maintained at < 1ppm and nitrogen content was at < 500ppm. The electrorefining cell is shown in Fig. 2. The cell which contained molten salt and liquid Cd was made of Ta tube with a half inch size in an outside diameter. A Ta wire of 1 mm diameter was used as a cathode in the cell. As shown in Fig. 2 (A) and (B), actinides-Cd alloy was used as an anode for the electrorefining of first stage and the anode was replaced by Li_2Sb for the second stage. All experiment was controlled by galvanometry in the range of 2 mA to 5 mA in the first stage and 2 mA to 3 mA in the second stage.

The initial amount of the elements in liquid Cd and molten salt were determined as Table 1. According to the ratio of actinides (U, Np, Pu and Am) to RE (Y, La, Ce, Nd and Gd) in HLW, excepting U, Cd alloy was prepared by mixing Cd with U-Cd, Np-Cd, Pu-Cd and Am-Cd alloy at about 773 K. The resulting concentration of each element in the alloy was determined by Inductively Coupled Plasma atomic emission spectrometry(ICP). The salt was prepared by mixing the weighted amount of LiCl-KCl eutectic salt with YCl_3, $LaCl_3$, $CeCl_3$, $NdCl_3$ and $GdCl_3$ according Table 1. The alloy and the salt were put into Ta tube and then, heated to 723 K.

Ta wire with 1 mm ϕ was immersed in the molten salt and was connected to the cathode. A liquid Cd alloy was then connected to the anode through Ta tube. The cathode of the first stage was covered on the alumina tube of a quarter inch in an outside diameter with a small window and a small amount of Cd was placed in the tube, in order to catch the dropped deposits. The molten salt and liquid Cd were stirred by Ta stirrer. After passing about 10 to 20 coulomb, the cathode deposit and /or a trace amount of Cd alloy and salt were taken

out for the analysis by ICP, and then the new cathode was inserted. The amount of metal deposit were derived by subtracting the amount of salt entrained in the deposit. The amount of entrained salt was estimated from the concentration of potassium in the deposits.

After removing actinides from Cd alloy, Cd was taken out from the cell and then, the anode was changed to Li_2Sb in order to remove actinides from the salt, as shown in Fig. 2 (B). After passing about 20 to 50 coulomb, the cathode deposit and the salt were analyzed.

RESULTS AND DISCUSSION

Figure 3 shows the concentration change in the salt with the total charge passed. It was observed that the U concentration decreased faster than Np with passing charge. While, the final deposit was consisted of ca.42 % - U, ca. 42% - Np, 0.7% - Pu, 1% - Am and 15% - RE. The total charge needed for removal of all actinides from Cd alloy three times as much as the calculated value of 77 coulomb. This was due to the drop of actinides deposited from Ta, because the content of U and Np in a catch Cd and a catch tube were higher concentrated than the other part. These results suggest that some portion of U deposits dropped into the salt. On the other hand, the concentration of Am in the salt was increased with increasing charge passed, and suggesting that Am was hard to deposit on the cathode. The content of RE in the salt didn't change with passing charge, which means to no deposition on the cathode at this electrolysis condition.

Figure 4 shows that the relationship between the current efficiencies and the total passed charge. The current efficiencies of cathode and anode were defined as the equations of (1) and (2),respectively.

$$\text{The cathode current efficiency} = \frac{\Sigma \text{ amount of deposit observed}}{\Sigma \text{ amount of deposit calculated from the coulomb passed}} \quad (1)$$

$$\text{The anode current efficiency} = \frac{\Sigma \text{ amount of elements removed from Cd phase}}{\Sigma \text{ amount of removed elements calculated from the coulomb passed}} \quad (2)$$

This figure indicates that the current efficiencies of the cathode and anode were ca. 20% and ca. 30%, respectively. If the dropped deposits were recovered by a catch tube, the anode current efficiency was still far less than 100%. Hence, most of the dropped deposit was returned to Cd anode through a window in a catch tube as a form metal fog [9]. The existence of the floating particles like metal fog was supported by salt entrained in the cathode deposit showed gray color with small black particles.

Figure 5 shows that the relationship between the separation ratio of actinides from RE at an use of Cd anode and total charge. This separation ratio was defined as the equation of (3).

$$\text{Separation ratio} = \frac{\dfrac{\Sigma \text{ amount of M deposit}}{\Sigma \text{ amount of RE depsoit}}}{\dfrac{\text{amount of M before the electrolysis}}{\text{amount of RE before the electrolysis}}} \quad (3)$$

(M : U, Np, Pu or Am)

The amount of M and RE were shown in Table 1. Figure 5 shows the separation ratios as ca. 20 for U, ca. 40 for Np, ca. 8 for Pu, ca. 1 for Am. Assuming that thermodynamic equilibrium are established, the separation ratio of actinides from RE can be derived from the standard redox potential in molten salt [7], The derived values of separation ratio of U was larger than that of Np, although the measured value of U was smaller than that of Np. This difference could be attributed to drop of U from the deposit as mentioned above. Figure 5 shows that the tendency of separation ratio among actinides was in order of Np > U > Pu > Am, which agreed with the prediction from the standard redox potential [7], except U. In this stage, only small amount of Pu and Am were deposited on the cathode, resulting in the small separation ratio of Pu and Am. It means that Am were still remained in the salt after most of actinides were removed from Cd anode in this stage. The averaged separation ratio of actinides kept ca. 20 during the electrolysis using Cd anode. This value was dominantly affected by U and Np, because the deposits consisted mainly of U and Np in the first stage.

Figure 6 shows the concentration of each element in the salt with passing charge at the use of Li_2Sb anode. It was seen in this figure that the concentration of all elements decreased with charge. In contrast at the case of Fig.3 with use of Cd anode, we observed the decrease of Am content, which indicated the deposition of Am on the cathode. Hence, the important factor in order to deposit Am could be that the concentration of Am in the salt increased an order of magnitude over the concentration of U and Np in this electrolysis. On the other hand, it was seen in Fig.6 that the concentration of RE was also decreasing with passing charge. Ce and Nd showed remarkable decrease among RE, especially, because the standard redox potential of Ce and Nd was close to Am [7], and then Ce and Nd were higher content in the salt than another RE as shown in Table 1. Consequently, the electrolysis accelerated to deposit RE in particular Ce and Nd as well as Am on the cathode. It might be predicted that much amount of RE was accompanied on the cathode when Am was further removed (> 99%) from the salt. As shown in Fig.6, the concentration of Ce and Nd in the salt decreased remarkably after 220 coulomb passed. In this last deposit, the content of Ce and Nd became higher than all actinides. It should be ascribed the extremely low concentration of Am in the salt after 220 coulomb passed.

The cathode current efficiency in the second stage was lower than that of first stage. This may be come from the minimized current for getting better separation and from increase of the drop of the deposit with decreasing the concentration of actinides in the salt.

Figure 7 shows the relationship between the separation ratio and the total charge passed at an use of Li_2Sb anode. This separation ratio was replaced the denominator in the equation of (3) with the amount of actinides and RE before using of Li_2Sb anode. It was seen in Fig. 7 that the separation ratio became ca. 8 for U, ca. 60 for Np, ca. 20 for Pu and ca. 2 for Am, except the last deposition. As compared with Fig.5, the separation ratio of Np, Pu and Am from RE increased. It was due to low the concentration of U in the salt and high the content of Np, Pu and Am in the deposit. The order of the separation ratio was Np > Pu > U > Am. This behavior of U does not agree with the prediction from the standard redox potential[7]. It may be due to the low concentration of U in the salt and the fall of U deposit. The separation ratio of all actinides from RE became 10 in the second stage and was a half value of the case using Cd anode. This is because the main deposit of actinides was changed from U and Np to Am. It means that U and Np were easy to be separated from RE, but Am was difficult.

The recovered ratio of TRU (Np, Pu and Am) to RE was defined as the total amount of deposited TRU in divided by that of RE, and was derived to be 1.2 for this experiment. Since the ratio of TRU to RE before the electrolysis was 0.14, the molten salt electrorefining can be multiply the TRU ratio to RE about 8.6 times in this experiment.

CONCLUSION

1. The separation ratio of actinides to RE became 22 by using Cd anode.

2. The separation ratio became 10 by using Li_2Sb anode and was a low compared with the case of Cd anode. It was due to the change of the main deposit of actinides from U and Np to Am.

3. The molten salt electrorefining could be separated 8.6 times TRU from RE in this experiment.

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Table 1   The initial composition of the experiment*

	Total (mg)	Cd Phase (mg)	Salt Phase (mg)
LiCl-KCl			4.4962 (g)
Cd		7.4214(g)	
U**	37.0	30.0	7.0
Np	15.0	9.0	6.0
Pu	1.6	0.8	0.8
Am	16.9	9.2	7.7
Y	11.7	D.L.	11.7
La	36.4	0.5	35.9
Ce	69.0	2.9	66.1
Nd	110.0	5.2	104.8
Gd	7.3	0.3	7.0

*:The chemical composition in the system was adjusted to the ratio of actinides to RE (Y, La, Ce, Nd and Gd) with HLW.

**:Uranium was one fourth of the simulated composition, and praseodymium was none in the composition.
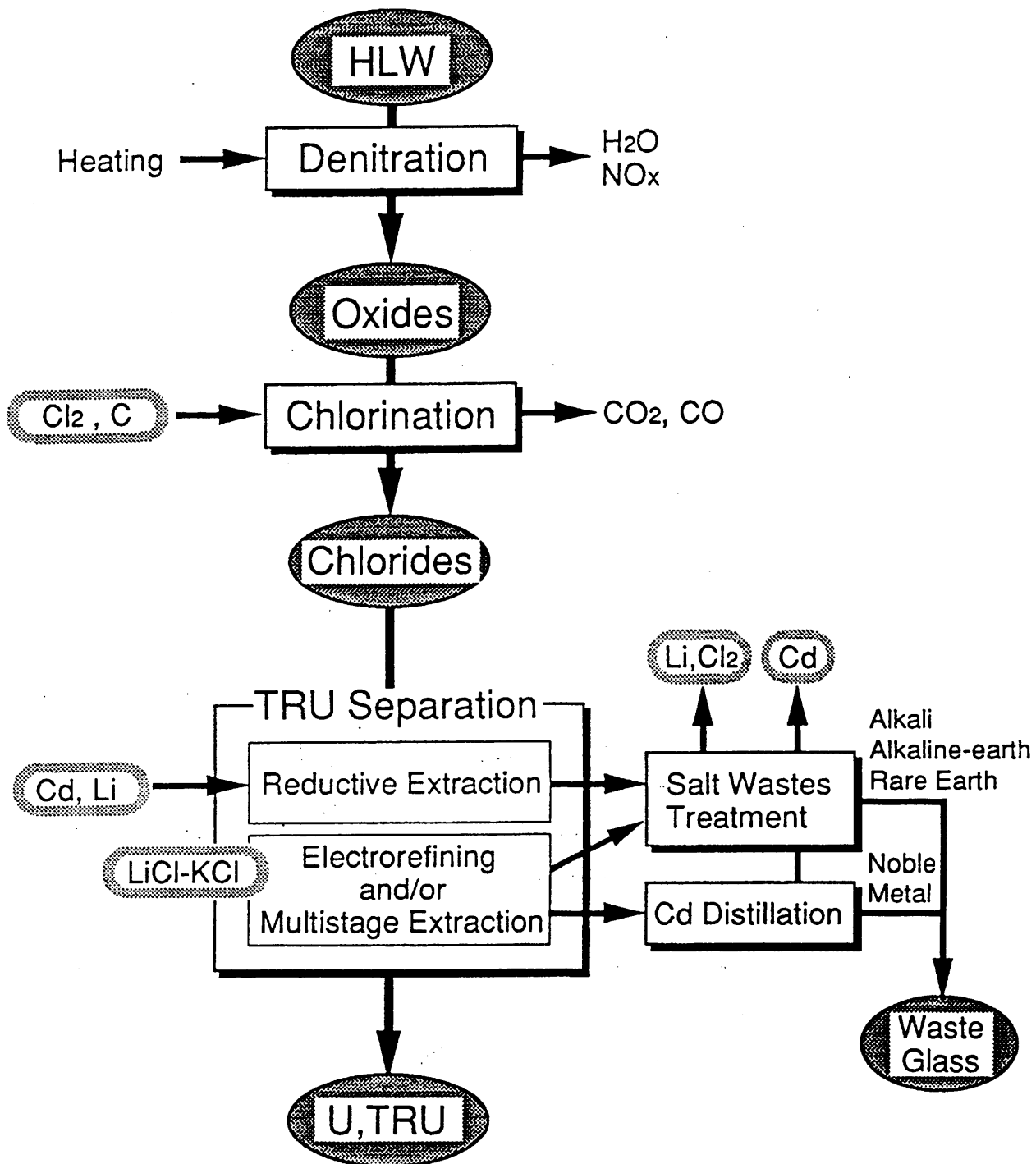
Fig. 1   Schematic flow diagram for TRU pyrometallurgical partitioning from high level wastes.
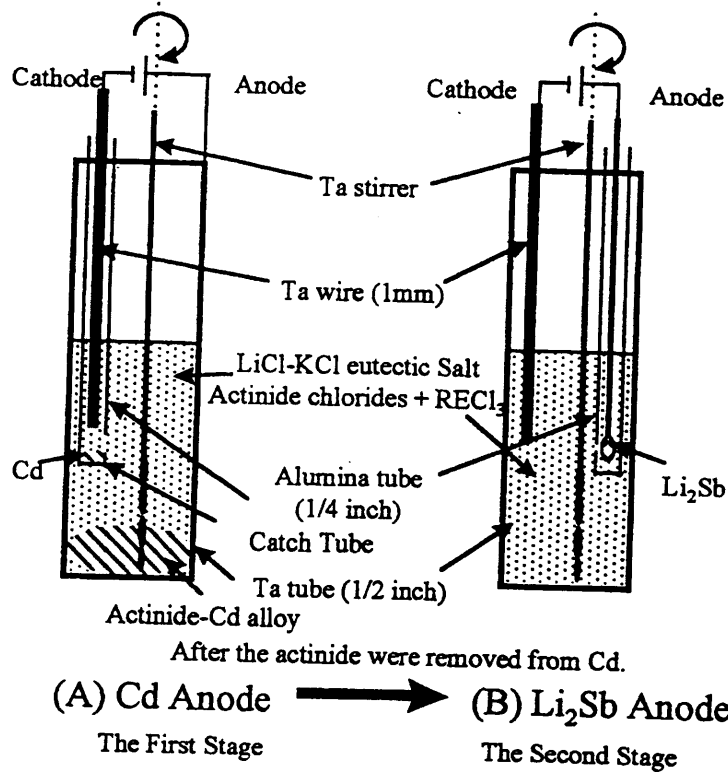
Fig.2 Schematic diagram of the experimental cell.
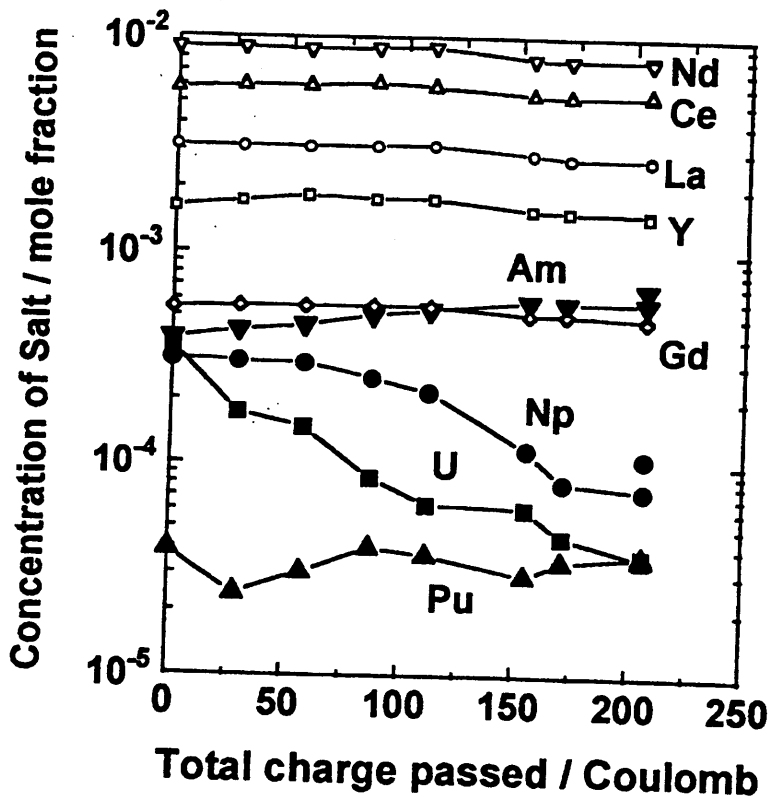(A) Cd anode (B) Li₂Sb anode

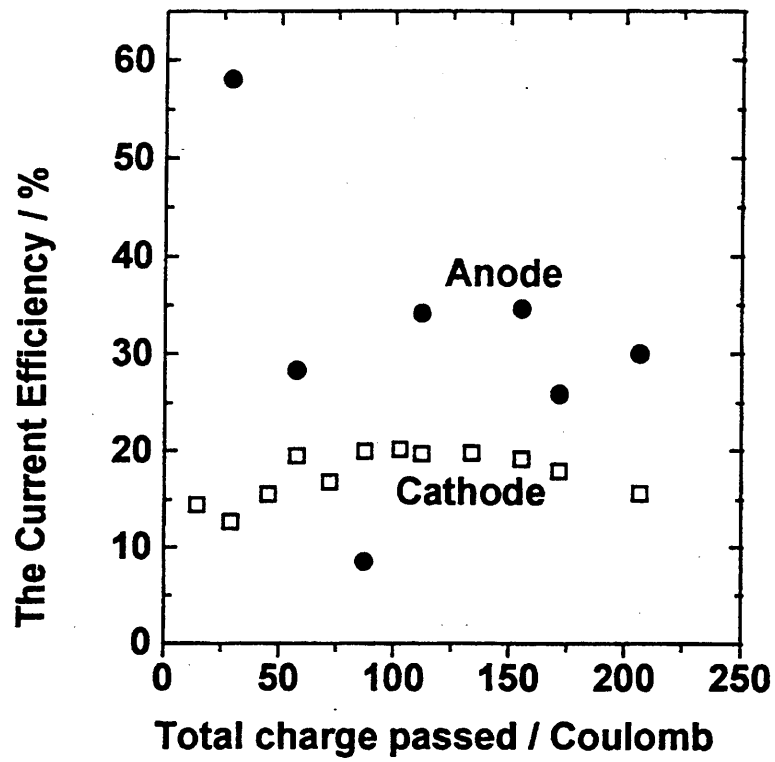Fig.3 The concentration change in the salt with the charge passed at an use of Cd anode.

Fig.4 The relationship between the current efficiencies and the charge passed at an use of Cd anode.
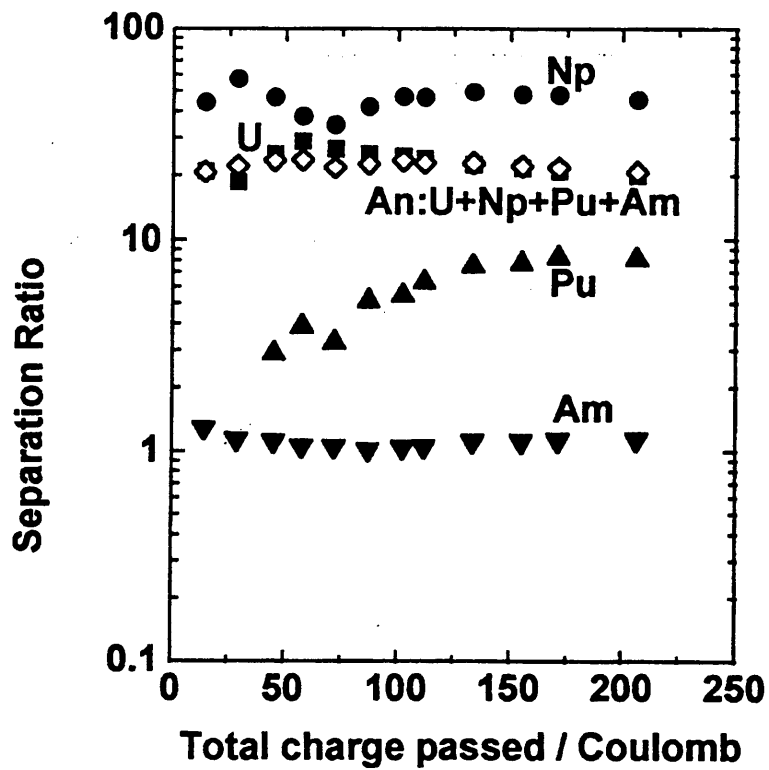

Fig.5 The relationship between the separation ratio at an use of Cd anode and the total charge.
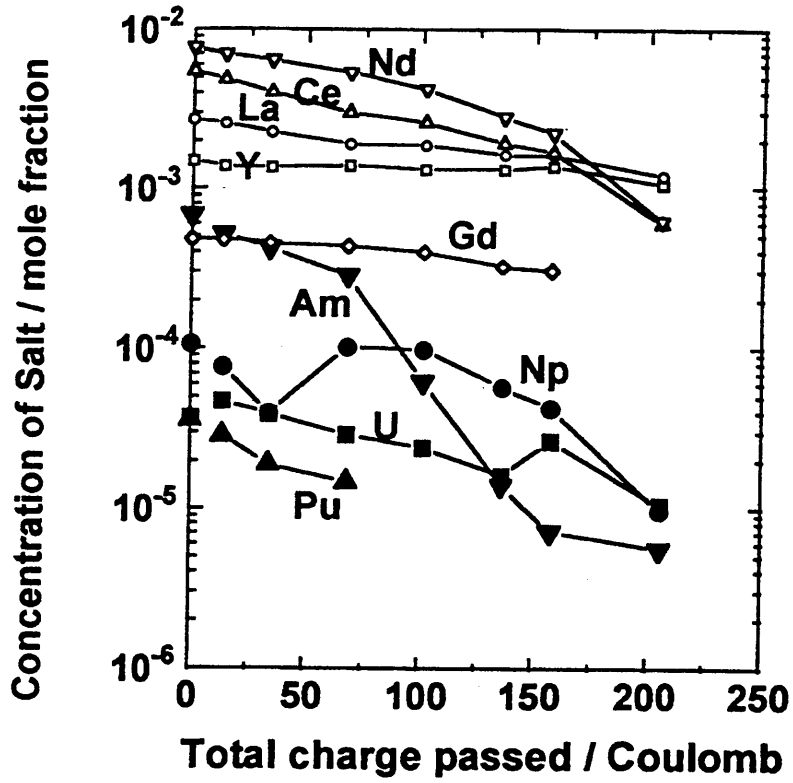
Fig.6 The concentration change in the salt with the charge passed at an use of Li$_2$Sb anode.
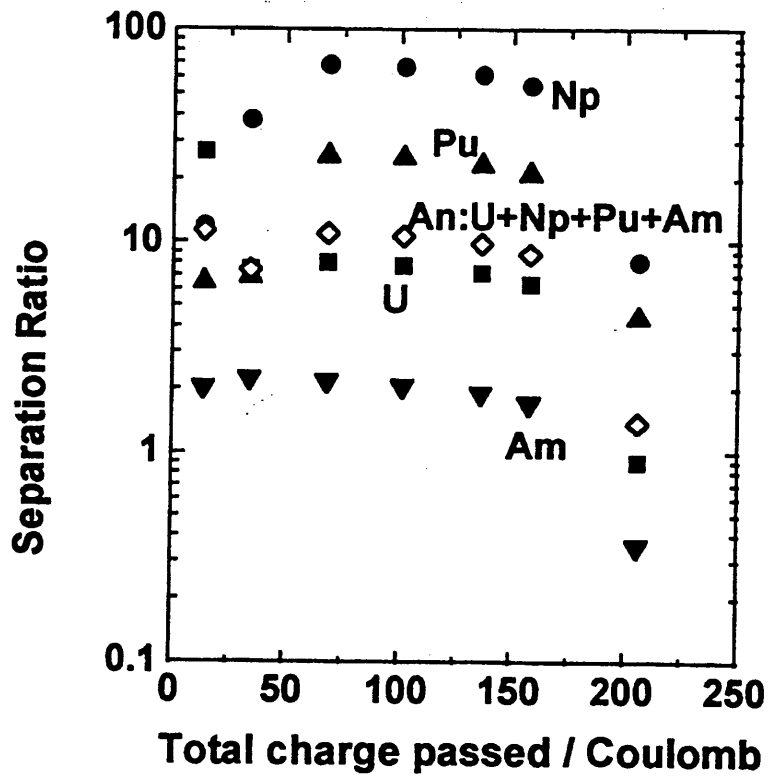

Fig.7 The relationship between the separation ratio at an use of Li$_2$Sb anode and the total charge.

PRODUCTS AND WASTES FROM FOUR GROUP PARTITIONING PROCESS DEVELOPED IN JAERI

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In the Japan Atomic Energy Research Institute (JAERI), a partitioning process has been developed to separate elements in a high-level liquid waste (HLLW) into four groups: transuranium elements (TRU), Tc-platinum group metals (PGM), Sr-Cs and the others.

The present paper deals with the partitioning process flow sheet, behaviors of objective elements and other consituents in the process, recoveries of objective elements, chemical purities of the products, the sorts and constituents of the secondary wastes, and the volume of solid materials generated from HLLW after the partitioning process.

The complete separation of TRU elements, including pentavalent Np, might be accomplished by using the partitioning process. However, further improvement will be required in the separation of Am and Cm from rare earths , back-extraction of U and Y from the DIDPA solvent, etc. to reduce the secondary waste generation and the handling liquid volume.

1. Introduction

Nuclear energy is the most promising option for the future generation when considering the grobal environmental protection. The management of high-level radioactive waste containing long-lived nuclides is one of the most important problems to be solved before the future deployment of nuclear energy in the global scale.

In 1988, Japan's Atomic Energy Commission published the report entitled "Long Term Program for Research and Development on Nuclide Partitioning and Transmutation Technology". In this program, a partitioning technology should be developed for separating elements in high-level liquid waste (HLLW) into four groups; transuranium elements (TRU), Tc-platinum group metals (PGM), Sr-Cs and the others. Among them, long-lived nuclides such as TRU nuclides should be transmuted by using an actinide burner reactor, FBR, etc.

2. Development of partitioning process

At JAERI, development of a partitioning method started about 23 years ago. From 1973 to 1984, a partitioning process was developed for separating elements in HLLW into 3 groups; TRU, Sr-Cs and others. The partitioning process consists of three steps; solvent extraction of U and Pu with tributylphosphate (TBP), solvent extraction of Am and Cm with diisodecylphosphoric acid (DIDPA), and adsorption of Sr and Cs with inorganic ion exchangers. The process was demonstrated by using an actual HLLW.

Since 1985, a four group partitioning process has been developed, in which a step for separating the Tc-PGM group was developed in addition to the three group separation. Effective methods for separating TRU, especially Np, and Tc have been developed.

3. Four group partitioning process

Through the fundamental study, the four group partitioning process has been constructed as shown in Fig.1. Main characteristics of this flow sheet are as follows: (1) All TRU elements including pentavalent Np are extracted with DIDPA after the denitration of HLLW, reducing the nitric acid concentration from 2 M to 0.5 M. (2) Tc and PGM are separated by precipitation through denitration or by adsorption with an active carbon. (3) Sr and Cs are separated by adsorption with inorganic ion exchangers, titanic acid and zeolite, respectively.

3.1 TRU separation

The TRU elements in the DIDPA solvent are sequentially back-extracted with 4 M nitric acid for Am, Cm and rare earths, 0.8 M oxalic acid solution for Np and Pu, and 1.5M sodium carbonate solution for U. A chemical flow sheet is shown in Fig.2. Back-extracted Am, Cm and rare earths are extracted again with DIDPA, and then Am and Cm are preferentially back-extracted with 0.05 M dietylentriaminepentaacetic acid (DTPA) solution, leaving rare earths in the DIDPA solvent.

Recoveries of TRU elements and chemical behaviors of fission products and corrosion products in each chemical step can be estimated with data so far obtained through experiments with actual or simulated HLLW. Following results might be expected under optimized process conditions.

Recoveries of Am, Cm, Pu and U are more than 99.99% and Np more than 99.95% in the DIDPA extraction step. More than 99.99% of Am, Cm and rare earths are back-extracted with 4 M nitric acid, more than 99.9% of Np and Pu with the 0.8 M oxalic acid solution, more than 99.9% of U with the sodiumcarbonate solution and more than 99.99% of Am and Cm with the DTPA solution.

As to the chemical behaviors of fission and corrosion products, rare earths and Fe are quantitatively extracted with the DIDPA solvent. Rare earths behave like Am and Cm, but finally are separated from them in the DTPA back-extraction step. The rare earth content in the Am and Cm fraction might be reduced to lower than 25% under the operating condition of 99.99% recoveries of Am and Cm. Among rare earths, the chemical behavior of Y fairly differs from those of other rare earths. Most Y is back-extracted along with U in the sodium carbonate back-extraction step. The Fe is back-extracted along with Np and Pu with the 0.8 M oxalic acid solution.

3.2 Tc and PGM separation

Two chemical methods have been developed for the Tc and PGM separation from the DIDPA raffinate; the precipitation method by a denitration with formic acid and the adsorption method with active carbon column. The former method might be more effective in practical use because of no generation of secondary wastes even though the recovery of Tc is estimated to be about 95% as compared with more than 99.9% in the latter method and the former method is not applicable to the solution in which concentration of Rh and Pd is lower than 0.005 M. More than 90% of Tc might be preferentially leached out, leaving PGM in the precipitate, with a hydrogen peroxide solution.

3.3 Sr and Cs separation

The adsorption method with inorganic ion exchangers, titanic acid and zeolite, has been developed for the Sr and Cs separation. More than 99.9% of Sr and Cs might be separated from the filtrate by this adsorption method after the Tc and PGM separation.

4. Products from four group partitioning process

4.1 TRU products

4.1.1 Am and Cm

The recovery which is the ratio of the amount in the product to the initial amount in HLLW might be more than 99.97% for Am and Cm under the estimation that less than 0.03% of them are losed in the chemical steps; DIDPA extraction, 4 M nitric acid back-extraction, DIDPA re-extraction and DTPA back-extraction. About 1 % of rare earths might be contained in the Am and Cm product and the chemical purity of the product might become about 75%.

In the chemical flow sheet as shown in Fig. 2, the Am and Cm product is obtained as the DTPA solution. Finally, a conversion method to oxide or nitride to be subjected to the nuclide transmutation should be developed.

4.1.2 Np and Pu

The recovery of Np might be more than 99.85% under the estimation that less than 0.05% is losed in the DIDPA extraction step and less than 0.1% in the 0.8 M oxalic acid back-extraction step. Almost all Fe and slight amounts of Rh, Ru, Zr and Mo might be contained in the Np and Pu product. The purification of the product from Fe and other impurities should be considered in the conversion step from the oxalic acid solution to oxide or nitride to be subjected to the nuclide transmutation.

Estimation of the Pu recovery is very difficult because more than 70% of Pu might be precipitated during the preparation step of HLLW from the TBP raffinate generated in the Purex

process, long-term storage of HLLW and the denitration step of HLLW prior to the DIDPA extraction even though the recovery of Pu from the filtrate after the denitration of HLLW is more than 99.9%. In order to accomplish the complete recovery of Pu, the dissolution of the precipitate and the separation of Pu from the resulting solution should be developed.

4.1.3 U

The recovery of U might be more than 99.9% under the estimation that less than 0.01% is losed in the DIDPA extraction step and less than 0.1% in the sodium cabonate back-extraction step. Almost all Y, slight amount of Fe, less than 0.1% of Np and less than 0.01% of Am and Cm might be contained in the U product which is obtained as the sodium carbonate solution. This product should be recycled to a fuel reprocessing plant.

4.2 Tc and PGM products

Estimation of the recoveries of Tc and PGM is difficult as the same as in the case of Pu because about 10% of Tc and about 20% of Ru and Rh might be precipitated during long term storage of HLLW and the denitration step of HLLW prior to the DIDPA extraction. In order to increase the recoveries of Tc and PGM up to more than 90%, a treatment method for the precipitate should be developed. However, higher recovery more than 90% for Tc will not be needed from the standpoint of reducing the potential hazard index of a vitrified HLLW.

The recoveries from the filtrate after the denitration of HLLW are estimated to be about 95% of Tc, 92% of Ru , 87% of Rh and 99% of Pd when the precipitation method is applied to the DIDPA raffinate. The Tc product obtained by the leaching of the precipitate with hydrogen peroxide might contain trace amount of PGM. Conversion of the Tc chemical form present in pertechnetate ion should be studied for the nuclide transmutation or a beneficial use. The PGM obtained as the precipitate might be present as a mixture of metal and oxide. Mutual separation of Ru, Rh and Pd should be studied for thier beneficial uses. However, the necessity of this study might not be so urgent since the PGM contains long lived nuclides of which half-lives are longer than one year and a very long-term cooling will be needed before practical use.

4.3 Sr and Cs product

The recoveries of Sr and Cs might be more than 99.9%. Most Ba and Ni might be also adsorped on the inorganic ion exchangers. The U and TRU contents compared to their initial amounts in HLLW might be less than 0.01% and less than 0.0001%, respectively.

The exchangers loaded with Sr and Cs can be solidified into a very stable form by direct calcination. This greatly contributes to the reduction of waste volume because the material used for the adsorption can be used as the mother material for the Sr and Cs solidification and the thermal stability of the product is very high compared with that of vitrified material. Therefore, large amount of heat generating nuclides can be included in the small volume of the solid material. Leachabilities of Sr and Cs are extremely low by a factor of four order of magnitude as compared with that for vitrified material.

The Sr and Cs product might be used as a heat source and a radiation source during the period of storage prior to a deep underground disposal.

5. Wastes from four group partitioning process

5.1 Others group

The others group in the four group partitioning process is waste in a direct sense. This group contains elements collected from 4 kinds of fractions; the precipitate after the denitration of HLLW, the rare earths fraction separated from Am and Cm, the effluent from the Sr and Cs adsorption column, the Fe and Y fractions separated from the Np and Pu fraction and the U fraction, respectively.

From the precipitate fraction, most Zr, Mo and Te are estimated to be recovered and transfered to the others group. The Pu quantity transfered to the others group is estimated to be less than 0.01%. The rare earth fraction is estimated to contain most rare earths and less than 0.01% of Am and Cm, the effluent fraction to contain Na which is released by an ion exchange reaction with Cs, and the Fe and Y fraction to contain most of them.

Total amount of elements to be contained in the others group is estimated to be 26 kg in their oxides for one ton of the spent fuel burned up to 33 GWd/t.

5.2 Solvent waste

The DIDPA solvent is estimated to contain less than 0.1% of U, less than 0.001% of TRU and trace amounts of Ru, Fe and Zr after treatment with the sodium carbonate solution. Total amount of the DIDPA solvent waste generated for one ton of the spent fuel is estimated to be 10 L , corresponding to 8.2 kg of $CaHPO_4$ under the conditions that 3000 L and 4000 L of the DIDPA solvent are used respectively for the TRU extraction step from HLLW and the separation step of Am and Cm from rare earths and the number of its recycle use in each step is estimated to be 50 and 100 times, respectively.

5.3 Washing solution

The DIDPA solvent after the treatment with the sodium carbonate solution should be washed with nitric acid to convert the Na form to H form for its recycle use. Therefore, the waste of the washing solution contains sodium ion of which amount is estimated to be 128 kg in $NaNO_3$ for one ton of the spent fuel. Amounts of U and Pu-TRU are estimated to be less than 0.0001% and less than 0.00001%, respectively.

5.4 Sodium carbonate solution and other wastes

In the U back-extraction step with sodium carbonate solution, about half of Na remains in the carbonate solution. Therefore, the amount of Na in the carbonate solution after the U back-extraction is estimated to be 128 kg in $NaNO_3$ for one ton of the spent fuel.

The liquid wastes generated after treatment of the Am and Cm fraction and the Np and Pu fraction are the DTPA solution and the oxalic acid solution, respectively. For these liquid wastes it might be possible to decompose to water and carbon dioxide which enable no generation of solid wastes.

6. Volume of the solid materials

Table 1 shows the volume of the solid materials generated in the four group partitioning process.

The volume of the Sr-Cs group was estimated for the solid material generated by the direct calcination of the inorganic ion exchangers loaded with most Sr, Cs, Rb, Ba and Ni, and the volume of the others group was estimated for the vitrified material containing 30 wt% of oxides of fission and corrosion products. This content might be not so high for the vitrification because the others group

contains less heat generators such as Sr-90 and Cs-137. Cementation was considered for the secondary wastes such as $CaHPO_4$ and $NaNO_3$.

Total volume of the four groups generated from the partitioning process was estimated to be 45 L which is smaller by a factor of 3.3 compared with that in the vitrification of HLLW without partitioning.

For the others group it might be possible to dispose directly into a deep ungergroud without any long term cooling. For the cemented waste, a shallow land disposal might be suitable because alpha activities concentration is estimated to be negligible.

7. Conclusion

The four group partitioning contributes to the reduction of the high-level waste volume and the enhancement of the utilization of valuable elements or nuclides in HLLW as well as the promotion of the transmutation of long-lived nuclides which contributes to the reduction of long-term burden into natural environment.

Complete separation of TRU elements, including pentavalent Np, can be accomplished by using the DIDPA solvent. However, a chemical method using a salt-free reagent should be further developed for the back-extraction of U and Y from the DIDPA solvent to reduce the secondary waste generation and an advanced chemical method should be considered for the separation of A m and Cm from rare earths to reduce the handling liquid volume. The recovery of TRU elements, especially Pu, should be studied for the precipitate formed during the preparation step to HLLW from the TBP raffinate generated in the Purex process, long therm storage of HLLW and the denitration step of HLLW.

Table 1 Volume of solid materials after partitioning for one ton
of the spent fuel burned up to 33 GWd/t

Group	Main nuclides or elements	Solid form	Volume (L)
TRU	Np-237 Am-241	oxide	0.09
Tc - PGM	Tc-99 Ru, Rh, Pd	metal	0.39
Sr - Cs	Sr-90 Cs-137	calcined product	14
Others	Zr, Mo, Fe rare earths	vitrified material	31
Secondary wastes	$NaNO_3$ $CaHPO_4$	cemented material	330

High—Level Liquid Waste

Formic acid ------> Denitration

Filtration ──> Precipitate

DTPA   Oxalic acid

DIDPA ------------> Solvent
                    Extraction   Selective
                                         Back—Extraction   ──> TRU Group
                                                                 (Am,Cm,Np,Pu,U)

                                         Rare Earths

Formic acid ------> Precipitation by
    or   Denitrtaion or
Active carbon -----> Column   ──> Tc—PGM
                    Adsorption   Group

Zeolite ------------> Column
Titanic acid -------> Adsorption   ──> Sr—Cs
                                                                 Group

Effluent   ──> Others
                                                                 Group

Fig. 1 The four group partitioning process

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Solvent
0.5M DIDPA
0.1M TBP

HLW Feed
HNO₃ ~ 0.5M

Scrub
0.5M HNO₃
1.0M H₂O₂

New Solvent

H₂O₂ Sol.

Used Solvent

Extraction I | Scrub
Raised Temperature

4M HNO₃

Raffinate

To Separation
of Cs, Sr, Tc
and PGM

Strip I
Raised Temp.

0.8M H₂C₂O₄

Acidity
Adjustment
HNO₃ ~ 0.5M

Strip II

1.5M Na₂CO₃

DIDPA Solvent

Strip III

Extraction II

Np-Pu | U

0.05M DTPA

Raffinate

Strip IV

4M HNO₃

HNO₃ Recycle

Solvent Recycle

Strip V

Am-Cm | Lanthanides

Fig. 2   The DIDPA extraction process including the separation of Am and
Cm from rare earths

SELECTIVE EXTRACTION AND TRANSPORT OF CESIUM WITH CALIX[4]ARENES CROWN FROM RADIOACTIVE LIQUID WASTES

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Cesium possesses two long lived isotopes ^{135}Cs and ^{137}Cs, the first one of which the half live is very long must be selectively separated either for transmutation, either for encapsulation in a very specific matrix. As for ^{137}Cs, it is interesting to remove it with strontium and actinides in order to decategorize immediate level radioactive wast. Cesium must be removed with a very high selectively in the first case from very acidic medium (HNO_3 3-4 M) in the second one from acidic high sodium nitrate concentration liquid waste. Calix[4]arenes crown or bis crown in the 1,3 alternate conformation exhibit a tremendous efficiency and selectivity for cesium. These exceptional performances, much higher than those obtained with the best crown ethers, were obtained on simulated wastes and confirmed in two hot tests by liquid-liquid extraction and by implementing supported liquid membranes.

1 - INTRODUCTION

Nuclear Fuel reprocessing operations produce both high and medium level activity liquid wastes. Studies are launched, in the framework of SPIN programm to selectively remove actinides or long lived fission products like ^{135}Cs in order to distroy them by transmutation or to dispose of them in very stable matrices. On the other hand medium level activity wastes are treated by evaporation this treatment leads to large volume of concentrates composed mainly of inactive salts. It is desirable to remove the long-lived radionuclides (actinides, ^{90}Sr and ^{137}Cs) from the concentrates, this allows these decontaminated wastes to be directed to surface repositories, only a small volume containing these radionuclides being disposed of in geological formation. We have to point out that in both cases, high or medium activity liquid wastes, it is interesting to selectively and efficiently remove cesium isotopes.

2 - EXTRACTION OF CESIUM BY ION EXCHANGERS OR EXTRACTANTS

For several decades, inorganic ion exchangers or absorbers were used to remove cesium, recent reviews concluded, from the study of these compounds that Cristalline Silico Titanates (CSTs) were the most promising (if reuse of material was not required) followed by ammonium molybdo phosphate, ferrocyanides and other phosphates [1][2]. However the authors concluded that elution, if possible, had to be studied in order to minimize the volume of waste produced.

Two classes of extractants were particularly studied for the extraction of cesium : Dicarbollides and crown ethers. Czechs carried out extensive studies for the synthesis and extraction properties of dicarbollides [3]. These lipophilic anions withstood protonation in very acidic medium and removed cesium effectively in nitric solution up to 3 M, the stripping occuring at higher acidity (5 M), but the extraction abilities sharply decreased in presence of sodium nitrate. Crown ethers, were also proposed for the extraction of cesium, bis (tert butyl benzo) 21 crown 7 or bis (hydroxyheptyl) 18 C 6 synergized by organic soluble anions like dinonyl (or didodecyl) naphtalene sulphonic acid were able to remove cesium from very acidic solutions but not in presence of high sodium concentration due to the high coextraction of sodium [4] [5]. *Blasius* showed that, among the classical crown ethers, DB 21 crown 7 was the only crown ether providing the required selectivity towards sodium, however to accomplish an extraction from sodium nitrate medium, the crown ether had to be combined with heteropolyacids or hexachloroantimony acid [6]. Lipophilic tert butyl (or decyl) benzo 21 crown 7 failed to quantitatively remove cesium from simulated acidic high sodium concentrates, we directed our efforts towards a new promising class of macrocycles functionalized calixarenes [7].

3 - CALIXARENES

Calix[4]arenes are macrocycles made up of phenolic units (generally n = 4 to 8) linked by methylene bridges. Butyl[4]calixarene, the cyclic tetramer, is an important building block because it can be synthesized in large amounts from inexpensive starting materials, it can be functionalized either using the phenolic oxygens, either by it's para position. Moreover calix[4]arene is conformationally mobile and can assume four conformations : cone, partial cone, 1-2 alternate, 1-3 alternate (Fig. 1). The analogy of calix[4]arene in cone conformation with a beaker (calix in greek) led *D. Gutsche* to call them calixarenes. The functionalization associated with the conformational properties led to a large variety of « tailored » macrocycles.

| cone | partial cone | 1,2-alternate | 1,3-alternate |
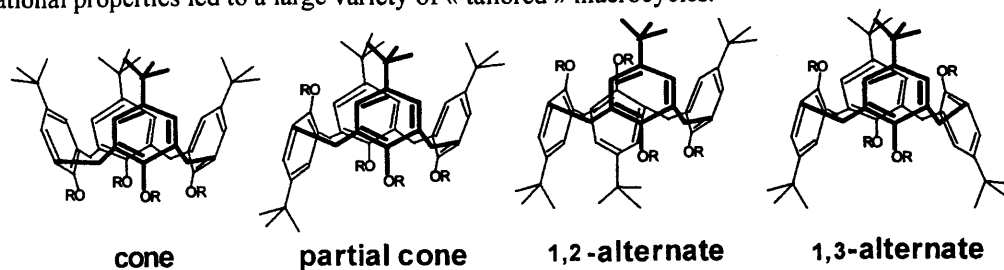
Figure 1
calix[4]arene conformations

In search for better extractants than crown ethers, efforts were devoted to crown ethers built on calixarene molecular platform. Since the synthesis of a crown compound with two opposite phenolic groups linked by a penta ethylene glycol chain many calix[4]arenes with crown ether moieties were produced and proved to be efficient for the complexation of alkali and alkaline earth cations due to the presence of the crown ether link [8]. The selectivities of the complexation were strongly dependent on the conformation of the calixarenes. R. Ungaro and J. Vicens, blocked the calixarene crown into a 1,3 alternated conformation by adding respectively, either two alkyl chains either a second polyethylene glycol on the two remaining phenolic units.

Thirteen calix crowns have been studied, the extraction results are given in Table 1, the main conclusions are :

For alkyoxy crown 6 and bis crown 6, the extraction is mainly dependent on conformation, the compounds in the 1,3 conformation displays the highest cesium distribution coefficients and very low sodium distribution coefficients hence the highest Cs/Na selectivity [10].

The extraction is at a lesser extent linked to the crown's size, the highest results are obtained for two classes of calixarenes with polyethylene glycol bridges containing six oxygens.

The exceptional selectivity of these two classes of calixarenes for cesium, much higher than those of the most efficient crown ethers, can be explained by the stabilization of the complexes calixarene-cesium by the bonding interactions with the four phenyl units of the calix[4]arene [11].

Table 1

Extraction of cesium and sodium - Selectivity Cs/Na

Aqueous feed solution, 5.0×10^{-4} M M^+ (NO_3^-) in 1 M HNO_3 ;
Organic solution, 10^{-2} M extracting agent in 1,2-nitrophenyl hexyl ether

	D_{Na}	D_{Cs}	α(Cs/Na)
1,3-calix[4] dimethoxy crown 6	3.10^{-3}	$4\ 10^{-2}$	
1,3-calix[4] hydroxy ethoxy crown 6	$4\ 10^{-3}$	4,2	≥ 4200
1,3-calix[4] dipropoxy crown 6	$2\ 10^{-3}$	19.5	≥ 19500
1,3-calix[4] di isopropoxy crown 6	$< 10^{-3}$	28.5	$\geq 28\ 500$
1,3-calix[4] di n oxtyloxy crown 6	$< 10^{-3}$	33	≥ 33000
1,3-calix[4] di methoxy crown 7	$4\ 10^{-3}$	$7\ 10^{-3}$	
1,3-calix[4] biscrown 5	2×10^{-3}	0.4	
1,3-calix[4] biscrown 6	1.3×10^{-2}	19.5	1500
1,3-calix[4] biscrown 7	$< 10^{-3}$	0.3	
1,3-calix[4] bis-p-benzo-crown 6	$< 10^{-3}$	2×10^{-2}	
1,3-calix[4] bis-o-benzo-crown 6	1.7×10^{-3}	32.5	≥ 19000
1,3-calix[4] bisnaphthyl-crown 6	$< 10^{-3}$	29.5	≥ 29000
1,3-calix[4] bisdiphenyl-crown 6	$< 10^{-3}$	7×10^{-2}	
n-decylbenzo-21-crown 7	1.2×10^{-3}	0.3	250
tert-butylbenzo-21crown 7	1.2×10-3	0;3	250

4 - TRANSPORT OF CATIONS THROUGH SUPPORTED LIQUID MEMBRANES

4.1. Supported Liquid Membranes

The selective extractants used for extraction are often very expensive and thus limit the use of the techniques mentioned previously ; work was therefore carried out in this study on the use of selective extractants with liquid membranes technology.

Supported liquid membranes (SLM) are made up of two-aqueous phases separated by an organic phase. The aqueous phase, called the feed phase, contains the radioelements to be extracted by means of the organic phase. They are then carried to the other aqueous phase, called the stripping phase. The organic phase, constituted by an extractant dissolved in a diluent, impregnates a microporous support placed between both aqueous phases. The driving force of the process is attributable to the difference of the nitrate concentrations in the feed phase [NaNO$_3$ (4 M), HNO$_3$ (1 M)] and in the stripping phase (no nitrate). The transport mechanism that takes place is called co-transport, as the cation and the extractant transit through the membrane in the same direction.

The use of neutral carriers, such as a calix[4]arene crowns, leads to a coupled co-transport of cations and nitrate anions through the SLM [12]. When concentrates or acidic solutions are used as feed solution, and demineralized water as stripping solution, the concentration gradient of the nitrate anions will force the transport of cesium against their own concentration gradient thus leading to their concentration in the stripping solution.

4.2- Permeability Determination

The transport of ^{137}Cs from synthetic aqueous solutions of NaNO$_3$ (4 M) and HNO$_3$ (1 M), was followed by regular measurement of the decrease of radioactivity in the feed solution by γ spectrometry analysis. This allowed graphical determination of the constant permeabilities P (cm.h^{-1}) of cesium permeation through the SLM by plotting the logarithm of the ratio C/C° vs.time, as described in the model of mass transfer proposed by *Danesi* [13]

$$\ln \frac{C}{C^\circ} = -\frac{\varepsilon.S}{V}.P.t$$

where
C is concentration of the cation in the feed solution at time t (mol.l^{-1}) ;
C° is initial concentration of the cation in the feed solution (mol.l^{-1}) ;
ε is volumic porosity of the SLM %) ;
S is membrane surface area (cm^2) ;
V is volume of feed and stripping solutions (cm^3)
t is time (h).

Transport experiments were carried out with the most promising compounds ; their permeability are given in the Table 2.

Table 2

^{137}Cs Transport Experiments through Flat Sheet-Supported Liquid Membranes :
Permeability Determination after 6 h of Permeation

Aqueous feed solution, NaNO$_3$ (4 M) and HNO$_3$ (1 M) ; aqueous strip solution, deionized water ;
organic solution, 10^{-2} M carrier in 1,2-nitrophenyl octyl ether.

P$_{Cs}$ (cm.h^{-1})

1,3-calix[4] hydroxy ethoxy crown 6	0.4
1,3-calix[4] dipropoxy crown 6	1.6
1,3-calix[4] di iso propoxy crown 6	1.3
1,3-calix[4] di n octyloxy crown 6	1.9
1,3-calix[4] biscrown 5	9×10^{-2}
1,3-calix[4] biscrown 6	1.3
1,3-calix[4] biscrown 7	4×10^{-2}
1,3-calix[4] bis-*p*-benzo-crown 6	3×10^{-3}
1,3-calix[4] bis-*o*-benzo-crown 6	2.8
1,3-calix[4] bisnaphthyl-crown 6	2.7
1,3-calix[4] bisdiphenyl-crown 6	0.1
n-decylbenzo-21-crown 7	9×10^{-2}

5 - TESTS ON REAL LIQUID WASTES

Two types of measurements (distribution coefficients, transport through SLMs) were carried out on two real wastes. The experiments were performed respectively in the *CARMEN* hot cell of CEA/DCC/DRDD on an acidic HA liquid waste provided by this Department and in the facilities of COGEMA Marcoule /Service on a M.A. concentrate provided by COGEMA Marcoule.

Several calixarenes were tested in the experiment carried out in CARMEN cell (bis crown-6-calix[4arene, 1,3 diisoproposy-2-4-crown-6 calix[4]arene and 1,3-di(2 nitrophenoxy octyloxy)-2,4- crown-6-calix[4]arene this calixarene has been conjointly synthesized by the Universities of Parma (Pr UNGARO) and Twente (Pr REINHOUDT), the latter was a very interesting compound due to its very high lipophilicity and to its great solubility in NPHE or NPOE but available in low amount. 1,3 di octyloxy-2-4-crown-6 calix[4]arene was used for decontaminating the concentrates.

compound 1   compound 2   compound 3   compound 4
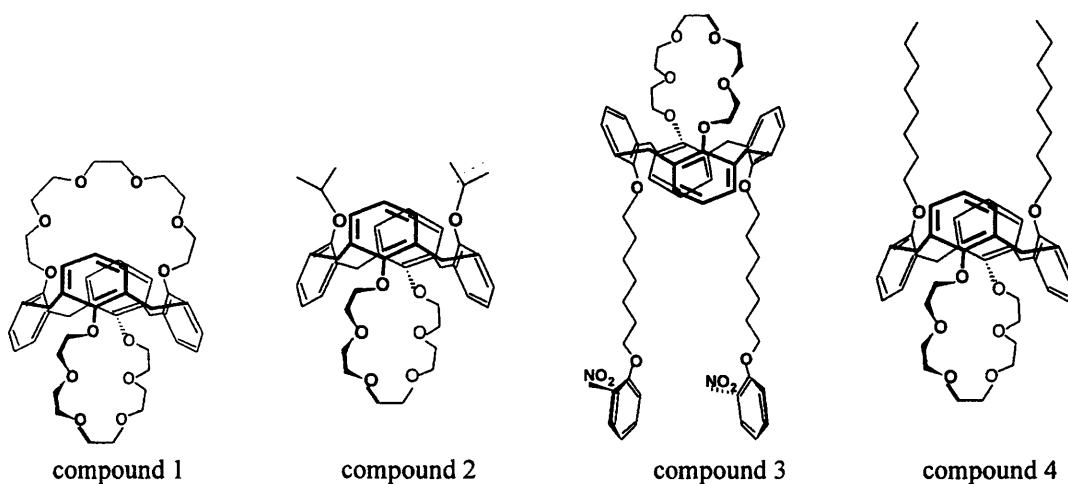
Figure 2
Structure of crown 6 calix[4]arenes

Compound 1 : bis crown-6-calix[4]arene
Compound 2 : 1,3-diisopropoxy-2,4-crown-6-calix[4]arene
Compound 3 : 1,3-di(2-nitrophenoxy octyloxy)-2,4-crown-6-calix[4]arene
Compound 4 : 1,3-dioctyl oxy-2,4-crown-6-calix[4]arene

5.1- Test on HA liquid waste

The H.A. liquid waste is a dissolution of a MOX Fuel (Burn up 34 650 MWJ/tU) where Uranium and Plutonium have been previously extracted by TBP (classical PUREX process). Composition of the waste is summarized in Table 3.

Table 3

Chemical and radiochemical composition of the real raffinate to reprocess

	Concentration (mol/l)	Activity (Ci/l)
Acidity	4	
Fe	4.5×10^{-4}	
Zr	5.1×10^{-3}	
Mo	4.9×10^{-3}	
Nd	4.9×10^{-3}	
Ce	3×10^{-3}	
Pu	$< 2 \times 10^{-5}$	
U	$< 4.2 \times 10^{-5}$	
Tc	$< 5. \times 10^{-5}$	
Np	$< 2.1 \times 10^{-5}$	
Cs	4.15×10^{-3}	
^{106}Ru		0.73
^{125}Sb		0.21
^{134}Cs		2.78
^{137}Cs		17.9
^{144}Ce		0.42
^{154}Eu		1.07
^{241}Am		1.22 (17.8 %)
^{244}Cm		5.57 (81.3 %)
^{242}Cm		0.024

Distribution coefficient measurements were carried out by putting into contact a calixarene crown 6, 0.1 M, diluted in NPHE, with the real waste, cesium distribution coefficients higher than 60 were obtained, then this cation was easily stripped in demineralized water (Table 4). Moreover the high selectivity of this class of calixarene, observed with synthetic waste was confirmed by this test : for all radionuclides (actinides or fission products : ^{106}Ru, ^{154}Eu, ^{125}Sb, ^{144}Ce) the decontamination factors (Ratio of initial activity of the elements in waste to activity of these elements in organic phase) were higher than 100 and ranging from 12 to 60 for Fe, Mo, Zr, Ce, Nd. (Table 5).

Table 4

Calixarènes	Cesium distribution coefficients (D_{Cs})			
	Extraction		Back-extraction	
	*	**	*	**
Compound 1	55±5	50±5	10±1	10±1
	55±5	46±5	11±1.1	12.5±1.2
Compoind 2	61±6	55±5	10±1	10±1
	71±7	78±8	6.7±0.7	7.2±0.7

* *aqueous phases mass-balance*
** *measurements of organic and aqueous phases*

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Table 5

of liquid-liquid extraction of a real raffinate (Table 1) by crown calixarenes.
Cesium distribution coefficients and cesium decontamination factors towards other elements

Calixarènes	Decontamination factors of cesium towards M, $DF_{(Cs/M)}$:										
	βγ emitters				Chemical elements				Actinides		
	^{106}Ru	^{125}Sb	^{144}Ce	^{154}Eu	Mo	Zr	Fe	Nd	Ce	α tot	Cm
Compound 1	9	>100	>100	>100	9	15	~60	24	19	~50	~50
	7	>100	>100	>100	11	11	22	17	20	~50	~50
Compound 2	73	>100	>100	>100	22	12	25	44	17	>100	>100
	36	>100	>100	>100	117	13	13	64	30	>100	>100

Calixarene 0.1 M in 1,2-NPHE, t = 30°C, stirring speed 1000 rpm, back-extraction : demineralized water.
note : two Dcs measurements were performed.
$D_{Cs} = [DCs]_{org}/[Cs]_{aq}$. $DF_{(Cs/M)} = D_{Cs}/D_M$.

A small percentage of nitric acid was coextracted (5 to 7 %) which is an interesting factor knowing that we observed a competitive extraction of nitric acid and cesium cation.

Calix[4]arene bis crown, diisopropoxy calix[4]arene crown 6 and di NPOE calix[4]arene (not available in sufficient amount to perform distribution coefficient measurements) were used as carriers in supported liquid membranes (0.1 M NPHE). Respectively 58.3 %, 77.5 % and 86.3 % of cesium was transported from liquid waste to the demineralized water, higher cesium activities could have been transported by increasing the duration of an experiment (Table 6). Only cesium was significantly transported during these tests, Molybdenum and Zirconium were detected in stripping phase at very low level when diisopropoxy calix[4]arene crown 6 was used, with di NPOE calix[4]arene crown 6 Molybdenum, Zirconium, Iron, Neodynium, Cerium were detected at a very low level. The decontamination (concentration of element in feed solution/concentration of elements in stripping solution) factors obtained were higher than 100 for all elements or radionuclides (Table 7).

Table 6

Extracted cesium percentage during transport experiments

Compound	Extracted cesium (%)	
	after 4 h	at the end of the rest
Compound 1	30.4	58.3 (13 h)*
Compound 2	55.7	77.5 (8h40)*
Compound 3	63.1	86.3 (9 h)*

* the transport test lasted (xh)

It is obvious that bis-crown-6-calix[4]arene was the less efficient molecule. This molecule is the less lipophilic one. Because of the high ratio (aqueous phases/organic phase) used in SLM experiments (~3000-4000), the loss of extractant molecule in the aqueous media is far from negligible.
Further transport kinetics of bis-crown-6-calix[4]arene were slower.

Cesium decontamination factors were highly satisfactory (Table 7). No other element (except Rubidium) was extracted at a higher level than 1-2 %.

Table 7

Cesium decontamination factors obtained during transport experiments

Calixarenes	Time (h)	βγ emitters				Chemical elements					Actinides	
		^{106}Ru	^{125}Sb	^{144}Ce	^{154}Eu	Mo	Zr	Fe	Nd	Ce	α tot	Cm
compound 1	13	>50	>50	>50	>50	>100	>100	>100	>100	>100	>100	>100
compound 2	8.7	>50	>50	>50	>50	>100	>100	>100	>100	>100	>100	>100
compound 3	9	>50	>50	>50	>50	>100	>100	>100	>100	>100	98	98

Top header spanning: Decontaminaiton factors of cesium towards M, $DF_{(Cs/M)}$:

Permeability coefficient and membrane fluxes were calculated. The results are indicated in the Tables 8 and 9.

According to Danesi's model, flux of cations were calculated from experiments carried out with the real waste and simulated waste for different nitric acid concentrations (2-6 M). A decrease of cation flux was observed with an increase of the acidity due to an higher transport of HNO_3. At a HNO_3 4 M conentration, the cesium flux was 10 % lowered real waste, this flux was included within the range of reproducibility of fluxes.

Table 8

Permeability coefficients obtained for Cs during transport experiments

Calixarenes	S_{eff} (cm^2)	time (h)	Cesium permeability (cm.h^{-1})	
			Feed compartment	back-extraction compartment
compound 1	12.6	13	0.66	0.72
compound 2	12.2	8.7	2.39	2.06
compound 3	12	9	2.19	2.67

Table 9

Membrane fluxes obtained for Cs during the transport experiments

Calixarenes	S_{eff} (cm^2)	time (h)	Membrane flux (mol.cm^{-2}.h^{-1})	
			Feed compartment	back-extraction compartment
compound 1	12.6	13	2.6×10^{-6}	3.1×10^{-6}
compound 2	12.2	8.7	6.7×10^{-6}	7.6×10^{-6}
compound 3	12	9	6×10^{-6}	6.7×10^{-6}

1,3-diisopropoxt-2,4 crown-6-calix[4]arene and 1,3-di(2-nitrophenoxy octyloxy)-2,4 crown-6-calix[4]arene gave better results than bis-crown-6-calix[4]arene (less lipophilic).

1,3- di (n octyloxy)-2,4 crown-6-calix[4]arene was diluted in 1,2 nitrophenyl hexyl ether (5.10^{-2} M) for the distribution coefficient measurements and transport experiments. The composition of the concentrate is given in Table 10.

Distribution coefficients of cesium exhibited 1,3-di-n-octyloxy-2,4- crown-6-calix[4]arene (Table 11) high affinity. The extraction and back-extraction percentages agreed with those obtained the high level liquid waste was decontaminated and were fairly satisfactory.

Table 11

Chemical and radiochemical composition of the real raffinate to reprocess [1]

Cations	g.l^{-1}	M	Anions	g.l^{-1}	M
Na	60	2.61	NO_3^-	340	
K	4.5	0.117	PO_4^{3-}	$1.7\ 10^{-3}$	
Mg	14.9	0.620	Cl$^-$	<0.1	
Ca	0.38	0.0095			
Al	0.5	0.0137			
Cr	0.05	0.000693			
Fe	0.98	0.0175			
U	1.3	0.00546			
Mo	<0.02	<$2.1\ 10^{-4}$			
Zn	0.07	$1.07\ 10^{-3}$			
Zr	<0.01	<$1.1\ 10^{-4}$			

Acidity : 1.05 M

Radioelements	Mbq.l^{-1}	mCi.l^{-1}
Pu 239 to 242	1.7	0.046
Pu 238 + Am 241	8.14	0.22
Cm 244	1.33	0.036
Cm 242	6.66	0.18
Sr 89 + 90	648	17.5
Co 60	3	0.1
Ru 106	720	19.5
Sb 125	40	1.1
Cs 134	180	4.9
Cs 137	3200	86.5
Ce 144	350	9.5
Pr 144	350	9.5
Eu 154	9	0.2

Table 11

Cs decontamination of the real effluent by liquid-iquid extraction

	Extraction		Back-extraction	
	D_{Cs}	% Extraction	D_{Cs}	% back-extraction
134Cs	15.8	91.1	4.37	17.3
137Cs	14.3	89.2	4.27	18.1

feed solution : TBP washed effluent, organic solution : calixarene octyl 5.10^{-2} M/NPHE, back-extraction : demineralized water.

Only residual plutonium after TBP washing and potassium are noticeably co-extracted. Sodium is not extracted at all and the Cs/Na selectivity is confirmed. Potassium is co-extracted but does not prevent Cs extraction.

The real effluent was introduced after TBP washing and acidification to 1 M HNO_3 in the central compartment of the double membrane system. (The 2 membranes contain the calixarene octyl 5.10^{-2} M diluted in NPHE). This two membrane device was used to reduce the duration of transport.

After 9 hours, practically all the cesium was transferred. Other elements were left in the feed solution. The tremendous selectivity of crown 6 calix[4]arenes was demonstrated by the decontamination factors higher than 50 or 100 (Table 12), except in the case of residual plutonium. The symetric behaviour of feed and strip concentrations confirmed that there was no cesium retention inside the membranes.

Permeabilities, reported in the Table 13, pointed out the transport's efficiency..

Table 12

Real effluent Cs decontamination by SLM. Solutions after 9 hours contact.
Decontamination factors of Cs

Element X	D.F
239-242Pu	2.5
238Pu + 241Am	148 $\cong$ >100
244Cm	154 $\cong$ >100
242Cm	803 $\cong$ >100
134Cs	-
137Cs	-
Na	>100
K	>105 $\cong$ >100
Mg	380 $\cong$ >100
Ca	58.7
Al	40.7
Fe	>1750 $\cong$ >100
Zn	>302 $\cong$ >100

Feed solution : real effluent after TBP washing and acidified to 1 M (HNO₃) , organic solution :
crown calixarenes 5.10^{-2} M/NPHE, back-extraction solution : demineralized water, double membrane system.

Table 13

Cs transport from a real effluent. Permeabilities according to Danesi
(calculated for the 4 first hours of the transport)

	Cs 137	Cs 134
Right	1.65	1.70
Left	1.62	1.71
Right + Left	3.27	3.41

Feed solution : real effluent after TBP washing and acidified to 1 M (HNO₃),organic solution : crown
calixarene 5.10^{-2} M/NPHE, back-extraction solution : demineralized water, double membrane system

CONCLUSION

Studies carried out with several calixarenes display the interest of using calix[4]crowns. These compounds are much more efficient than crown ether for the extraction of cesium from acidic medium and exhibit a tremendous selectivity cesium/sodium, moreover the extraction is reversible, cesium can be recovered in demineralized water, this property allows volume of waste to be strongly decreased. Some preliminary tests indicating a good stability towards irradiation of calix[4]arene crown 6 must be confirmed. Calix[4]arenes seem very promising for the removal of ^{137}Cs from liquid containing sodium salts at high concentration and also for the selective separation of ^{135}Cs before transmutation or disposal in a specific matrix.

ACKNOWLEDGMENTS

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PARTITIONING OF MINOR ACTINIDES FROM RARE EARTHS BY SOLVENT EXTRACTION WITH DI(2-ETHYL HEXYL) PHOSPHORIC ACID

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ABSTRACT

A flowsheet of the solvent extraction process to separate minor actinides(MA) from rare earths(RE) was devised and experimentally tested. The process is based on the high extractabilities of minor actinides and rare earths by di(2-ethyl hexyl) phosphoric acid at low nitric acid concentrations. The extraction process, composed of one extraction and three selective strippings in series, was installed with four miniature mixer-settler banks of a total of 44 stages in a glove box. The operation was performed by using a simulated waste solution containing 15 inactive compounds as the stands-in for rare earths and other fission products, and ^{241}Am and ^{237}Np as radioactive tracers for the minor actinides. For each element fed to the extraction bank, more than 99% of Am, Np, and rare earths were extracted by 1M HDEHP/n-dodecane. Then each of the Am, Np, and RE was selectively back extracted into the aqueous phase by 0.05M DTPA, 6M HNO$_3$, and 0.5M H$_2$C$_2$O$_4$, respectively, in consecutive stripping processes. In these steps, 99.8% of Am, 97~99% of rare earths elements and 99.4% of Np were separated from one another. The Am and Np products, however, may require further purifications because of other impurities accompanied these elements into their respective product streams.

BACKGROUND ON PARTITIONING & TRANSMUTATION STUDIES IN KOREA

In Korea, 11 nuclear reactors (10 PWRs and 1 CANDU) are currently in operation with total generating capacity of 9.6 GWe. In addition, 7 reactor units are under construction which will be completed in the years from 1997~2002. Accordingly, the total nuclear generating capacity will reach 15.7 GWe in the year 2002. The amount of spent nuclear fuels annually arising from the current operating reactors accounts for 280 MTHM and the cumulative amount reaches about 2800 MTHM (PWR 1600, CANDU 1200 MTHM). The spent fuels are now in storage at each reactor site. However, they are to be stored at a central interim storage facility for the time being before they are reprocessed or disposed of. This program addresses the national policy of just "wait & see" because the procedure for a back-end fuel cycle has not been established yet.

Reactor wastes, namely, low-level wastes are also in storage at each reactor site. They will be disposed of in a final repository in the future. For the last 10 years, lots of effort has been devoted to find a candidate repository site in the midst of strong anti-nuclear movement throughout the country. As a result, a tiny island in the west sea was determined as the candidate site in 1995. However, it was immediately canceled because an active fault was discovered near the island in the survey of geological characteristics. Consequently, the national program on radwaste disposal has changed in that the project should be transferred to the Korea Electric Power Corporation from the Korea Atomic Energy Research Institute (KAERI).

At present, we have no high-level wastes in Korea because we do not have any fuel recyling activities. However, it might be necessary in the future to complete the nuclear fuel cycle in view of the Korean situation, that is, it depends not only on import for almost all of its energy resources, but also on nuclear energy for the major part of its electricity generation. In addition, the amount of spent fuels accumulated will increase year by year. Moreover, it might become more and more difficult to get public acceptance for the direct disposal of the spent fuels in the Korean peninsula. An alternative prospective solution for this might be the transmutation of long-lived radionuclides.

Though several countries are planning to dispose of vitrified high-level wastes at a deep underground repository, there are no countries yet in the world which have put it into action. In fact, even the enviromental impact of high-level wastes disposal has not been fully elucidated yet. Actually, there is lots of concern as to whether they can be sustained without the release of radioactive material to the biosphere for hundreds of thousands of years when buried in the geologic repository. In this

respect, it would be attractive to convert the long-lived radionuclides into short-lived or stable nuclides. Residual waste management after transmutation could result in the reduction in the final disposal cost at hand, as well as in the possible contamination of the environment in the future.

With this background in Korea, both partitioning and transmutation studies are being carried out in preparation for future application. In parallel with this, the development of high-level wastes disposal technology is also being performed in KAERI. The future objective facilities for transmutation in Korea include a liquid metal reactor, and an accelerator-driven subcritical reactor (the same as a few other countries). A research project on the former is being carried out with the target of proto-type reactor completion by 2011. As to the latter, a new research program is under planning in order to establish a concept of the reactor.

A study on partitioning is also being conducted with simulated waste solutions in KAERI focused on the development of MA, Cs, Sr and Pt-group metals separation methods. It is also considered to include such research area in the near future as thorium fuel cycle with pyroprocessing which is known as an alternative fuel cycle favorably applicable to the subcritical reactor.

INTRODUCTION

Most of minor actinides contained in the typical high-level liquid waste (HLLW) from reprocessing of spent nuclear fuels are composed of long-lived radionuclides. These radionuclides, if they are intended to be transmuted, must be separated from HLLW and then made into the form of target for transmutation.

One of the prospective methods to recover MA from HLLW is the extraction of them at low nitric acid concentrations using di(2-ethyl hexyl) phosphoric acid (HDEHP) as an extractant [1~6]. In this process, however, most of RE and MA have similar properties in their extractability and thus RE elements are accompanied with MA in the organic phase. Another process for the mutual separation of MA and RE is, therefore, necessary to recover the MA alone. A representative process to separate Am and Cm from RE is the reverse-TALSPEAK process [1,6] where Am and Cm can be selectively stripped from the organic phase of HDEHP by di-ethylenetriamine pentaacetic acid (DTPA). As for Np, it exists in the state of Np (IV), Np(V), and Np(VI) in nitric acid solution by the disproportionation. The extractability of Np(IV) or Np(VI) with HDEHP is high without regard to the nitric acid concentration, whereas that of Np(V) is much lower. These properties lead to the possibility of separation of Np from either Am or RE. However, Np tends to have

TABLE 1. CHEMICAL COMPOSITION OF THE SIMULATED WASTE SOLUTION

Component		Concentration
TRU	^{241}Am	5.90×10^4 Bq/ℓ
	^{237}Np	1.66×10^4 Bq/ℓ
RE	Eu	1.05×10^{-3} M
	La	2.96×10^{-2} M
	Ce	3.47×10^{-2} M
	Nd	5.07×10^{-2} M
	Y	7.90×10^{-3} M
FP	Cs	3.48×10^{-2} M
	Ba	2.37×10^{-2} M
	Rb	7.72×10^{-3} M
	Pd	6.58×10^{-3} M
	Fe	2.02×10^{-2} M
	Ni	4.09×10^{-3} M
	Mo	1.36×10^{-2} M
	Sr	2.08×10^{-2} M
	Zr	4.82×10^{-5} M
	Rh	4.66×10^{-3} M
Media	HNO$_3$	0.1 M
	H$_2$O$_2$	1.0 M

Apparatus for Extraction and Stripping

Four banks of miniature mixer–settler made of acrylic plastic were used for extraction and selective strips. The volume of each mixer, same with that of settler, was 13 mℓ. Like conventional mixer–settlers, this apparatus was also fabricated so that the aqueous and organic phase move in counter-current flow. Air pulsation produced by a membrane type pulse generator and distributed to each mixer through a pulse header was used to mix aqueous and organic phases. All the four banks of mixer–settler, as shown in Fig. 1, were installed inside an α-tight glove box in order to shield the α activities of ^{237}Np and ^{241}Am. Whenever they are started to run, blank-operation was carried out for over 4 hours by feeding 0.1 M HNO$_3$ instead of the simulated solution and by adjusting the interface level in the settlers so that they can reach an optimal hydraulic condition in advance. Then the regular operation was started by switching the feed to the simulated solution.

more stable form of Np(V) in larger proportion at lower concentration of nitric acid and thus it is necessary to reduce it to the state of Np(IV) or to oxidize to Np(VI) in order to extract it into the organic phase. These characteristics make it possible to combine a few unit processes to a probable process for the partitioning of Am, Cm group, RE group and Np one another. On the basis of the above concept, a partitioning process constituted of one extraction and three selective stripping was drawn out and its validity was experimentally tested in this study. The experiments were conducted with a simulated waste solution containing 17 metal elements. The simulated solution was prepared with 15 inactive compounds as the stands-in for RE and other fission products, and with tracers of ^{241}Am and ^{237}Np as the stands-in for Am and Np, respectively. Four banks of miniature mixer-settler with a total of 44 stages were used for extraction as well as selective stripping apparatus. The stripping agents, DTPA, HNO$_3$ and H$_2$C$_2$O$_4$ were respectively employed for back extraction of Am, RE and Np.

EXPERIMENTAL

Preparation of a Simulated Waste Solution

A simulated waste solution was prepared to contain major metal components of the typical high-level liquid waste from the reprocessing of spent fuels. Inactive compounds of rare earths, Fe, Ni, Mo, Sr, Zr, Cs, Ba, Rb, Pd and Rh were dissolved in the medium, 0.1 M HNO$_3$, in order that they have similar concentrations to those of the high-level liquid waste. Trace amounts of ^{241}Am and ^{237}Np were also added to the solution as stands-in for minor actinides, to track the behaviors of Np, Am and Cm in the partitioning process. Hydrogen peroxide [7, 8] was added to the stock solution to control the oxidation valence of Np as Np(IV) because it has higher extractability with HDEHP. Chemical composition of the simulated waste stock solution is illustrated in Table 1.

Extraction of TRU and RE

A 14-stage bank (A1) as shown in Fig. 1 was used for extraction. The simulated solution (aqueous feed), 0.1 M HNO₃ (scrub) and 1M HDEHP/ n-dodecane (extractant) were respectively injected into the 10th, 14th and 1st stage. The operation conditions of the banks are listed in Table 2.

TABLE 2. FEEDING MATERIALS AND THEIR FLOW RATES IN EACH BANK

Bank No.	Feed	Feeding stage	Flow rate($m\ell/hr$)
A1	① : simulated waste	10	80
	③ : 0.1 M HNO₃	4	15
	② : 1M HDEHP	1	80
A2	④ : loaded HDEHP	5	80
	② : 1M HDEHP	1	15
	⑦ : 0.05M DTPA in 1.5M Lactic acid	14	95
A3	⑥ : loaded HDEHP	1	95
	⑪ : 6M HNO₃	8	30
A4	⑧ : loaded HDEHP	1	95
	⑮ : 0.5M H₂C₂O₄	8	95

Stripping of Am

A 14-stage bank(A2) was used to strip Am from the organic phase. 0.05M DTPA and 1.5 M lactic acid mixture (pH : 3.1) [9] was fed to the 14th stage as a stripping agent while the organic feed containing MA and RE was supplied to the 5th stage. 1M HDEHP/n-dodecane, injected to the 1st stage, served as the scrubber of aqueous stream by extracting Np and RE again to the organic phase.

Stripping of RE

RE elements were stripped from the organic phase by 6 M HNO₃ in the 8-stage bank A3. In this bank, only RE were selectively washed out to the aqueous phase leaving Np still in the organic phase.

Stripping of Np

Finally Np was stripped from the organic phase by 0.5 M $H_2C_2O_4$ [10] through the 8 stages of the bank A4. The Np-loaded solvent was injected into the 1st stage while oxalic acid was fed into the 8th stage.

Chemical Analyses

Radioactivities of ^{237}Np and ^{241}Am were measured using a multichannel analyzer (Afora Model LP-4900B) with Ge(Li) detector. Since the elements Ba, Sr, Eu, La, Zr, Ce, Nd and Y are inactive, their concentrations were obtained by an Inductive Coupled Plasma Spectrophotometer. The concentrations of Cs, Rb, Fe, Ni, Pd, Mo and Rh were measured with an Atomic Absorption Spectrophotometer (Hitachi Model 180.80).

Solvent Regeneration

The used solvent, containing Fe and mono-ethylhexyl phosphoric acid (H₂MEHP) as the major degradation components, was washed with the mixture of 5% $(NH_4)_2CO_3$ and 2M manitol.

Definition of Relative Concentration

In order to evaluate the state of extraction or stripping of a metal component, the relative concentration (C*) of the metal component concerned was defined as follows :

$$C^* = \frac{M_i \cdot F_i}{M_f \cdot F_f} \tag{1}$$

M : concentration of the metal component (Bq/ℓ or mole/ℓ)
F : flow rate (mℓ/hr)

where the subscripts f and i denote feed stream to the bank A1 and internal stream in the corresponding bank, respectively.

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RESULTS AND DISCUSSION

Extraction of TRU and RE

Over 99 % of Am and Np were found to be extracted by 1M HDEHP/n-dodecane in the bank A1. The contents of Np and Am released to the raffinate were less than 50 Bq/ℓ which were the measurable limits of radioactivity. Fig. 2 shows the steady state concentration profiles of Am, Np, and Eu for the relative concentrations as defined in Equation (1). The high extractability of Np was due to the valency control of Np (Np(V) $\rightarrow$ Np(IV)) by means of H_2O_2.

Among the impurities contained in the stream of Np and Am, the major ones were found to be RE, Zr, Mo and Fe because 99% of RE, Zr and Fe and 97.8 % of Mo were extracted into the organic phase together with Np and Am. Though Ba, Ni, Sr, Cs, Rh, Pd and Rb were also accompanied into the organic phase, their contents lay within the range of only 1 ~ 4 % out of the quantities in the feed. Since these impurities tend to cause the forming of the third phase, it would be quite desirable to remove them prior to the solvent extraction.

Selective Stripping of Am

Experimental results show that 99 % of Am was selectively stripped from the organic phase in the bank A2. Fig. 3 shows the steady state aqueous concentration profiles of Am, Np, and Eu in the aqueous phase of the bank A2. Np content in the aqueous outlet stream was measured as less than 50 Bq/ℓ assuring that Am and Np can be mutually separated by this selective strip. However, 2.3 % of RE, 7 % of Fe, 85 % of Mo and 0.01~ 2 % of Ba, Ni, Sr, Cs, Rh, Pd and Rb were accompanied with Am into the aqueous outlet stream. Among the RE elements, Eu showed the largest portion of stripping by displaying 2 % of the original amount in the feed was liberated to the aqueous phase, which is over 100 times higher than those of other RE elements. These experimental results show that additional purification procedures must be introduced if pure Am product is required.

Selective Stripping of RE

Since the distributions of all RE elements by 1 M HDEHP/n-dodecane are very low at high nitric acid concentrations, the loaded RE could be stripped with 6 M HNO_3. Experimental results show that over 98 % of RE were stripped whereas other elements, Np, Ba, Ni, Sr, Cs, Rh, Pd and Rb, were washed out by only 0.01 ~ 2 %. Fig. 4 shows the steady state aqueous concentration profiles of La, Nd, Y, and Np in the bank A3. When the aqueous concentration profiles of La, Nd and Y are compared

one another, as shown in Fig. 4, they represent almost same pattern of profiles meaning that RE elements have very similar behaviors in the extraction and the strippings.

Stripping of Np

The Np loaded in the organic phase was finally stripped with 0.5 M $H_2C_2O_4$. More than 99.4 % of Np was stripped back into the aqueous phase accompanying 6.6 % of Fe whereas other elements were back extracted from the organic phase by less than 0.1%. The steady state aqueous concentration profile of Np in the bank A4 was illustrated in Fig. 5.

Composition in the Aqueous Outlet Stream of Each Bank

The aqueous outlet streams of the bank A1 and A3 correspond to raffinates while those of A2 and A4 correspond to products. The compositions of these outlet streams, expressed as relative concentrartions of the unit of percentage ($C^* \times 100$), are given in Table 3. The Am product stream of the bank A2 shows that 99.8 % of Am was recovered from the original simulated waste. However, it contains appreciable amounts of impurities such as 86.4 % of Mo and 7.3 % of Fe. The Np product stream of the bank A4 also shows that 99.4% of Np was recovered, however, containing 6.6 % of Fe as the only considerable amount of impurity.

Solvent Regeneration

The Fe still left in the organic phase was favorably removed by treating with the washing agent mentioned earlier. However, the H_2MEHP, one of the degradation products of HDEHP, was removed only in part from the used solvent.

TABLE 3. THE RELATIVE CONTENTS OF THE VARIOUS ELEMENTS
IN THE AQUEOUS OUTLET STREAM OF EACH BANK (Unit : %)

Element	A1 (Raffinate)	A2 (Am product)	A3 (RE stream)	A4 (Np product)
Am	0.03	99.83	0.04	0.02
Np	<0.31	<0.31	0.34	99.37
La	0.01	trace	98.1	trace
Ce	trace	0.08	99.7	"
Nd	"	0.03	99.7	"
Y	0.02	0.03	99.4	0.01
Eu	0.08	2.32	97.5	0.09
Cs	98.75	1.05	0.06	trace
Rb	98.18	0.32	0.11	"
Ba	98.65	0.05	0.03	"
Sr	98.24	0.16	0.2	"
Pd	99.43	0.43	0.86	"
Rh	97.5	0.48	0.77	"
Fe	0.51	7.26	0.08	6.58
Ni	96.2	1.73	1.11	trace
Mo	2.2	84.61	0.77	0.01

trace : < 0.01

CONCLUSIONS

It was shown that the Am and Np, can be effectively recovered from the simulated waste solution by extraction with HDEHP followed by selective strippings. In addition, Am, Np, and RE could be independently separated from each other. As a result, the recovery ratios of Am and Np were found to be 99.8% and 99.4%, respectively. However, the Am and Np products were carrying some amounts of impurities, that is, 7.3% Fe and 84.6% Mo in the former, and 6.6% Fe in the latter, with respect to the original quantities contained in the feed. 97.5 ~ 99.7% of rare earth elements were removed into the RE outlet stream of the bank A3.

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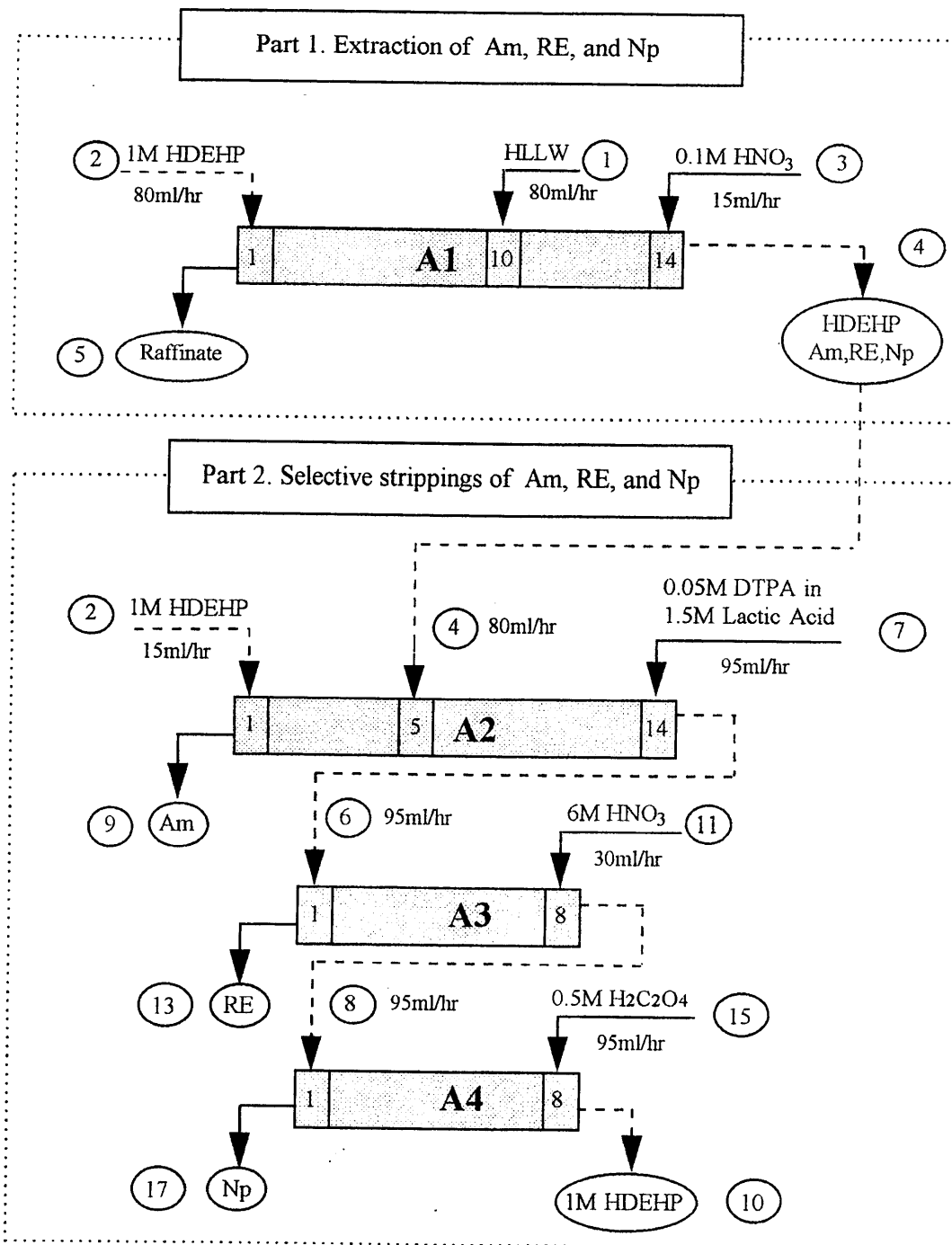
Figure 1. Flowsheet for respective partitioning of Am, RE and Np
by extraction with HDEHP and selective strippings
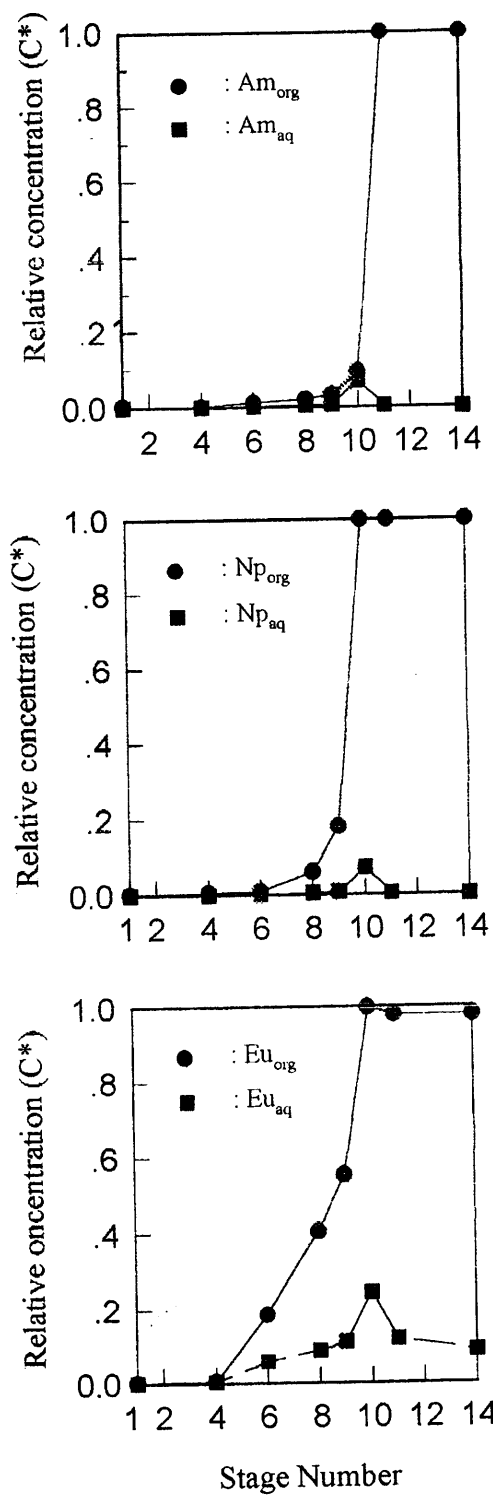
Figure 2. Concentration profiles of Am, Np, and Eu in the organic and aqueous phases of the bank A1
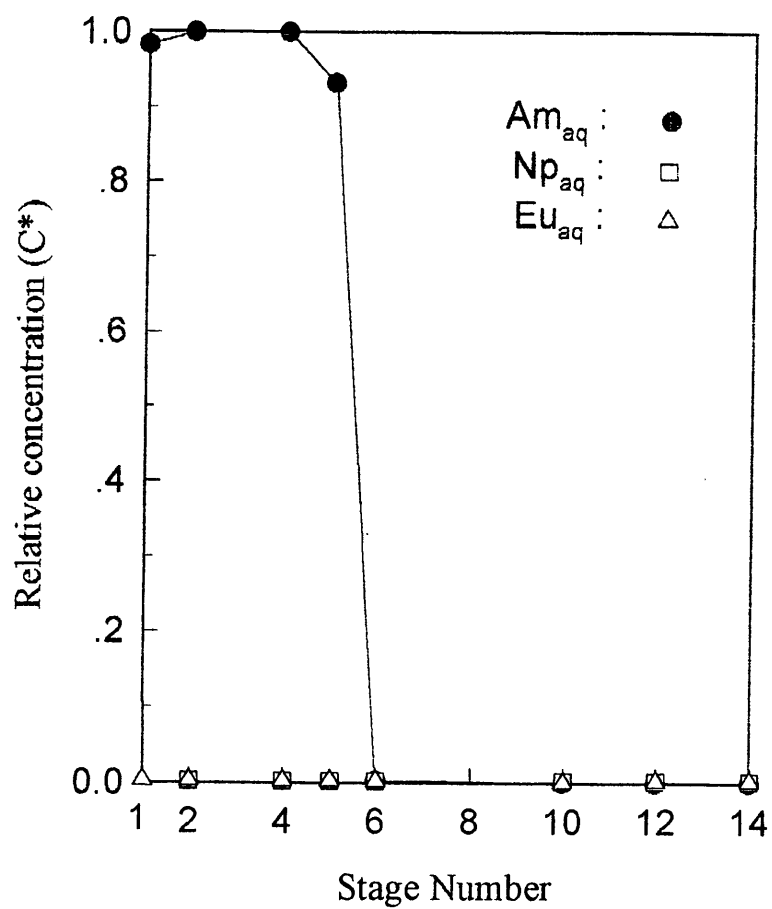
Figure 3. Concentration profiles of Am, Np, and RE in the aqueous phase of the bank A2
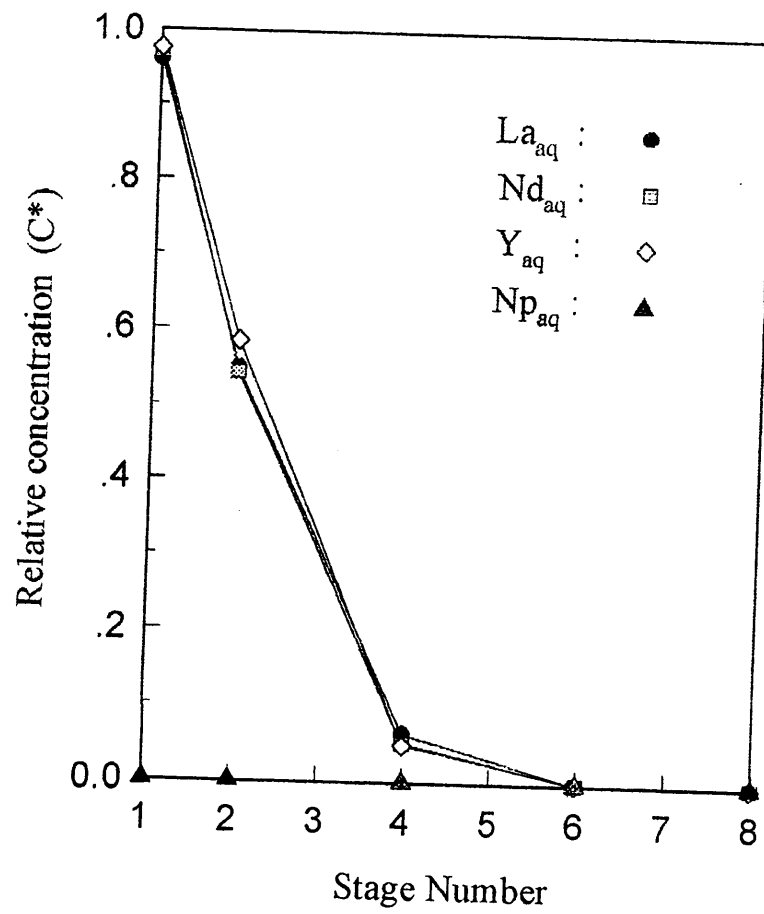
Figure 4. Concentration profiles of RE(La, Nd, Y), and Np in the aqueous phase of the bank A3
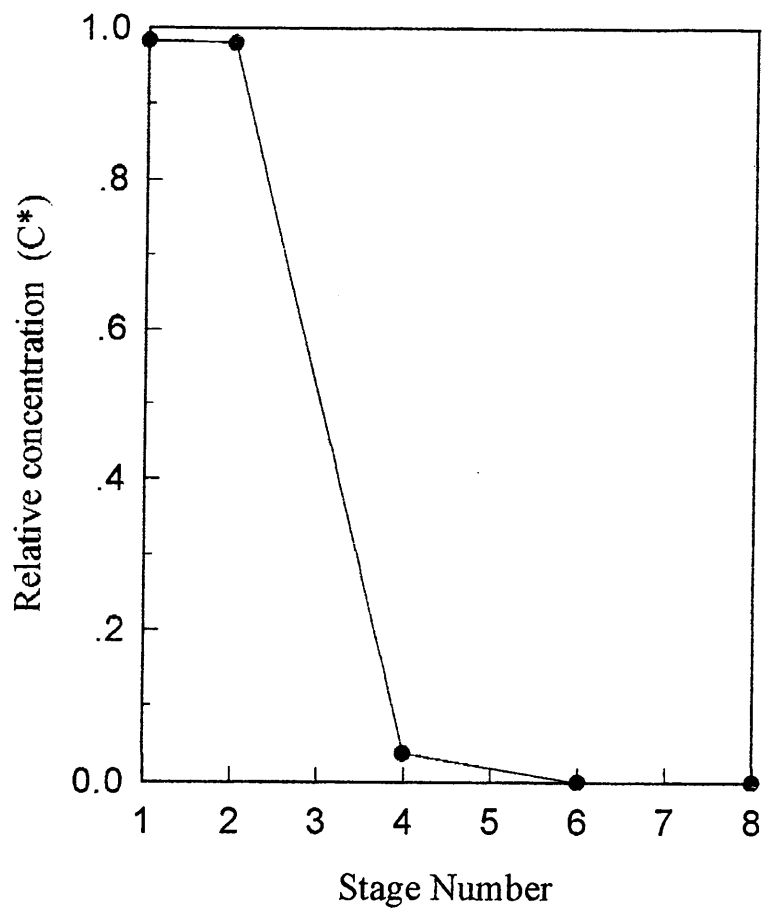
Figure 5. Concentration profile of Np in the aqueous
phase of the bank A4

PYROMETALLURGICAL PROCESSING TECHNOLOGY DEVELOPMENT

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ABSTRACT

Current status of development of pyrometallurgical reprocessing technology by CRIEPI was summarized. As for the electrorefining process, three different electrodes were developed for getting higher process efficiency. The prismatic anode basket which rotates during electrorefining was found to accelerate the fuel dissolution. Collection efficiency and morphology of electrodeposited uranium on steel mandrel cathode was found to vary with anode/cathode area ratio. Paddle-shaped stirrer was developed for liquid cadmium cathode which collects TRUs and uranium simultaneously. Optimal operational conditions such as cathode current density and Reynolds number of stirring were determined for collecting uranium without forming dendrite. As one of the promising way to immobilize the water-soluble salt waste, to synthesize natural occurring mineral which contain halide salt in three dimensional cage structure was proposed. Measured leachability from synthesized mineral which contained FP simulating elements was as low as those from vitrified waste form.

I. INTRODUCTION

As the most promising way to reconcile safety and economy, Central Research Institute of Electric Power Industry (CRIEPI) have been focusing on the metal fuel cycle (MFC) that originally developed by Argonne National Laboratory.[1] Pyrometallurgical reprocessing combined with injection fuel casting gives the key features such as compactness, economy and diversion resistance to the MFC[2][3]. CRIEPI has been studying MFC technology since 1986 in order to establish the technical basis of MFC[4][5][6]. Presently, applicability of pyrometallurgical technology is extended around the fuel cycle, as shown in Fig. 1. In this presentation, current status of technological development of the pyrometallurgical processing shown in Fig. 2 was summarized with emphasis on the molten salt electrorefining and waste salt immobilization.

II. ELECTROREFINING PROCESS

An operational sequence of electrorefining step is schematically shown in Fig. 3[2]. The chopped spent metal fuels or reduced oxide fuels are loaded into an anode basket, and actinides are anodically dissolved. They are reduced and collected at two types of cathodes. One is a solid cathode which collects essentially pure uranium, and another is a liquid cadmium cathode where all of the actinides (uranium, plutonium, neptunium, americium and curium) are recovered. Chemically more active FPs such as cesium, barium, cerium, etc. accumulate in the electrolyte salt in the forms of their chlorides. Less active FPs such as ruthenium and

molybdenum remain in anode basket or fall into liquid cadmium layer at the bottom of the electrorefiner. Development of each electrode in the electrorefiner is described bellow.

A. Anodic Basket for Fuel Dissolution

Anode basket should offer good contact between chopped fuel pins and fresh bulk electrolyte to prevent accumulation of oxidized actinides in the electrolyte around fuels and to facilitate transport of them[7]. Hence, two types of anode baskets with different configuration of perforated stainless steel panels were tested. Fig. 4 shows the dissolution rate of uranium segments, 10 mm in diameter and 20 mm in length, charged in these baskets. The higher anode current efficiency was obtained for the prismatic baskets arranged at right angles. It was also found that the dissolution rate is increased with faster rotation of anode baskets.

B. Solid iron cathode for uranium recovery

Due to the highest redox potential among actinides and chemically active FPs[8], uranium predominantly deposits on solid (steel) cathodes. Uranium electrotransport tests were carried out with various concentration of uranium in the electrolyte salt by using the steel cathodes in three different diameters. No deposit was collected on any cathodes at lower concentration (about 0.5 wt%), while dendritic deposits were obtained for any cathodes at higher concentration (about 2.0 wt%). Fig. 5 shows the photographs and the collection efficiency of these deposits. With using the cathode of 15 mm dia. where anode to cathode area ratio was 10.8, needles of the dendritic deposit were thin, long and likely to be broken off from the cathode. That seems to be why the collection efficiency was extremely low in this case. In the case of 30 mm dia. cathode where anode to cathode area ratio was 5.4, the dendrite was much more adherent so that the collection efficiency was quite better. When cathode area was increased further to diameter of 70 mm where anode to cathode ratio was 2.3, concentration polarization was arose at the liquid cadmium anode and the transport of uranium was interrupted, although collection efficiency was fairly good.

C. Liquid cadmium cathode for TRUs recovery

When liquid cadmium cathode is used, TRUs are collected together with uranium because of their significantly reduced chemical activities in liquid cadmium[8]. One of the problems regarding to the liquid cadmium cathode is the formation of dendritic uranium[9]. When uranium deposits faster than it is taken into the bulk cadmium, uranium dendrite forms at the surface of the cathode as shown in Fig. 6. Once the dendrite grows up, current is concentrated on it and liquid cadmium cathode works as a solid cathode where only uranium continues to deposit.

In order to avoid this problem, stirring of cathode cadmium was considered to facilitate the transport of uranium in cathode cadmium from surface to the bulk. Suitable conditions for depositing uranium on stirred liquid cadmium cathode have been studied by using the puddle shaped stirrer. Fig. 7 shows the effect of stirring with different cathode current density on dendrite formation. The height of each bar indicates how much uranium can be collected without liquid cadmium cathode before dendrite begins to grow up. It shows much

more uranium can be collected without forming dendrite with more impetuous stirring[10]. In these tests, uranium was collected up to 10 wt% into the cathode with current efficiency of approximately 100 %.

D. Computer code development for design optimization

(i) simulation of electrochemical behavior

Practically, conditions for electrorefinig operation such as composition of the spent fuel and of electrolyte salt cannot be kept constant. Hence, a computational code, TRAIL, was developed for analyses and prediction of the electrotransport behavior of elements in various condition[11]. This code employs diffusion-limited electrochemical reaction model described in Fig. 8. A comparison between actual result of the electrotransport test of uranium and plutonium reported by ANL[12] and calculation is shown in Fig. 9. Good agreement between composition of the cathode products in both cases indicates that the behavior of each element in electrorefining step can be predicted by this code.

(ii) potential distribution calculation of specific electrorefiner

Decrease of the cell resistance is necessary for developing high throughput electrorefiner. Cell resistance strongly dependent on the geometrical configuration of the electrodes in the electrorefiner. Hence, a computational code, CAMBRIA, was developed for analyses of the cell resistance of the electrorefiner with various electrode configuration.[13] This code enables to calculate the 2-dimensional potential distribution and current distribution in the electrolyte by solving the Laplace equation with using Finite Element Method. It should be noted that this code calculates the configuration resistance without polarization. As shown in Fig. 10, however, it works well for rough prediction of the cell resistance.

III. IMMOBILIZATION of SALT WASTE

Salt waste generated at electrorefining step contains much amount of chemically active FPs such as alkali, alkaline earths, and iodine in the form of halides. Because these halides are highly soluble into water, this salt has to be converted into a stable chemical form for disposal. Alkali halides and alkaline halides are, however, hard to be converted directly into oxides, and to be dissolved into bolosilicate glass in high concentration. Hence, method to immobilize waste salt has to be developed. At present, two different immobilization methods are under study in CRIEPI. One is an electrolysis of waste salt into metal and chlorine gas followed by vitrification. It is found that the use of different cathode materials made it possible to separate the radioactive elements from nonradioactive base salt. The detail of the experimental results of this method will be reported in this conference[14]. Another method is to synthesize natural occurring mineral that contains halide salt stably in it's structure from the waste salt[15]. The three dimensional sodalite structure (Fig. 11) was found to be synthesized according to the following dry reaction,

$$6NaAlO_2 + 2NaCl + 6SiO_2 \Rightarrow Na_8[(AlO_2)_6(SiO_2)_6]Cl_2, \tag{1}$$
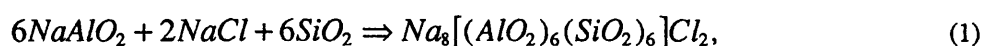
where a mixture of $NaAlO_2$, SiO_2 and simulated waste salt were pressed at 200 MPa and heated at a temperature of 973 - 1173 K for 50 - 100h. Products were identified as of sodalite structure by X-ray diffraction. Leachability was measured for the synthesized sodalite specimen before or after irradiation by γ-ray. As shown in Table 1, measured leachability of the relevant elements are as low as the values reported for vitrified waste form or zeolite form[16].

V. SUMMARY

Major progress and present status were summarized on electrorefining process and waste salt immobilization process. Although it is still in an early stage of development comparing to the conventional PUREX process, any problems regarding to actual application of pyrometallurgical processing technology was not found, yet. This technology was originally developed in the United States, however, CRIEPI is now planning to continue research and development activities to establish its practicability as an advanced reprocessing technology.

ACKNOWLEDGMENT

The authors wish to acknowledge the contributions from the joint study with Toshiba Corp. for electrorefining and Hitachi Ltd. for waste salt treatment. They also acknowledge the information exchange with Argonne National Laboratory about pyroprocess technology.

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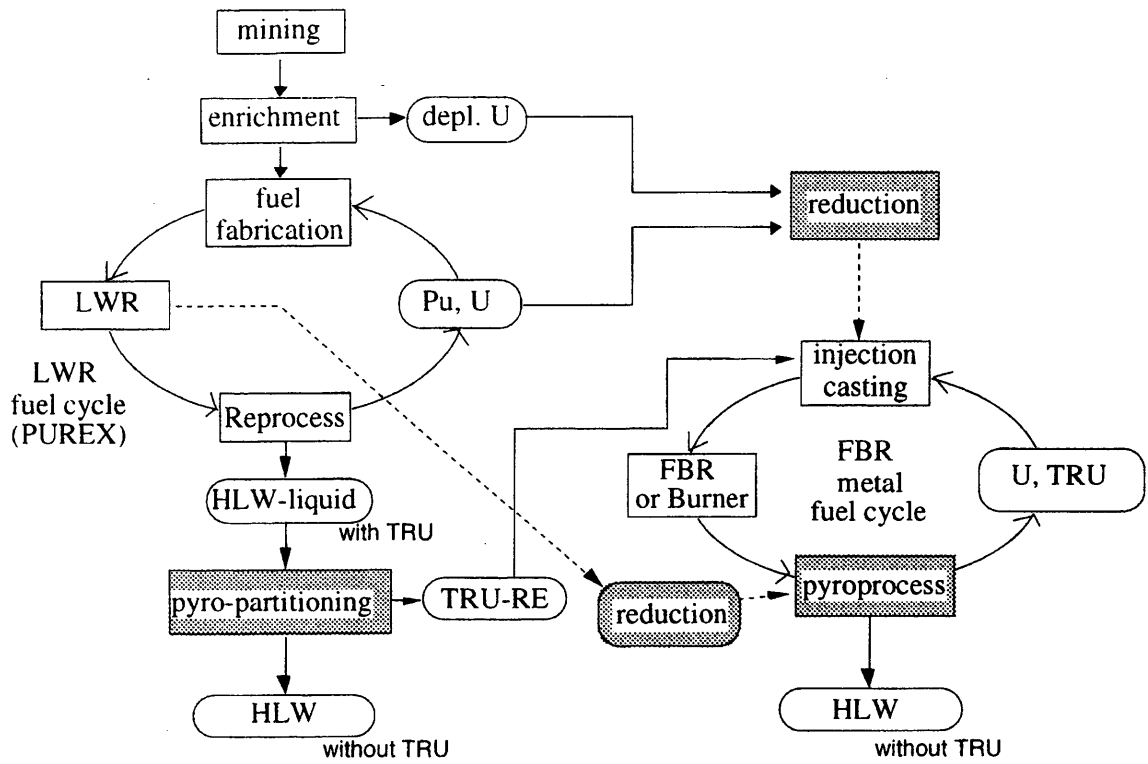[16] M. A. Lewis et al., *J. Am. Ceram. Soc.*, **76**(11), 2826(1993).

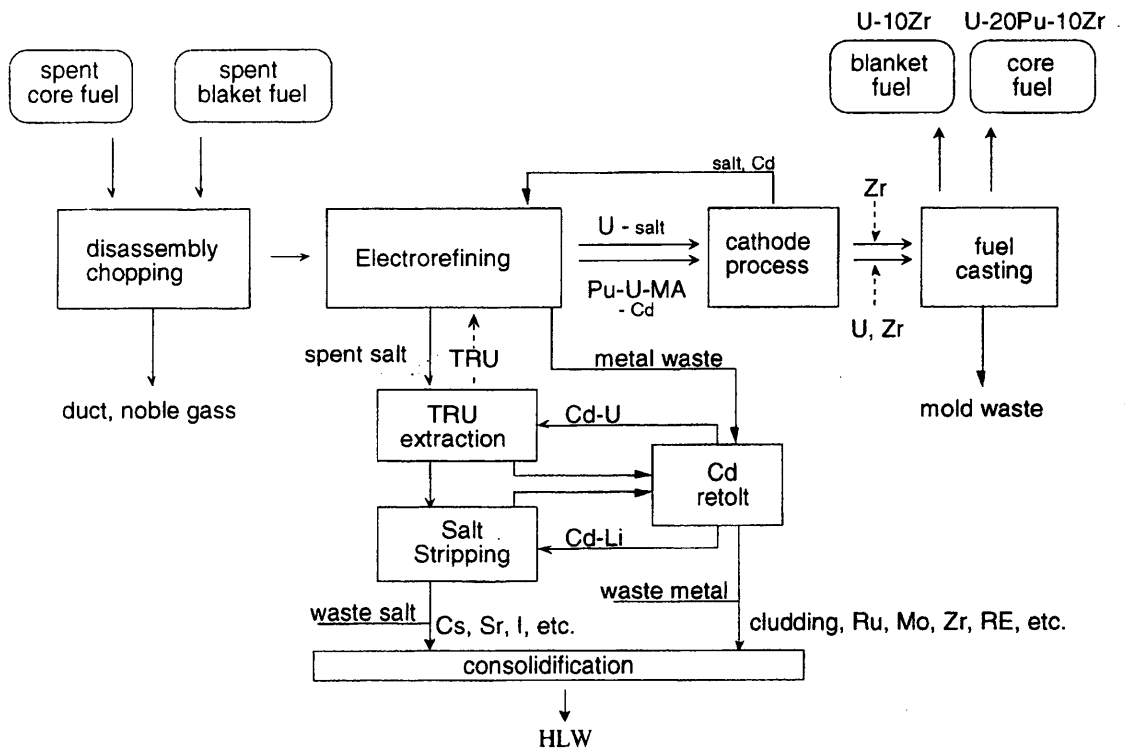Fig. 1 CRIEPI's PYRO program in fuel cycle.
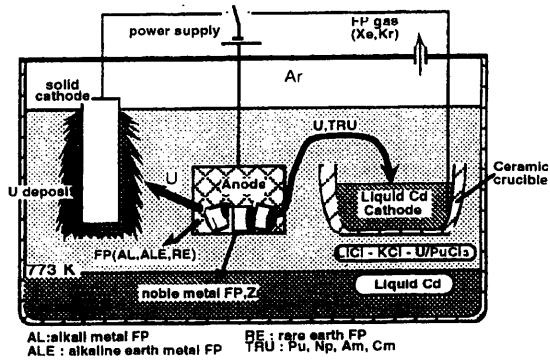
Fig. 2 Pyrometallurgical reprocessing process.

Fig. 3 Sequence of electrorefining process.

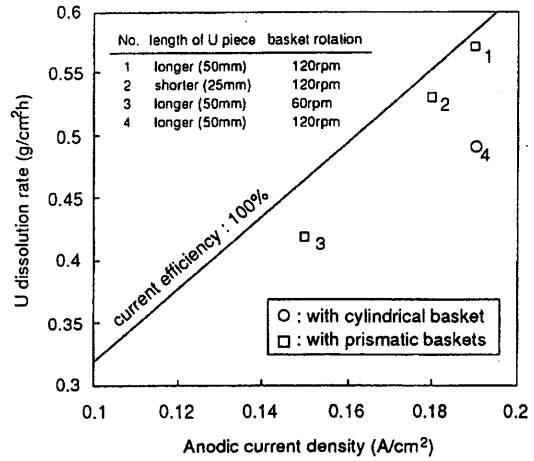Fig. 4 U dissolution rate with different anode baskets.

| anode/cathode area ratio | 10.8 | 5.4 | 2.3 |
| collection efficiency | 9.3 % | 77 % | 65 % |

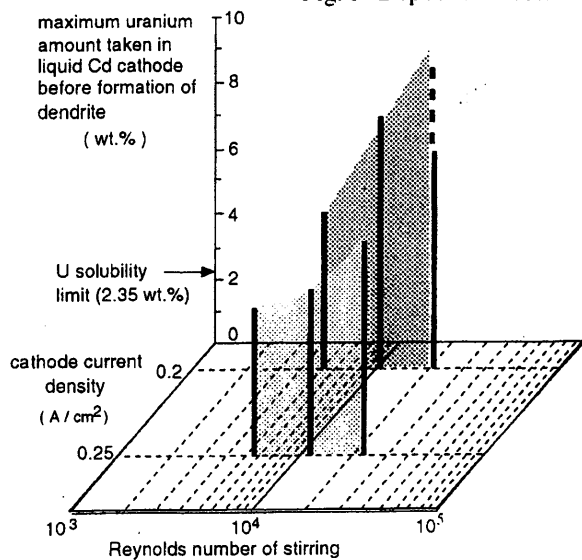Fig. 5 Deposits on solid cathodes of different diameter.

Fig. 6 Uranium dendrite on liquid cadmium cathode.
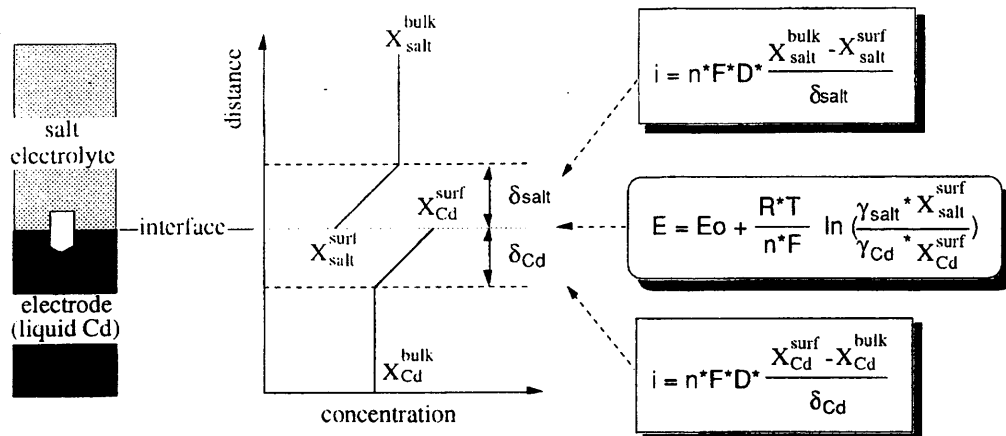

Fig. 7 Deposited U amount before dendrite iformation.

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Fig. 8 Model for ectrorefining simulation code.
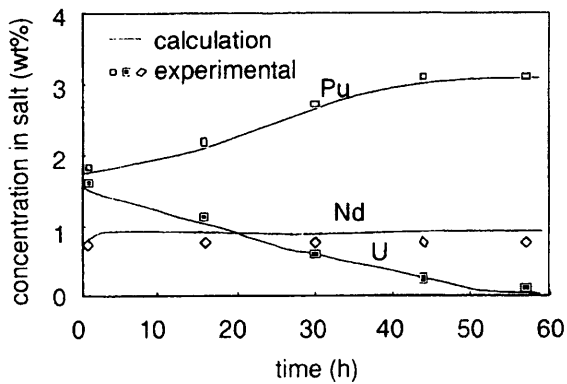
cell resistance
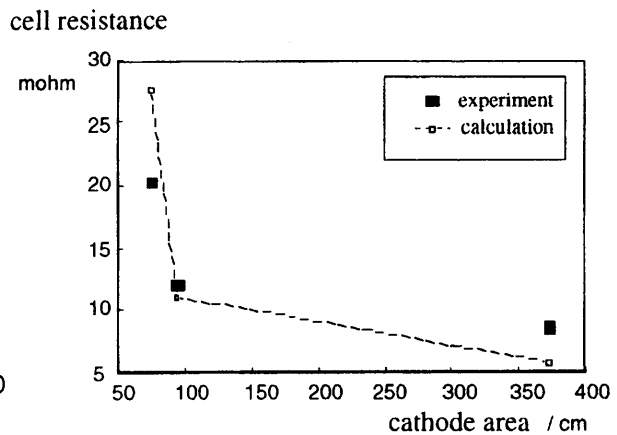

Fig. 9 Electrorefinig behavior reported by ANL.

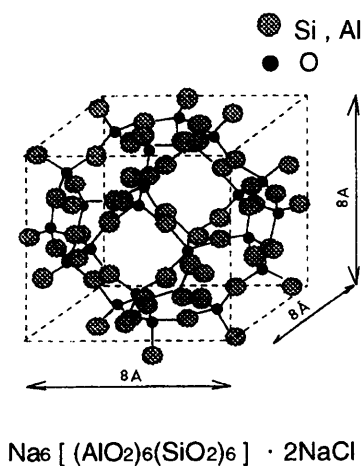Fig. 10 Cell resistance of electrorefiner.

Na₆ [(AlO₂)₆(SiO₂)₆] · 2NaCl

Fig. 11 Sodalite structure with 3-D cage.

Table 1 Leachability (g/cm²d) from sodalite, zeolite and glass.

	sodalite	zeolite *	bolo-silicate glass *
Li	0.0047	0.12	0.29
K	0.0061	0.031	0.22
Na	0.0023	0.018	0.28
Cs	0.0013	0.0066	NM
Sr	0.00035	< 1.0E-5	NM
Ba	0.000069	< 1.0E-5	NM
Al	0.0015	0.0048	0.14
Si	0.0017	0.0041	0.23
Cl	0.0022	NM	NM
I	0.0029	NM	NM

NM: not measured

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MINOR ACTINIDE SEPARATION

RECENT ADVANCES AT THE CEA

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ABSTRACT

In the frame of the french SPIN programme, R&D work has been undertaken at the CEA in order to develop minor actinides separation. The main route concerns solvent extraction processes, and in particular :
- PUREX process adjustment for Np selective recovery;
- DIAMEX process development for Am and Cm extraction from PUREX raffinate.

Important advances have been recently achieved, especially in the field of Am and Cm separation : optimization of diamide formula, flowsheet improvement to prevent FP extraction, progress in An(III)/Ln(III) separation using new extractants.

Main R&D results are presented and discussed.

1. INTRODUCTION

In December 1991, the French Parliament passed a law on research into radioactive waste management. One of its Articles required the "finding of solutions for the separation and transmutation of long-lived radionuclides present in high-level long-lived wastes". The law set a time limit of fifteen years.

This request is connected with the chemical separation of certain elements and radionuclides of spent fuels to transmute some of their long-lived radioactive isotopes liable to incur long-term hazards. The target elements of this strategy are primarily the so-called minor actinides (neptunium, americium and curium), due to their large contribution to the waste radiotoxic inventory after 1000 years.

Given the large amounts of irradiated fuels to be reprocessed, any valid separation process must be industrial, implying processes as reliable as possible, and always striving to minimize the doses to the personnel and the production of effluents and secondary wastes.

The field is hence limited by these restrictions. The CEA accordingly decided to develop original processes, by relying on considerable basic research conducted for a better understanding of the separation mechanisms. This paper reviews the methods selected and sheds light on recent developments.

2. PROBLEMATICS OF THE SEPARATION OF MINOR ACTINIDES

Irradiated fuel reprocessing by the PUREX process generates a high-level effluent containing all the soluble fission products and minor actinides. This effluent is concentrated today, and then, after interim storage of about one year, the elements it contains are encapsulated in a glass matrix which guarantees high-quality conditioning.

Table 1 lists the quantities of minor actinides contained in one ton of reference UOX fuel, irradiated to 33 GWd/t and cooled for three years.

element	isotope	half-life (years)	mass (g/t)
Np	237	2.1×10^6	430
Am	241	430	220
	243	7400	100
Cm	243	28	0.3
	244	18	24
	245	8500	1

Table 1 : Minor actinides contained in reference UOX fuel

It is important to develop separation processes whose feasibility can be proved before 2006, the deadline set by the law. It was decided to assign priority to developing liquid/liquid extraction processes, which are extremely efficient and could be integrated with the present PUREX process.

The separation of minor actinides raises two very different technical problems according to the element concerned.

- In some conditions, neptunium can be extracted in tri-n-butylphosphate (TBP), the solvent used in the PUREX process. In the operating conditions of the standard PUREX process, it is estimated that about 3/4 of the neptunium is extracted by the TBP in the first extraction cycle, and then separated in the second uranium purification cycle. To guarantee more complete separation of this element, the PUREX process conditions must therefore be adjusted to achieve the desired performance.

- Americium and curium are not extractable by TBP and remain in the aqueous phase produced by the PUREX process. The separation of these elements will require finding new classes of extractants, or the development of different separation techniques. It goes without saying that the latter problem is far more complex than the former.
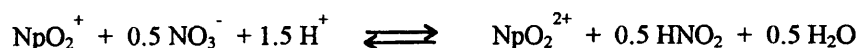
3. SEPARATION OF NEPTUNIUM

Neptunium, whose stable oxidation state in nitric medium is (V), is relatively inextractable as this species by TBP. However, the dissolution liquors fed to the first extraction cycle of the PUREX process contains significant amounts of nitrous acid, which oxidizes a portion of the Np(V) to Np(VI), a form in which neptunium can be extracted in the organic phase.

Once the neptunium is extracted by the TBP, it follows the uranium stream, and can be separated easily from this stream in the second uranium purification cycle, by changing its oxidation state.
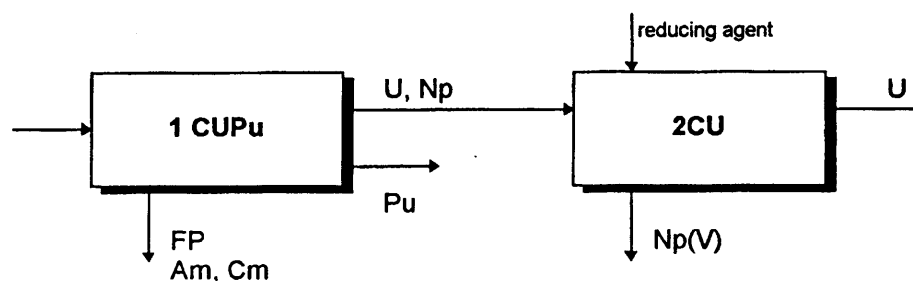
The basic principle of intensive neptunium separation consists in privileging its oxidation to the hexavalent state by the following reaction:

$$NpO_2^+ + 0.5\,NO_3^- + 1.5\,H^+ \rightleftharpoons NpO_2^{2+} + 0.5\,HNO_2 + 0.5\,H_2O$$

This reaction is reversible and catalysed by the nitrous acid produced by the reaction.

To develop this process, two types of investigation were conducted :

- Consolidation of the PAREX code used to predict the behavior of neptunium in the PUREX process. Backup laboratory tests were also performed to consolidate know-how on the redox mechanisms of the Np(V)/Np(VI) system in the presence of the pair HNO₃/HNO₂.

- Comparison of the results of the model with experiments performed in a laboratory-scale installation of α pulsed columns.

These studies revealed that relatively simple changes to the standard PUREX process should significantly improve the neptunium extraction yield. The overall target is a yield of 99.9% (99% in the PUREX process and complementary 0.9% in the DIAMEX process).

If the separation performance is insufficient in terms of the objective assigned, the oxidation of neptunium would have to be intensified by using a specific oxidant of the element, such as vanadium (V). This method has not undergone any development at the CEA for the time being.

4. SEPARATION OF AMERICIUM AND CURIUM

The high-level raffinate from the first extraction cycle of the PUREX process contains the whole americium and curium inventory, and most of the fission products from the irradiated fuel. The CEA is developing two types of process to extract and separate these minor actinides from the fission products. The first is based on extracting the actinides at their stable degree of oxidation in nitric medium, An(III), and the second process chiefly relies on the selective oxidation of americium in degree (IV) or (VI), followed by its selective separation by extraction or nanofiltration. This process, named *SESAME*, is not dealt with here.

In developing the extraction process for actinides in oxidation degree (III), two requirements were decided from the outset.

- To perform the extraction of An(III) without adjusting the nitric acidity of the high-level raffinate, to eliminate any risk of undesirable precipitation of fission products.

- To minimize the production of secondary wastes by only using totally degradable organic compounds (extractants or reagents). This principle was named *the CHON principle*, by reference to the substances used, which exclusively contain the atoms C, H, O and N.

The diamide extractants and especially those of the malonamide family (in which the two amide functions are separated by a single carbon atom) can extract An(III) while meeting the above two requirements. This process was named *DIAMEX* (DIAMide EXtraction).

Like the other compounds developed to extract An(III), diamide extractants display no selectivity for all trivalent elements. In particular, the elements of the lanthanide family which have external electron structures and dimensions comparable to those of Am^{3+} and Cm^{3+} ions, are extracted jointly. This entails the need for a supplementary step to separate the two families.

In brief, the separation process for americium and curium is a two-step process:

- An(III)-Ln(III) co-extraction by the *DIAMEX* process,
- An(III)/Ln(III) partition.

A detailed description of this process is given below.

4.1. DIAMEX process

The extraction of trivalent cations from strongly acidic nitric medium is a difficult operation due to the weak extraction ability of An(III) nitrates and the strong competition which occurs between the extraction of nitric acid and that of the An(III) nitrates.

Diamides, which have two donor oxygen atoms, react with the metallic ion to form a six-apex chelation ring, which is extremely stable. This property considerably increases the affinity of the extractant for trivalent cations.

A first compound was selected in 1991 for the development of the *DIAMEX* process, dimethyl-dibutyltetradecylmalonamide (DMDBTDMA), with the following semi-developed formula :
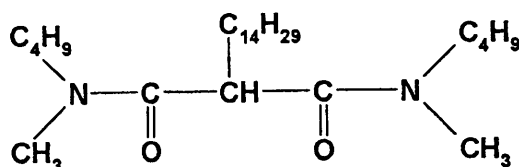
This substance was used for the first tests performed on real active solutions in 1993. These tests confirmed the possibility of quantitatively extracting americium and curium (a yield in excess of 99.5% was obtained with only six extraction stages), and then to strip them using a weakly acidic aqueous solution.

However, many flaws were identified at the time:

- a very limited operating range due to a low threshold of third phase appearance,
- undesirable extraction of some fission products, such as Zr, Mo and Ru.

Two research directions were pursued in parallel to solve these problems:

- optimization of the formula of the diamide extractant to improve its properties related to third-phase formation,
- the development of a flowsheet designed to increase the extraction selectivity.

Extractant optimization

The properties of diamide extractants can be adjusted by selecting the types of radical carried by the nitrogen atoms of the amide functions and by the central methylene bridge.

Third-phase formation in an extraction process is due to exceeding the solubility of the ligand/cation complex in the organic phase, and results in separation of the organic phase into two phases.

Increasing the length of the alkyl groups helps to increase the lipophilic property of the extractant and of its solvates, increasing the solubility of these products in the organic phase. However, this elongation may have two harmful effects :

- it increases the size of the molecule and, in some situations, decreases the accessibility of the amide functions, to the detriment of the extractive properties,
- it increases the risk of the formation of long-chain degradation products, which may have undesirable surfactant properties, and are difficult to remove from the degraded solvent by aqueous washing because of their insolubility in water.

Hence, optimization of the extractant involves finding the best compromise between the foregoing antagonistic effects. A new compound is currently being identified. It will be synthesized and tested to check that the improvements anticipated are effectively achieved.

Increasing extraction selectivity

The alternatives considered to minimize the undesirable extraction of Zr and Mo are based on the formation of inextractable complexes. Several processes have been envisaged, including :

- a separate complexation of the two elements (ketomalonic acid for Zr and hydrogen peroxide for Mo), which necessarily demands two distinct steps because these two compounds interact with each other,
- a combined complexation of both elements by oxalic acid.

It is also necessary to control the behavior and extraction of ruthenium. This is a much more difficult problem, because this fission product has an extremely complex and still virtually unknown chemistry within the *DIAMEX* process conditions.

4.2 Actinide(III)/lanthanide(III) partition

When they leave the *DIAMEX* process, the actinides(III) are in dilute nitric acid solution, mixed with lanthanides(III). The latter are much more abundant because the molar ratio R = number of moles Ln/number

of moles An is close to 50 for standard UOX fuel. It was decided to assign priority to developing processes for the extractive selection of An(III), leaving the most abundant elements in the initial aqueous solution. This helps to limit the solvent inventory and the size of the extraction units.

Actinide(III)/lanthanide(III) partition is certainly the most difficult step to design in a separation process for minor actinides. This is because very selective compounds have to be found, capable of recognizing elements with very similar properties, and which also have sufficient extraction properties.

All known processes for the separation of the actinide/lanthanide group in oxidation state (III) use the selective properties of ligands containing 'soft' donor atoms. These form stronger complexes with An(III) than with Ln(III).

The most common explanation for this is the existence of a stronger degree of covalence in bonds with actinides, due to a larger spatial extension of the 5f orbitals (actinides) in comparison with the 4f orbitals (lanthanides).

Since trivalent actinides and lanthanides are 'hard' cations in the HSAB (Hard Soft Acid Base) classification, the bonds with 'hard' ligands, such as those which have oxygen donor atoms, are essentially electrostatic, and this partial covalence can only occur with less electro-negative donor atoms than oxygen, i.e. nitrogen or sulfur.

The CEA pursues the following basic objective :

- Selective extraction of An(III) which account for the minority portion of the elements present, by developing an extractant compound which has 'soft' donor atoms.
- Use of an extractant which raises no new problems in waste management and preferably complies with the CHON principle. This limitation reduces the choice to nitrogen molecules and excludes the use of sulfur atoms.
- Direct operation on the aqueous solutions produced by the DIAMEX process, without intermediate acidity adjustment. This implies the presence of an extractant system which operates at relatively high acidity (0.5 to 1 mol/L).
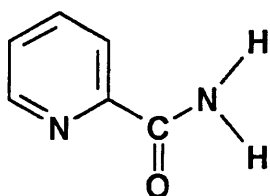
The approach adopted is to design an extractant compound based on a selective complexant for the actinides, made lipophilic by the addition of organic groups.

Two nitrogen complexants were selected :
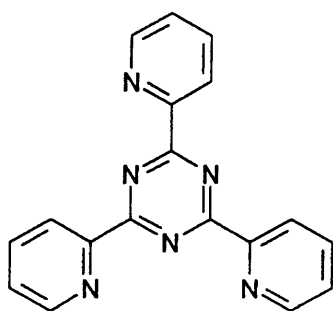
TPTZ (tripyridyltriazine)

This compound has a coordination site with three nitrogen atoms, which favors good selectivity for An(III) versus Ln(III).

Pyridine 2 carboxamide (picolinamide)

also capable of selective complexation of the actinides, probably via the nitrogen/oxygen site.

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Nevertheless, this type of ligand forms weaker bonds with metallic cations than those obtained with oxygenated ligands. This factor underlies the chief difficulty in the application of the processes : competition with oxygenated ligands (e.g. molecules of solvation water), during the extraction process, in which the total or partial dehydration of the metallic ion is required.

The grafting of alkyl groups on these complexing molecules has not made it possible so far to guarantee the intrinsic lipophilic property of the complex to obtain its extraction in the organic phase in the desired acidity range.

This problem is being dealt with by examining the possibility of associating a more lipophilic anion with the extraction process than the nitrate anion, such as the conjugate base of an organic acid:

$$An^{3+} + 3HA + L \rightleftharpoons AnA_3L + 3H^+$$
HA is the organic acid and L the nitrogen ligand.
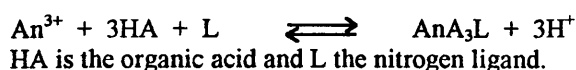
The nitrogen complexant/acid exchanger pair forms a synergistic mixture whose extraction efficiency is increased in comparison with that of the two constituents considered separately. The nitrogen complexant cannot extract the actinide nitrates from the aqueous solution by itself, because of the insufficient lipophilic property of the complex formed. Conversely, the acid exchanger cannot distinguish the actinides from the lanthanides because it only has 'hard' donor atoms.

To be effective in relatively acidic medium, the organic acid must be sufficiently strong to ensure the lability of the H^+ proton in this medium. Synergistic systems includind α-bromodecanoic acid and TPTZ or TtBPTZ (tri-tertiobutylpyridyltriazine) were studied.

The following results were obtained :

- americium is extracted better than europium with a separation factor of around 10,
- TtBPTZ offers better metal ions distribution coefficients than TPTZ, demonstrating the influence of the lipophilic property of the nitrogen agent on the extracting power of the synergistic mixture.

The entire challenge of this approach is thus contingent on finding strong organic acids, which comply with *the CHON principle*. Investigations so far have focused on carboxylic acids with an electron attractor group in the α position, such as -CN and -OH.

5. CONCLUSIONS

Major breakthroughs have been achieved in research under way at the CEA on the development of separation processes for the minor actinides.

The intensive separation of neptunium appears feasible if a limited change is made to the PUREX extraction flowsheet. This theory will have to be corroborated in a perfectly representative situation.

The development of actinide(III)/lanthanide(III) co-extraction is highly advanced. It remains to be optimized, by examining the behavior of ruthenium, which appears as an undesirable element.

Work on separating actinides and lanthanides appears to be making headway thanks to the use of synergistic extraction systems. Conditions will have to be found in which these systems comply with *the CHON principle* and remain effective in slightly more acidic media than today.

These investigations are in the laboratory stage for the time being, and much obviously remains to be done before they can be applied industrially.

ACKNOWLEDGEMENTS

THE STATE OF THE ART ON NUCLIDES SEPARATION
IN HIGH LEVEL LIQUID WASTES BY TRUEX PROCESS

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ABSTRACT

For the advancement of the back-end of nuclear fuel cycle, novel CMPO–TRUEX process was studied for separating minor actinides from fission products in high level liquid waste using real radioactive solutions from PUREX experiments, so as to support PNC's actinides recycling program using fast reactor. The present PUREX process was also studied to improve the separation of ^{237}Np, ^{106}Ru and ^{99}Tc, the most interfering-natured nuclides in both PUREX and TRUEX processes, by utilizing electrochemistry-based salt-free methods which can eliminate the secondary radioactive waste.

The state of the art of separation technologies are described by summarizing the extraction behaviors of nuclides in recent hot counter-current runs using CMPO–TRUEX process with mild salt-free stripping reagents. The degradation and regeneration characteristics of CMPO/TBP/n-dodecane mixture solvent were also simulated by semi-hot experiments. Several experiments to separate minor actinides and lanthanides from the TRUEX mixture product using aqueous aminopolycarboxylate complexant, DTPA, resulted in reasonable MA/Ln separation profiles in multiple mixer-settler stages and allowed a unique separation flowsheet adaptable to the TRUEX process to be proposed.

Application of electrochemistry to assist both solvent extraction processes, *e.g.*, "anodic oxidation" to destroy PUREX and TRUEX solvent waste in the presence of electron transfer mediator Ag^{2+} or "cathodic reduction" for electrolytic extraction of Pd^{2+}, $RuNO^{3+}$ and $^{99}TcO_4^{-}$ from 3 M nitric acid medium is under study.

1. Introduction

Radioactive waste, especially high level liquid waste (HLLW) containing α emitters, have become a central issue from the interest in decreasing long lived toxicity on their long term storage and reducing the cost of the nuclear fuel cycle. Minor actinides (MA), usually lower than 1 % by weight, will sustain major toxicity of vitrified HLLW; actinides practically account for ca. 45 % of the total initial toxicity (one year after storage), but their contribution will increase up to ca. 70 % over 100 years for the case of LWR–HLLW. Such α toxicities of HLLW lie in MA, ^{241}Am, ^{244}Cm, ^{237}Np, and also $^{238,\,241}$Pu derived from the PUREX process. The researches regarding α- and salt-free HLLW will become a key for a new reprocessing system.

Characteristics such as excellent extractability from highly acidic solutions, sufficiently fast kinetics for mass transfer, high radiolytic/hydrolytic stabilities and biological safety of extractants are essential for the process design of any novel solvent extraction system. An extraction process using neutral bifunctional organophosphorus Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (O$\emptyset$D(iB)CMPO or simply CMPO) [1,2] is a candidate to satisfy such requirements.

The first questions about the TRUEX process are its efficiency as a separation tool in a highly acidic and very complicated solution mixture for producing α-free HLLW, and the second is the quality of the recovered actinides if they are recycled in a reactor. For this evaluation, both optimization of the main TRUEX chemical flowsheet and introduction of a complexant to separate lanthanides (Ln) from MA were carried out by counter-current experiments. This paper describes the state of the art on TRUEX process development at PNC. The first part deals with some flowsheet improvements of the TRUEX process for actinides separation in a real highly active raffinate (HAR) solution, the second part describes the application of a chelating reagent, diethylenetriaminepentaacetic acid (DTPA) to a TRUEX flowsheet for MA/Ln separation. Auxiliary electrochemical process to assist both PUREX and TRUEX processes are thirdly described. All information is abstracted in attached summary tables.

2. TRUEX as a Tool for α-free Radioactive Wastes

2.1 Fundamental distribution properties of actinides and fission products

Fundamental distribution ratios (Ds) of 4f, 5f elements and fission products were verified in 0.2 M CMPO/1.0~1.4 M TBP/n-dodecane using not only real FR–HAR but also concentrated LWR–HLLW. Element compositions and concentrations of HAR and HLLW are shown in Figure 1, where a HLLW was obtained by commercial LWR spent fuel (less than 33000 MWD/T) reprocessed in the Tokai Reprocessing Plant (TRP) and HAR was originated in reprocessing experiments of FR Joyo spent fuel (burn up at ca. 55000 MWD/T, cooled for ca. 4 years). Relationships between various parameters such Ds and nitric acid concentration have already been given in other papers [3,4]. The distribution characteristics of trivalent f-elements: ^{241}Am, ^{244}Cm and Lns are moderate, suggesting that they will be well extracted and recovered very simply by changing aqueous nitric acid

concentration from *ca.* 5 M to 0.01 M in the general TRUEX flowsheet.

Especially, the increase of nitric acid concentration causes desirable effects in decreasing the extractability of Ru and increasing that of Np. Distribution ratio of Np was confirmed at each acidity by equilibrating both phases over 24 h. At high acidities disproportionation of Np^{5+} into Np^{4+} and Np^{6+} might shift the valency of Np to Np^{6+}, which is easily extracted. An opposite tendency of Ru against Np was found either in batch experiments using trinitratonitrosyl ruthenium, $RuNO^{3+}$, and in counter-current tests using real HAR containing ^{106}Ru. These results suggested that different kinds of extraction mechanisms were operative for Ru and Np, and specific variation in distribution tendencies of Ru seemed to be attributed to the diversity of ruthenium species that were affected by even slight differences in extraction conditions. Since Ru behaved similar in batch and counter-current experiments, we concluded that Ru behaved in the form of $RuNO^{3+}$ in counter-current runs. Simple adjustment of the feed solution higher than 5 M nitric acid concentration was therefore recommended as an effective method to handle these two key nuclides. Neutral bidentate organophosphorus CMPO alone could make this procedure possible.

The Ds of all other major elements were measured for diluted LWR–HLLW using normal TRUEX solvent (0.2 M CMPO/1.0 M TBP/n-dodecane). Dilution was necessary for preventing third phase formation. It was confirmed that there was little difference in Ds of trivalent f-elements and Ru for HAR or HLLW in the range 0.5~4 M nitric acid. Third phase limit concentrations almost agreed with the predictions from mono element solution system. This suggested that there were probably no mutual interactions among these elements in HLLW and also among the extracted species [5].

Although tetra- and hexavalent elements needed no special treatment for their forward extraction, perfect back extraction of these might require either strong complexants or higher pH reagents, such as salt-free hydrazine oxalate or hydrazine carbonate as previously reported [4]. The suitable concentrations are different for each reagent; recommended concentrations of these salt-free reagents are for example 0.5 M (at least higher than 0.2 M) to obtain 90% stripping of $RuNO^{3+}$ and Zr^{4+} at trace level in a single contact with TRUEX solvent, even with irradiated solvent by 10^7 R.

2.2   Improved TRUEX flowsheet based on "Salt-Free" concept

Several TRUEX counter-current runs employed to partition actinides in real HAR led to the flowsheet "TRUEX PNC Salt-Free Version" [6, 7]. Its block flow and typical material balance are shown in Figure 2. The feed composition of HAR is indicated in Figure 1. The higher acidity (*ca.* 5 M) was selected for the feed HAR due to the aforementioned reasons and the dual scrubbing was employed to decrease extraction of both $RuNO^{3+}$ and free nitric acid. Addition of oxalic acid was minimized to eliminate oxalate precipitation of f-elements, in spite of concerns of lowering decontamination factor of fission products (DF_{FPs}) and causing accumulation of extractable species. Expecting complete fractional stripping, we prepared 3 banks composed of 51 stages in total, despite having only 6 stages for extraction in this case. Material balance was made based on the flow rates and α, γ and element concentration. Experimentally, steady state operation had been confirmed within 4–5 hours from the start. Each sample was taken from the settlers after ten hours operation.

Although there was some experimental fractiousness, it was confirmed that most of the f-elements were extracted within the 6 extraction stages, and they were quantitatively recovered again in the aqueous phase. Extractability of Np from highly acidified HAR was sufficiently high in the presence of oxalic acid in the aqueous phase as confirmed by no leakage in the raffinates. Stripping of Np however unexpectedly occurred with dilute nitric acid prior to the contact with HAN. The neighboring transition elements, Zr^{4+}, Nb^{4+}, Mo^{6+} and TcO_4^-, were also extracted in this condition. Once extracted in the solvent phase, Zr and Mo were retained until strip-III, the scrubbing of hydrazine oxalate. Therefore more sensible management is necessary for both elements because of their abundance in spent fuel.

The typical stripping profile for major nuclides indicates that the organic concentrations of $^{238, 239, 240}Pu$ and ^{106}Ru were peculiarly high in the stripping banks until strip-III. In normal TRUEX process Pu and Ru used to be retained in the spent organic phase at ca. 20 – 95 % and ca. 2 – 8 % respectively after stripping with dilute nitric acid. For Ru, however, hydration seemed to transform extractable trinitrato nitrosyl species into less extractable mono- or dinitrato nitrosyl species in the alkali scrubbing stages (strip-III and IV) [8]. Consequently, high decontamination of ^{106}Ru could be attained by high pH scrubbing with hydrazine carbonate at the end of solvent regeneration step, offering $DF_{Ru-106} > ca$. 10, by combining high acidity scrubbing at scrub-1 banks with $DF_{Ru-106} > 10^2$. The stripping behavior of Pu was similar to that of ^{106}Ru; namely, DF_{Pu} was ca. 10 with hydrazine oxalate and ca. 20 with hydrazine carbonate. These steps were also capable of removing UO_2^{2+}, HDBP and other acidic degraded species. Scrubbing efficiency of HDBP was tentatively ca. 60 % in the two steps of solvent regeneration.

In this modified TRUEX flowsheet, where complex ions composed of hydrazine oxalate and hydrazine carbonate worked well under high pH conditions, the final amounts of remaining Pu and Ru were respectively reduced to 0.5 % and 0.25 % of their initial concentrations. They are, then, no longer troublesome nuclides in this salt-free TRUEX flowsheet and the final two steps of solvent regeneration become an effective "plutonium/ruthenium barrier". Generally, while the addition of complexants will have trade off the elements between precipitation and third phase formation, the elimination of precipitates highly helped to improve the recovery rates of the elements in this case. The actinide concentrations in the raffinate were usually lower than the detection limits (around 10^4 Bq/mL), giving a DF_α of $\geq 10^3$, a few more stages would be necessary to absorb process fluctuations.

2.3   Stability and safety of CMPO

Solvent degradation of CMPO/TBP by γ radiolysis/hydrolysis and its effects on the stripping of the extracted elements were studied. Irradiation experiments using a ^{60}Co source (ca. 7×10^4 Ci) on pure CMPO and on 0.2 M CMPO/1.0 M TBP/n-dodecane mixed solvent preequilibrated with 3 or 5 M HNO_3 showed that two major peaks, assigned to neutral methyl(n-octyl)(phenyl)phosphine oxide (MOØPO) and n-octyl(phenyl)isobutyl-carbamoylmethylphosphine oxide (OØ(iB)CMPO), were distinct and such radiolytical damage became dominant over 10^7 R. For irradiations higher than 10^7 R, the practical radiation bounds in partitioning process, TBP's damage was more substantial than CMPO's. Alkali scrubbing with sodium carbonate, tetramethyl ammonium

hydroxide (TMAH) and hydrazine oxalate offered quantitative scrubbing effects only for the former degradation species (probably in the form of octyl(phenyl)phosphinic acid) as well as for Ru, Zr and HDBP. The slow kinetics of each scrubbing treatment necessitated sufficient contact time (> *ca.* 10 min.) and concentration for each reagent (> 0.2 M). Neutral degradation species are generally very lipophilic, therefore some solid absorbents such as magnesium silicate or activated alumina are recommended as a secondary clean up system.

Thermochemical data [6] of OØD(iB)CMPO, obtained by thermogravimetric analysis and differential thermogravimetry (TG-DTA), indicated that its degradation exothermally proceeded in two steps at least, around 260 °C and 294 °C, and was completed at 300 °C even in the form of amorphous of it with TBP and Ru. The flash and combustion temperatures of CMPO were also quite a bit higher than those of TBP. These results indicate that CMPO is thermochemically stable in the usual operation.

The biochemical data [6] represented by 50% lethal dose, LD_{50}, also suggest that OØD(iB)CMPO should be categorized neither as a poison nor as a toxin, and that it is as safe as TBP whose LD_{50} for rats has been reported to be 3000 mg/kg. Furthermore, negative results in reverse mutation assay for Salmonella Typhimurium and DNA molecular repair assay for Bacillus subtilis indicated that CMPO is neither a chemical carcinogen nor a hereditary toxicant.

3. Actinide (III) and Ln Separation in CMPO Mixed Solvent System

3.1 Criteria for Am and Cm recovery

In our "Advanced Fuel Recycle System" which is based on MOX fuel, Am is recycled in fast reactors, and Cm is stored for several decades, waiting for ^{244}Cm decay [9]. The incineration of Am needs to separate Cm and lanthanides from Am. On the other hand, contamination with Ln would be allowed in Cm recovery.

It is considered that there is quite a large difficulty in Am/Cm separation by solvent extraction. Thus, TRUEX process must be coupled with some Am/Cm/Ln separation methods. If light lanthanides which are major fission products were removed, the scale of Am/Cm separation process could be reduced. For totally process simplification, it is favorable to add a function of lanthanides rejection to the TRUEX process.

3.2 Utilization of DTPA

A chelating reagent diethylenetriaminepentaacetic acid (DTPA) has been utilized in An(III)/Ln separation based on cation exchange and solvent extraction such as the TALSPEAK process. In a neutral extractant TBP system, DTPA is used with high concentration of nitrate as a salting out reagent [10].

Light lanthanide elements are less selectively extracted by CMPO than heavy lanthanides from nitric acid solution, and tend to make strong complexes with DTPA. Therefore it is expected that light lanthanides could be rejected in CMPO extraction system, utilizing DTPA complexation. In the studied process, the nitrate concentration was lowered and a higher pH than in the TBP system was used in the extraction experiment.

In order to realize the process using DTPA, stabilization and/or control of pH in the separation process is essential. Certainly, basic distribution data for CMPO–TBP mixed solvent / DTPA–nitrate solution are

required.

3.3 Control of pH

One of the advantages of CMPO is the extraction ability from high acidity solution. However, as the loaded solvent which is contacted with highly acidic waste solution contains considerable amount of nitric acid, it would interfere DTPA–metal complexation. Therefore, it is needed to reduce the acid concentration in the organic phase. Fortunately, the extent of distributions of metal and acid differ using nitrate salt at low acidity. It is considered that the selective stripping of acid from the loaded solvent can be conducted by using proper concentration of nitrate solution.

DTPA has carboxyl groups. Since the first and second dissociation constants are around two, buffering effect could be expected in the acidity range near 0.01 M which is appropriate for separation.

3.4 Basic data on lanthanide distribution

Since the separation system is rather complicated, many factors affect the distribution of trivalent metals. The acidity of the aqueous phase is the most important parameter. In Figure 3, the distribution ratios of four lanthanide elements are plotted as a function of pH. As pH become higher, dissociation of DTPA proceeds, resulting in a decrease of the distribution ratios. And the effect of metal complexation emerges as the difference of the values. As the stability constants of Dy is near that of Am, it is expected that Am could be stripped while major light lanthanides such as Ce and Nd would be kept in the organic phase. The separation factors are almost consistent with the ratio of stability constants of metals. Then it is considered that the separation is mainly governed by selectivity of DTPA complexation.

The higher nitrate and lower DTPA concentration enhance the extraction of metal. Higher temperatures lower the distribution ratios. And the kinetics of stripping of metal from loaded solvent are rapid enough for the use of mixer-settlers as contactors.

3.5 Concept of flowsheet

We made a basic flowsheet for An(III) recovery with lanthanides rejection using DTPA–nitrate solutions. The process is composed of four sections; namely, extraction–scrubbing, acid stripping, An(III) stripping and Ln stripping as shown in Figure 4.

In the first extraction–scrubbing section, the trivalent metals are extracted from acidic solutions. The operation procedure is basically the same as the original TRUEX. The acid in the loaded solvent is removed in the second acid stripping section using a nitrate solution of low acidity. The aqueous waste solution will contain only little activity. Trivalent actinides are back extracted in the third An(III) stripping section with a DTPA–nitrate mixed solution, the pH of which is adjusted around two. It is anticipated that mid lanthanides such as Sm and Eu would be simultaneously recovered with Am and Cm in a certain extent. As the product solution contains a high concentration of nitrate, further treatment will be required to obtain nitric acid solution as product. With dilute nitric acid, retained lanthanides in the organic phase are stripped in the fourth Ln stripping

section. (Recently, we call this process flowsheet as SETFICS * for convenient.)

* Acronym of "Solvent Extraction for Trivalent f-elements Intra-group Separation in CMPO–complexant System"

3.6 Results of counter-current experiment

Based on the conceptual flowsheet as stated before, we conducted counter–current hot experiments using a TRUEX product which was previously obtained in the hot tests and acidified to 2 M HNO_3 for extraction. The trivalent metals were well extracted in the first section. In the second stripping section, 0.5 M $NaNO_3$ solution (pH 2.0) was used. Since re-extraction was not conducted from experimental restriction, approximately 10 % of the metals were streamed into aqueous waste. The acid concentration of discharged solvent was lower than 0.01 M.

In Figure 5, the profiles of concentrations and distribution ratios of major nuclides are plotted. The composition of the An(III) stripping solution was 0.05 M DTPA–4 M $NaNO_3$ solution (pH 2.0). Americium-241 and ^{244}Cm were stripped into product solution while ^{144}Ce was retained in the organic phase. As the behavior of ^{155}Eu was similar to that of ^{241}Am, the greater part of ^{155}Eu was recovered with An(III) product. The distribution ratio was varied with acidity of aqueous phase. The pH value became higher in the upper stream of solvent feed point. This tendency resulted in a decrease of distribution ratios and an increase of An(III) recovery.

Table 1 Material balance and decontamination factor

Material balance ;

unit : %

	^{144}Ce	^{154}Eu	^{155}Eu	^{241}Am	^{242}Cm	^{244}Cm	La	Ce	Pr	Nd	Sm
Feed					100						
Acid waste	9.0	8.9	9.5	6.2	6.4	8.6	10*	10*	10*	10*	10*
An(III) product	0.89	45	46	64	56	67	1.2	<6.1	2.3	1.4	27
Ln waste	85	15	15	5.6	1.6	0.75	52	97	69	71	34
Total	94	68	70	76	64	77	63	<110	81	82	72

* Evaluated values equal to those of radionuclides

Decontamination factors to ^{241}Am ;

^{144}Ce	^{154}Eu	^{155}Eu	^{242}Cm	^{244}Cm	La	Ce	Pr	Nd	Sm
72	1.4	1.1	1.1	0.95	52	>10	28	46	2.3

The material balance and decontamination factors are summarized in Table 1. Because of the short operation time, the steady state was not attained. Especially, the sum of the output of An(III) and Eu was quite

low. The decontamination factors of light lanthanides were obtained in several tens, and, at least, 80 % of lanthanide were removed from An(III) product solution. Therefore, the main contaminants of An(III) were Sm and Eu.

3.7 Further subjects

It has been found that CMPO mixed solvent / DTPA–nitrate solution system has a potential for light lanthanides removal. It is considered that the improvement of An(III) recovery and the reduction of nitrate in stripping solution should further be studied.

4. Supporting Electrochemical Technique for Separation Process

4.1 Electrolytic extraction of platinum group elements and technetium

Precious metals such as Ru, Pd, Rh, Ag and Tc amount to several kilograms per ton of ordinary spent fuel. The ionic state of these elements, especially extractable $RuNO^{3+}$ and TcO_4^-, behave in a rather complicated manner and eventually dominate the final decontamination factors of the PUREX and successive TRUEX processes. In that sense, their separation prior to both solvent extraction processes is meaningful and worthy to improve decontamination in a limited number of extraction stages and cycles as well as to prepare future multiple usage of precious metals from spent fuel.

Pure cathodic deposition behaviors of Ru^{n+} and Pd^{2+} in 3 M nitric acid were studied using Pt-Ti cathode (20 cm^2) in an electrolysis cell equipped with cation exchange membranes. The volume of catholyte and anolyte was 100 ml each, temperature was set at 50 °C, and Ru^{n+} and Pd^{2+} were mixed together at 100 ppm each. In accordance with electrolysis time, both metals were deposited dendritically together. A yield $\geq$ 90% was obtained for both Ru and Pd in a few cases employing high cathodic current density $\geq$ 100 mA/cm^2 during 3 hours. In the case of low 10 mA/cm^2 electrolysis with less amount of hydrogen evolution, only Pd was deposited with the same high yield. Low deposition yield of Ru (less than 30%) suggests that its redissolution might occur at such a cathodic density. The reported value of E^0 for the amorphous TcO_2/TcO_4^- electrode is 0.746 V (vs. SHE) [11],

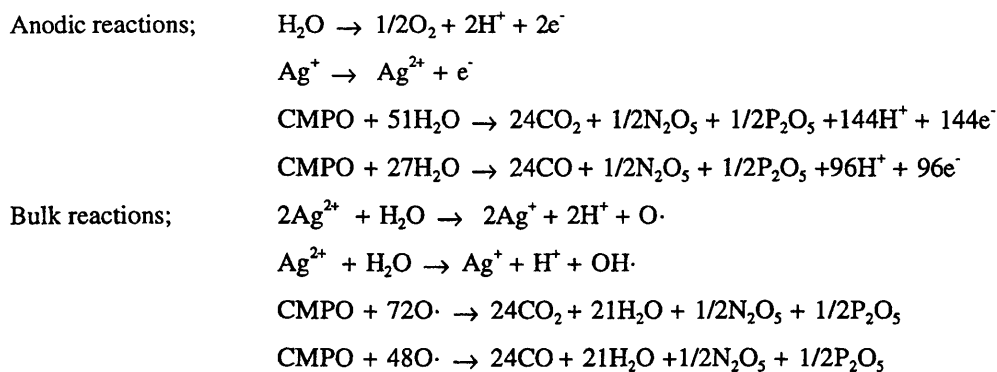$$TcO_4^- + 4H^+ + 3e^- \leftrightarrow TcO_2 \cdot xH_2O + (2-x)H_2O$$
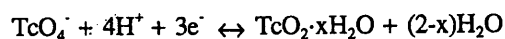
thereby suggesting electrochemical deposition of Tc in nitric acid. The further electrochemical tests by cyclic voltammogram (CV) measurement and galvanostatic electrolysis are in progress for Pd^{2+}, $RuNO^{3+}$, $^{99}TcO_4^-$ and ReO_4^- with 3 M nitric acid.

4.2 Mediated electrochemical destruction of solvent waste

Electrolysis tests were carried out to search for the possibility of electrochemical destruction of PUREX and TRUEX solvent waste [12]. Cyclic voltammogram measurements suggested that adsorption and the direct oxidation of emulsified CMPO (and also TBP) by Pt anode in nitric acid (3 M) was easier than that of n-dodecane.

About 90% of CMPO was decomposed within 3 hours electrolysis with much excess of Ag^{2+} (initial

Ag^+/CMPO/decalin molar ratio was 1500 : 1 : 30), 500 mA/cm^2, 50 °C in 3 M nitric acid. Mainly phosphoric acid (*ca.* 80 %) and carbon mono-, dioxide (*ca.* 10 % in total) were detected in the aqueous phase and in gas phase, respectively. The presence of Ag^{2+} mediator in the electrolysis system considerably accelerated oxidation kinetics by *ca.* 5 times and improved current efficiencies as compared to that from the direct electrode reaction. Nevertheless, still lower individual current efficiency calculated on the basis of gaseous compositions with the following assumed reactions suggests that electrolysis conditions can furthermore be improved.

Anodic reactions;
$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$$
$$Ag^+ \rightarrow Ag^{2+} + e^-$$
$$CMPO + 51H_2O \rightarrow 24CO_2 + 1/2N_2O_5 + 1/2P_2O_5 + 144H^+ + 144e^-$$
$$CMPO + 27H_2O \rightarrow 24CO + 1/2N_2O_5 + 1/2P_2O_5 + 96H^+ + 96e^-$$

Bulk reactions;
$$2Ag^{2+} + H_2O \rightarrow 2Ag^+ + 2H^+ + O\cdot$$
$$Ag^{2+} + H_2O \rightarrow Ag^+ + H^+ + OH\cdot$$
$$CMPO + 72O\cdot \rightarrow 24CO_2 + 21H_2O + 1/2N_2O_5 + 1/2P_2O_5$$
$$CMPO + 48O\cdot \rightarrow 24CO + 21H_2O + 1/2N_2O_5 + 1/2P_2O_5$$

The formation of O· and OH· radicals was essential in this mechanism (*i.e.*, double mediatory system), and cation exchange property of diaphragm was very important to prevent consumption of Ag^{2+} mediator in the anolyte. Mediation effect of Co^{3+} was lower than Ag^{2+}, and addition of Ni^{2+} or Ce^{4+} unexpectedly brought only negative effects.

Direct and/or mediated electroredox technique can push out separation function and provide new waste minimizing system in the solvent extraction process.

5. CONCLUSION

Basic distribution studies of actinides and FP as well as several TRUEX counter-current runs using real HAR from PUREX experiments successfully led to an original flowsheet "TRUEX PNC Salt-Free Version". With this flowsheet, an α- and salt-free HLLW was obtained, ensuring a $DF_a \geq 10^3$. The DTPA has been successfully adapted with a reasonable separation of MA from light lanthanide in counter-current runs using TRUEX product solution. General process safety on the TRUEX process were preliminarily verified by original experiments. Electroredox methods for separating precious metals and destroying solvent waste have been studied in the frame of salt-free concept.

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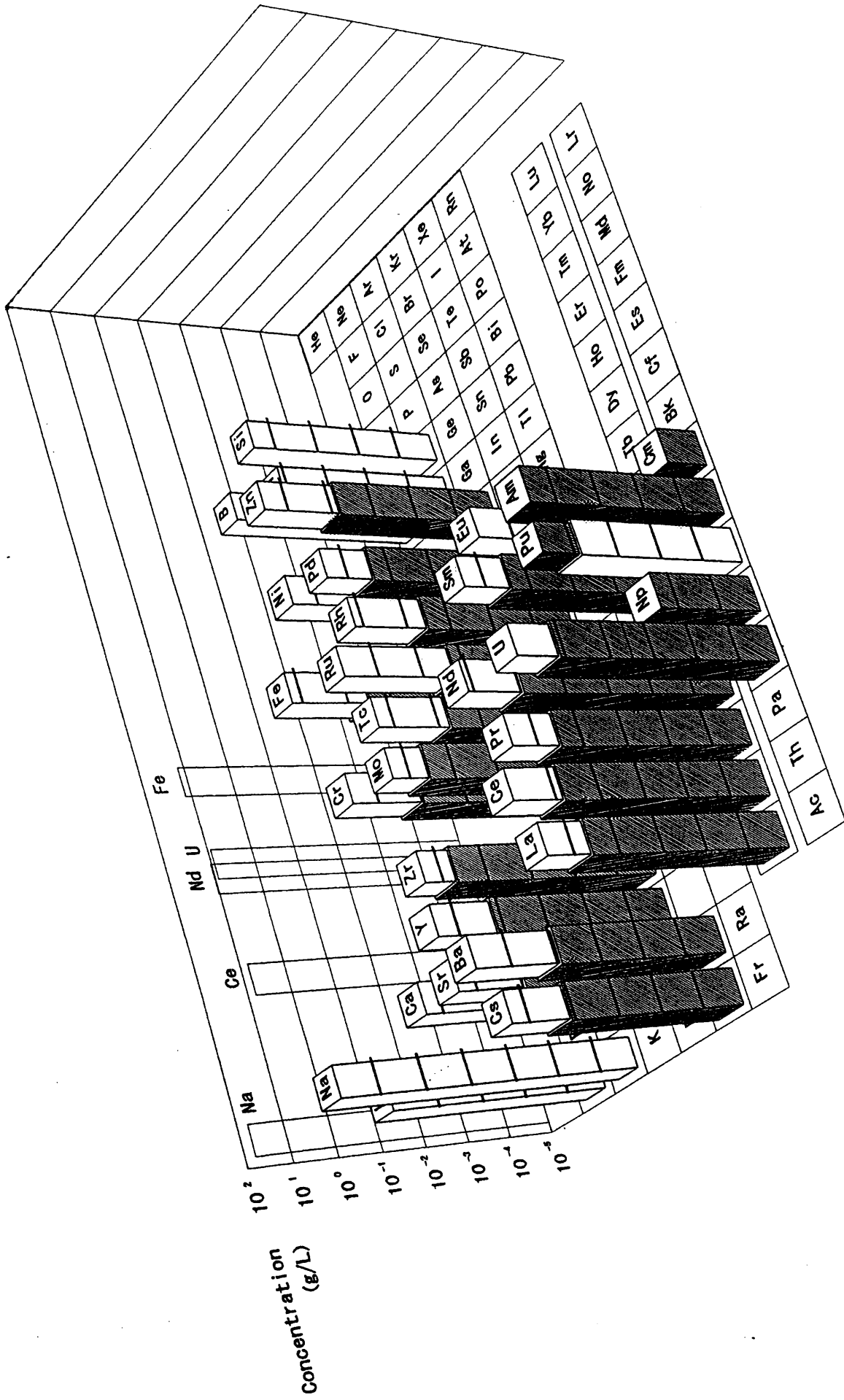
Figure 1 Typical Composition of HAW

⬡ : HAR by FR reprocessing, volume: *ca.* 15 L/kg•SF

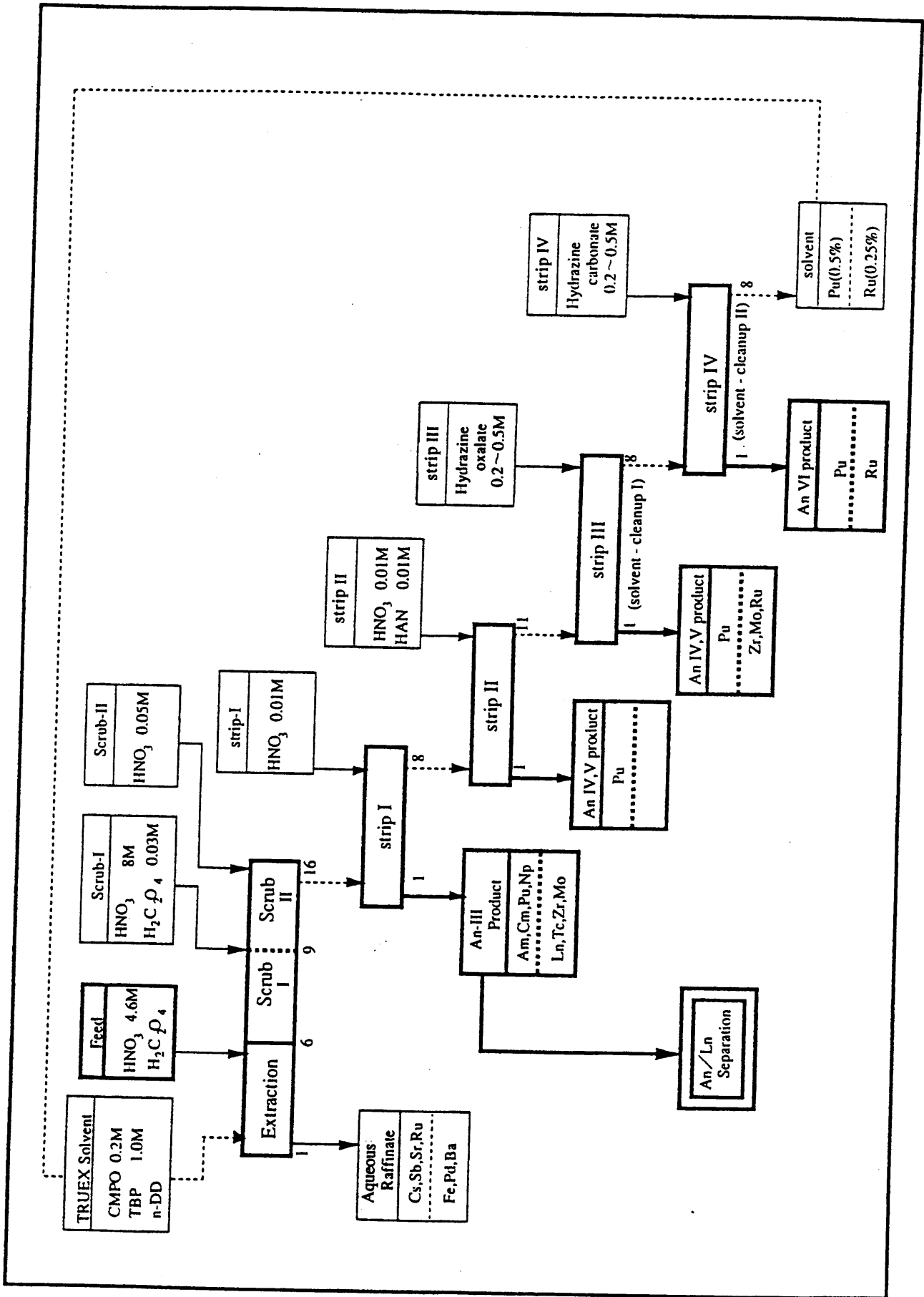⬡ : HLLW by LWR reprocessing, volume: *ca.* 1 m³/t•SF

Figure 2(a) Improved TRUEX Flowsheet : PNC TRUEX Salt-Free Version

Figure 2(b) Typical Distribution of Elements
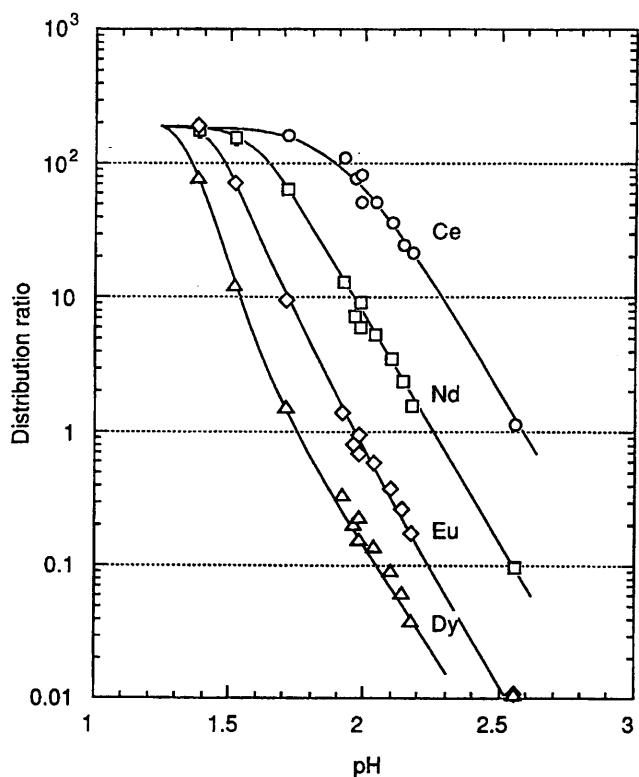(TRUEX : PNC TRUEX Salt-Free Version)

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Figure 3   Lanthanide distribution between CMPO mixed
solvent and DTPA–nitrate solution

Organic solvent :   0.2 M CMPO–1.0 M TBP–n-dodecane
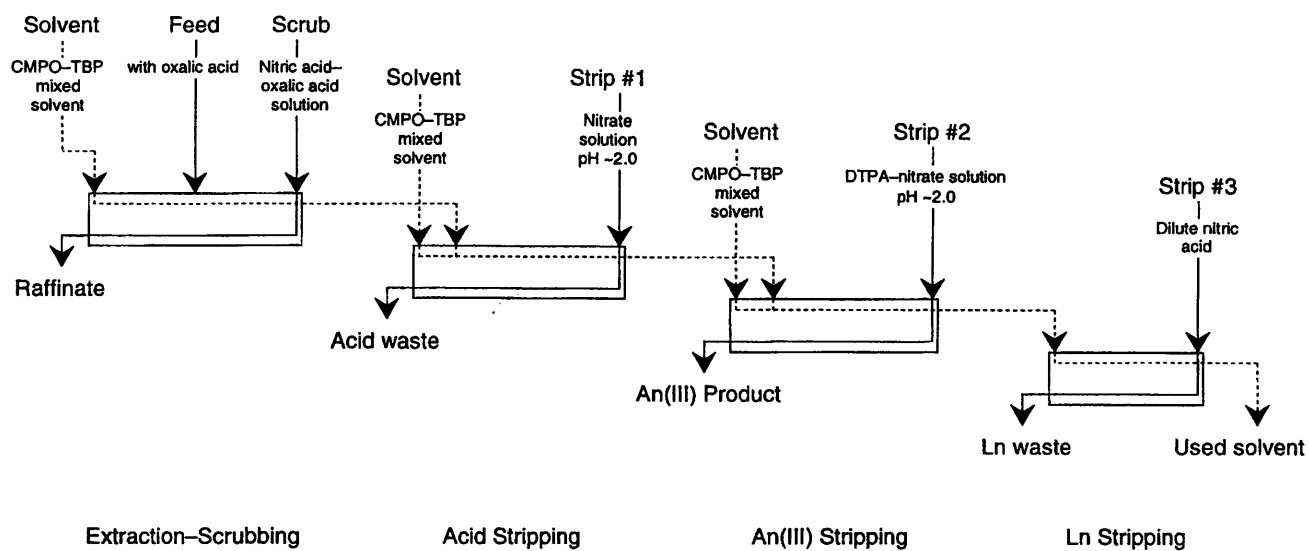Aqueous solution :   0.05 M DTPA–3 M NaNO$_3$

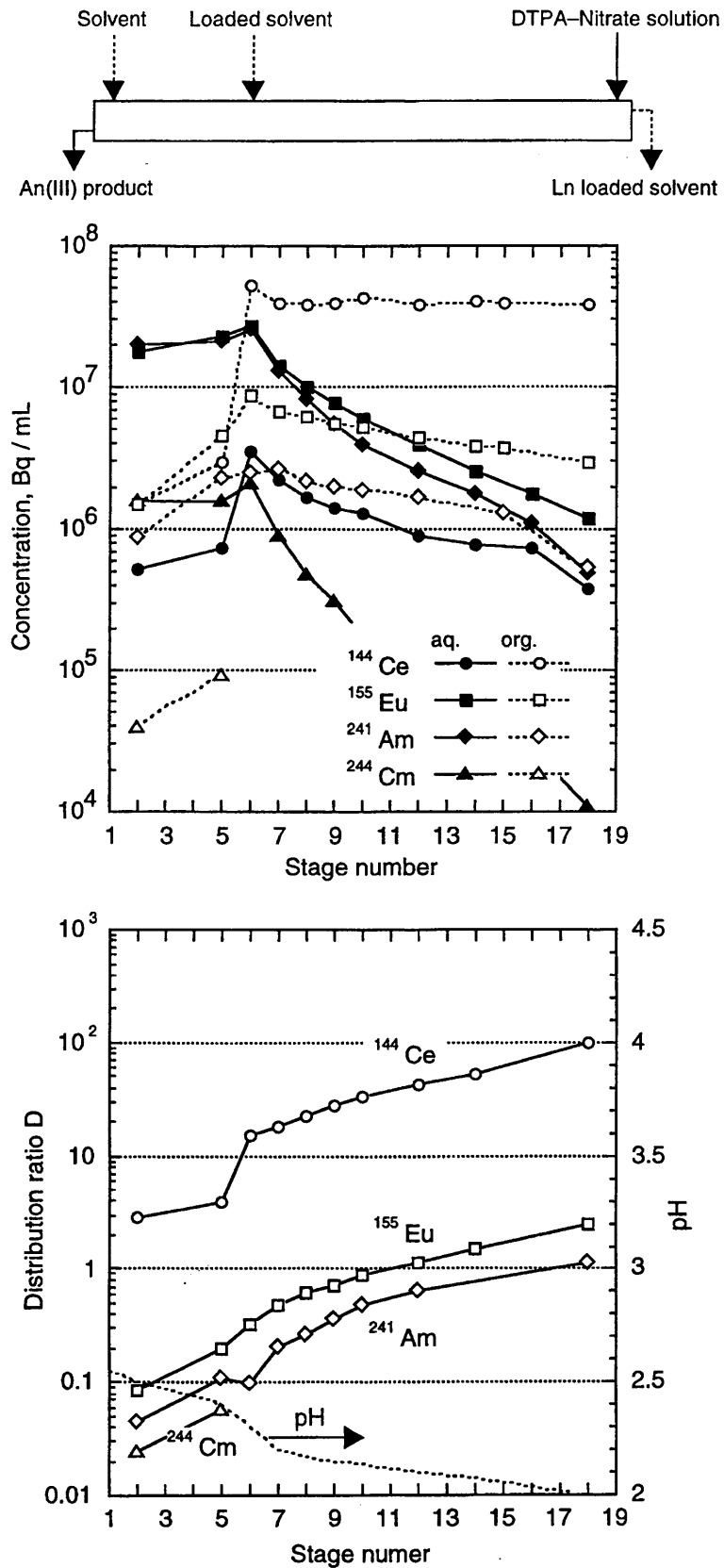Figure 4   Conceptual flowsheet for An(III)/Ln separation

Figure 5   Profiles of concentration and distribution ratio of major nuclides in An(III) stripping Section

APPENDIX

Summary Table

	TRUEX	Others (reference)
Extractant	OØD(IB)CMPO	
Synthesis		
– Method (synthesis & purification)	established	
– Cost (as a mixed solvt.)	500$/kg= 41kYen/L	40$/kg=3kYen (diamide)
Stability		
– γ ^{60}Co	highly stable up to 10^7R	
	(Over 10^7R, TBP as well as CMPO	
	will be significantly degraded)	
– Nitric Acid	(acceptable up to 7 M HNO_3 in	
	process)	
– Thermal decomposition temp.	272.3~313.2 °C	
Solubility		
– Into$\emptyset_{AQ}$(at 0.01~ 3 M HNO_3)	TBP ≤ 300ppm	
	CMPO ≤ 10ppm	
Toxicity		
– Mortality(LD_{50}) for		
5 mice (male): oral	> 3000 mg/kg	
	3000 mg/kg (for TBP)	
5 mice (male): dermal	> 2000mg/kg	
– Reverse mutation assay	negative	
– DNA repair assay	negative	
Burnability		
– Flash point	243.6 °C	
Incinerability	imperfect	perfect (diamide)
	(*e.g.*, Ag^{2+} process is under	
	investigation)	
Process Flowsheet		
Solvent	0.2 M CMPO/1.0 ~ 1.4 M TBP	
Diluents	n-dodecane	
Target waste solutions		
– Highly active raffinate	applicable	
– HLLW	needs more investigations	
Feed adjustment	*ca.* 5 M HNO_3 with $H_2C_2O_4$	
Process sensibility for extraction	durable for acidity changes	

	TRUEX
Typical mass transfer time	
Forward ext. at C_H 3 M	Nd (< 5 min) << Ru < Zr
Strip at C_H 0.2 M	Nd (< 5 min) << Ru, Zr
FPs scrubbing	"dual" scrubbing with a $H_2C_2O_4$
Selective stripping method	
→ 1st Step	dilute HNO_3 : 0.01 M HNO_3
	* An^{3+}, Ln^{3+}, TcO_4^-, Zr^{4+} and Mo^{6+} were separated
→ 2nd Step	reducing reagent : 0.01 M HAN
	* Pu^{4+} was separated
→ 3rd Step	complexant : 0.2~0.5 M $(N_2H_5)_2C_2O_4$
	* Pu^{4+}, Zr^{4+}, Mo^{6+}, $RuNO^{3+}$ were separated
→ 4th Step	high pH complexant: 0.2~0.5 M $(N_2H_5)_2CO_3$
	* Pu^{4+}, UO_2^{2+}, $RuNO^{3+}$ were separated
Separability of actinides from FP	
– DF for actinides from HAR	$> 10^3$
– SF for Am/Cs	$> 10^4$
for Am/Tc, Mo, Zr	to be improved
for MA/Ln	to be improved
Separation of MA from Ln	Applicability of DTPA is under investigation
Third phase formation	
– Constituents (confirmed)	H^+, Ln^{3+}, Fe^{3+}, UO_2^{2+}
– Limit concentration (at	Nd^{3+}: 0.04~0.045 M (0.02 M *)
0.2 M CMPO/1.2 M TBP/nDD,	Pu^{4+}: 0.03 M
C_H 3 ~ 6 M, 25 °C)	UO_2^{2+} : 0.025~0.03 M (0.012 M*)
	* in the case of 1.0 M TBP
Solvent clean up	
– Major degraded material identified at 10^7R	HDBP
	methyl(n-octyl)(Ø)phosphine oxide
	n-octhyl(Ø)isobutylcarbamoylmethylphosphine oxide
– Mass transfer rate of FPs during salt-free scrubbing for irradiated solvent at 10^7R.	
Scrub at $C_{HYD.CARB.}$	Nd (1 min.) << Zr, Ru (10 min.)
Scrub at $C_{HYD.OXAL.}$	Nd (1 min.) << Zr, Ru (20 min.)
→ 1st Clean up method	a salt-free method for acidic degraded materials and FPs.
	(see Step 3rd and 4th)
→ 2nd Clean up method	active Al_2O_3 or floridine

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THE COMPARATIVE CHARACTERISTIC OF METHODS PARTITIONING HLW IN RUSSIA FOR TRANSMUTATION OF RADIONUCLIDES.

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Methods of recovery long-lived radionuclides from HLLW with the purpose more safe isolation from environment and transmutation the most toxic radionuclides, are considered.

For separation of minor actinoids and fission products are offered extraction, membrane extraction, ion-exchange chromatographic, precipitation and pyrometallurgical methods with use neutral monodentate and polydentate compounds including carbonyl, amide and phosphoryl groups, phosphorus-organic acids and their salts, cobalt chlorinated dicarbollyde.

The basic problems, arising by use of phosphorus-organic acids (POA) for isolate of pure fractions of minor actinoids from HLW, are discussed.

Opportunity of use new extractant on a basis of acid zirconium compounds salts (ZCS) of POA for partitioning HLW is shown.

Acid zirconium compounds salts (ZCS) of HDEHP and n-alkil(C_8C_{10}) phenyl-phosphonic acid may be used for deep extraction of TPE and other α-nuclides from HLW with concentration up to 2 mol/l HNO_3 . The extraction process of long-lived radionuclides from the solutions, characterized by complex salt composition and high radiactivity level, can be fulfilled by two succesive stages. In case ZCS of HDEHP on first stages we separeted light REE and TPE, on the two stages REE yttrium group. Sheme of TPE, Ln and ^{90}Sr extraction with simultaneous removal of other α -nuclides from HLW includes TPE and Ln extraction with 0,9 mol/l n-alkil(C_8-C_{10})phenylphosphonic acid solution in n-paraffin dissolvent and ^{90}Sr extraction with 0,15 mol/l solution of zirconium salt of the indicated acid .

The perspective approach by choice of technology partitioning consists in combined extraction, sorbtion and precipitation methods for preparation radionuclides to transmutation. The minimization of secondary waste of partitioning is connected with development of new selective reagents, methods of multistage processes organization and also physical methods separation.

Partitioning HLW - the separation long-lived radionuclides from salts, is expedient for reduction of volume the most toxic wastes and for recovery of fractions radionuclides with the purpose transmutation [1]. Both purposes assume deep removal long-lived radionuclides from HLW, and recovery of fractions radionuclides in the form, necessary for inclusion in a matrix with the purpose of reliable disposal or transmutation.

In Russia a number of technologies on partitioning HLW of a working radiochemical plant RT-1 (Mayak) is developed. First of all it concerns to technology partitioning HLW, developed in ARSRIIM after A. A. Bochvar (Moscow) as the part of complex technology of reprocessing spent fuel VVER, based on use HDEHP for extraction of transplutonium (TPE), rare earths elements (REE) and strontium-90 [2]; technologies of removal cesium-137 and strontium -90 extraction CCD, developed in Khlopin Radium institute (St. Peterburg) [3] and soption cesium -137 on ferrocyanide FC-10, developed in the Institute of Physical chemistry (Moscow) [4].

To new development on partitioning HLW use bidentate extractants for removal α-nuclides from HLW (ARSRIIM, Khlopin Radium Institute, Vernadsky Institute of Geochemistry and Analytical chemistry of RAS) [5-9], use of acidic zirconium compounds salts of phosphorus-organic acids(ZCS POA) for extraction α-nuclides and strontium-90 from nitric acid solutions (ARSRIIM) [10]; of extraction system on basis of crown-ethers for extraction strontium-90 and cesium-137 (ARSRI Chemical Tecknology) [1, 11];

A number of processes of separation radionuclides: use cationic chromatography for separation TPE and REE [12,13], extraction and precipitation TPE [14, 15], can be directly used in technology partitioning HLW, in particular for partition more short lived curium. Methods partitioning HLW by use of heavy water blanket [16] and molten fuel [17,18] for transmutation radionuclides are developed.

At the moment on a plant on reprocessing spent fuel RT-1 total losses U, Pu and Np with raffinate of the first and second cycle make accordingly 0,01; 0,025 and 0,5 %. Practically whole Pu and Np through oxalic precipitation are transformed in dioxides and are directed on storage (part Np is used for reception ^{238}Pu) [19]. Work on partition Tc will be carried out at processing spent fuel, thus more than 95 % the localization Tc [20] is expected. Generation of Ru from Tc will potentially allow to pay back a part of expenses on transmutation[21].

HLW concentrate by evaporation and direct on temporary storage and solidification [22]. At evaporation of acidic HLW it is possible remove practically the whole nitric acid, thus rate of evaporation is determined solubility of nitrate HLW [23]. At the given stage there is the basic opportunity of physical partition of HLW in view of various solubility of nitrate radionuclides .

The flow sheet of complex reprocessing spent fuel VVER, developed in ARSRIIM included operations evaporation raffinate after extraction U, Pu and Np for removal of a nitric acid (final acidity - 0,2 - 0,3 mol/l establishments pH 4-4,5 for maintenance of conditions extraction strontium-90 by introduction sodium acetate and citric-ion in quantit 120 % from stoichiometry for linkage Fe, Cr and Ni; joint extraction REE, TPE and strontium-90 by a solution 0.6 mol/l HDEHP in paraffine diluent; stripping strontium-90 0,1 mol/l by a solution of a nitric acid; selective stripping TPE by a solution, containing 0,8 mol/l of lactic acid and 0,05 mol/l of DTPA; stripping REE 3 mol/l by a nitric acid; carbonate regeneration of extractant [2].

By extraction of α-nuclides the aforesaid complexone it is not required. In such variant the process ARSRIIM can be used for partitioning evaporated raffinate of Purex-process at concentration HNO3 0,2 - 0,3 mol/l.

In spite of the fact that the purposes of reprocessing HLW and the requirements to parameters of process of separation long-lived radionuclides have at the moment changed, extractants on a basis of phosphorus-organic acids remain the most effective for group separation of transplutonium and rare earth elements.

For deep extraction TPE and other α-nuclides from HLW with concentration up to 2 mol/l HNO3 can be used of ZCD HDEHP and of a n-alkyl(C_8C_{10})phenylphosphonic acid (n-APPhonK).

By use ZCD HDEHP the technological flow sheet includes [10]: evaporation HLW up to final concentration [HNO3] 1,5 - 2 mol/l; extraction of a sum α-nuclides and REE from HLW; stripping of a sum REE and TPE 6 mol/l HNO3; regeneration extractant with removal of the rests α-nuclides.

The flow sheet of separation TPE, REE, ^{90}Sr by simultaneous removal from HLW other α-nuclides includes extraction REE and TPE 0,9 mol/l; by a n-APPhonK in n-paraffine diluent and extraction ^{90}Sr 0 ,15 mol/l by a solution ZCD of the specified acid [24].

The salts of POA with polyvalent cations as Zr and Hf are effective extractants for alkaline earth elements (AEE) , REE and TPE from of nitric acid solutions. In a complex H_2ZrA_6, where A - anion POA, under influence central cation there is the strengthening of extraction properties of coordinated molecules HA in relation to one elements and suppression extraction of other elements. Extraction of metals proceeds on the cation exchange mechanism. The solutions ZCS POA in n-paraffine diluents are characterized by significant radiating and chemical stability, keep high extraction ability and capacity on taken metals after boiling (5-6 hours) with 3 mol/l nitric acid and practically do not change of extraction properties up to a doze of absorbed energy $4 * 10^5$ Gr. The water solutions fof reprocessing spent fuel have complex radiochemical and chemical composition. At transition from POA to ZCS POA there is the suppression extraction number salt cations HLW in particular of products of corrosion (Ni, Cr) and some radionuclides, that increases selectivity of separation TPE and ^{90}Sr from HLW. The essential increase of extraction properties POA by linkage them in the form of zirconium salts at simultaneous increase of selectivity of partitioning long-lived radionuclides from HLW opens prospect of wider use extractants of the given class in practice of reprocessing HLW [25].

For removal α-nuclides from HLW are offered extractants on a basis carbamoylphosphine oxides and diphosphine dioxides [5-6]. The effect anomalous aryl strengthning of the complexes of actinides provides high extraction ability diphosphine dioxides at clearing HLW from actinides [6].

On experienced laboratory plants an opportunity of deep removal (factor of distribution on one step membrane extraction is 10-20) and concentration actinides membrane extraction ditolyldibutylcarbamoylphosphine oxide the house is shown: from 0,01 mg/l up to 80 mg/l on Pu [7].

With the purpose of minimization secondary wastes, formed at partitioning HLW, enchanged explosion- and fire-safety of process in Khlopin Radium institute in quality diluents of neutral bidentate pyhosphororganic compounds are offered fluorcontained ethers. At partitioning offered extractants 3-8-divisible reduction of volume HLW is received at a degree of clearing from α-nuclides - 10^4 [8].

Essential lack bidentate extractants, offered for partitioning α-nuclides from HLW, is low selectivity. For sparation REE and partition actinides on a fraction search selective reactants and new ways of realization of multistep processes will be carried out. Is shown, that by use 1,2,4,- tris-(diphenylphosphinmetyl)benzene at extraction from 3 mol/l of a nitric acid factor of separation Am/Eu is equal 7 [9]. The selectivity extractants of the given class is determined by a mutual stereosequence of diphosphine groups. For selective separation radionuclides bidentate extractants engineering extraction chromatography with the purpose of increase of steps of separation can be used, however is more perspectiv, in our opinion, development of engineering liquid chromatography with a free liquid phase [26].

In Khlopin Radium institute partitioning of HLW is developed by use a solution chlorinated cobalt dicarbollide (CCD): $H^+\{[p-(3)-1,2-B_9C_2H_{11}C_{l2}]_2 Co\}$ and polyethylene glycol in a mix polar nitroorganic and nonpolar solvents [3, 27 - 29]. The most effective extractant can be used for removal Cs and Sr. At extraction directly from raffinate of Purex-process removal Cs and Sr is achieved more than 99 % with a degree of clearing from impurity $10^3 - 10^4$. With increase of cation charge the efficiency extraction falls, therefore a sum TPE and REE CCD takes from solutions with [HNO3] no more than 0,5 mol/l, and the extraction actinides with higher charge is problematic.

The complex flow sheet partitioning HLW of extraction CCD includes operation evaporation HLW, decrease of concentration nitric acid (no more than 0,5 mol/l) with subsequent extraction and fraction stripping REE, TPE, ^{90}Sr and ^{137}Cs.

The Institute of Physical chemistry (Moscow) has developed the sorption partitioning of ^{137}Cs from spent fuel solutions. Copper ferrocyanide-based sorbent (FC-10) used is delivered by the Perm State Univercity manufacturing department.

When sorbing from the PUREX raffinate , the FC-10 capacity is 100±5 mg/g at 0.3 mole/l HNO_3 and 5±0.5 mg/g at 3 mole/l HNO_3 . With hydrazine addend for combining with nitrous acid, the sorbent capacity is much higher in acidic solutions. Table 1 lists data on the Cs sorption from imitated solutions having 0.05 N_2H_4 as a function of the HNO_3 concentration.

Capacity FC-10 on Cs by sorption from imitation solution contained 0,05 mole/l N_2H_4 * HNO_3

[HNO_3], mole/l	Dynamic capacity FC-10, mg/g	
	before detection	entire
2.0	83±4	160±8
3.0	78±4	155±8
4.0	55±3	145±7

As can be seen, the gitlds good results at 4 mole/l HNO_3. When desorbing ^{137}Cs by 6-10 mole/l, no liss than 95 % of sorbed is are washed out with the first fire column volumes of eluate.

The sorbent can be regenerated (to convert Fe(III) to Fe(II)) by the following solution, g/l: sodium nitrite , 18; potassium nitrate, 40; (pH 6-8).

Average sorbent losses during 20 successive sorption - desorption - regeneration cycles amount 0.3-0.5 % per cycle.

Major stages of the ^{137}Cs recovery are: pH adjustment; hydrazine addition; ^{137}Cs sorption by FC-10; ^{137}Cs desorption by HNO_3; sorbent regeneration; ^{137}Cs desorbate evaporation to cerium nitrate.

Within 1988-93 about $8 \cdot 10^6$ m^3 of diverse process solutions was reprocessed to yield $4 \cdot 10^6$ [137]Cs.

In ScientificResearch Institute Nuclear Reactors (SRINR) extraction HDEHP is used for separation individual TPE from irradiated targets [13]

The clearing TPE from Al, Fe, Zr will be carried out extraction 0,5 mole/l HDEHP in n-paraffine diluent from citric solutions. For separation TPE and REE is used similar extraction system, but in addition in 0,3 моль/л citric solution (pH 3-3,5) is entered 0,015 mole/l DTPA. The separation Bk, Cf and Es will be also carried out extraction 0,5 mole/l by a solution HDEHP, and separation Am and Cm precipitation double carbonate K and Am after oxidation Am of amonium persulfate. The basic characteristics of separation TPE and REE are resulted in tab. 2.

Table 2
Parameters of separation TPE and REE at processing irradiated targets

Element	D	Factor of separation		
		Ce/TPE	Pm/TPE	Eu/TPE
Cm	0,05	120	40	70
Cf	0.20	30	10	7

For separation Am and Cm in SRINR is investigated a carbonate method. Process of preparations of fractions Am and Cm with the contents Cm in a fraction of Am up to 0,1 % and Am in a preparation of Cm up to 0,3 - 0,5 % is developed [15].

For recovery individual radionuclides are offered of extraction system on a basis dicyclohexane-18-crown-6 for ^{90}Sr and dibenzo-21-crown-7 for [137]Cs [30]. The technological flow sheet with use of crown-ethers differ by simplicity; from concentrate Sr and Cs desired products can be received by precipitation radionuclides or evaporation of solutions.

Pyrometallurgical (dry) methods of the reprocessing HLW for transmutation radionuclides in blanket molten fluoric salts are developed at the moment in SRINR [18]. The basic flow sheet provides removal »of noble fission products from a flow and plant of electrochemical processing of molten fuel. The electrochemical processing of molten fuel includes electrolyzer for separation Zr and minor actinides, electrolyzer for clearing fuel salt from REE and unit of updating of composition of fuel salt.

From considered methods of recovery and the separations long-lived radionuclides at the moment for practical application in Russia are the most fulfilled water extraction and sorption processes. For reprocessing HLW, formed on working radiochemical plants RT-1, in Russia three methods with use POA, CCD and bidentate extractants for removal α-nuclides are offered. Use POA allows thus also to take and ^{90}Sr, and in a case CCD to them radionuclides is added and цезий-137.

Despite essential advantages bidentate extractants, first of all an opportunity of removal α-nuclides directly from raffinate Purex-process and simplicity stripping, POA, in our opinion can quite compete at economic comparison of the given technologies. It is connected to expediency evaporation HLW for reduction of their volume. In process evaporation acidity HLW can be lowered up to value, at which can be used POA or them zirconium compounds. The important advantage POA in comparison with bidentate extractants is high selectivity ФОК at group separation TPE and REE. For regeneration POA - strong extractants heavy REE, Fe, Zr and similar cations, phosphoric acid by analogy to processes in a uranium industry [30] can be used . The formed product can be directed on vitrification.

Use CCD as universal extractants for partitioning HLW is limited first of all by its difficulty extraction fourthvalent actinides.

For recovery from raffinate of Purex-process Sr and Cs crown-ethers, however the published losses given not enough for an estimation extractants can be used at processing HLW.

For recovery Cs is well fulfilled copper ferrocyanide-based sorbent (FC-10). Essential advantage given sorbent is an opportunity of its long-duration use in cycles sorption-desorption, that allows to minimize accumulation ferrocyanide waste at partitioning HLW.

For separation TPE and REE are used Talspeak-process and its updatings. . But the capacitance of extractants used to REE and supplementary recovery of TRE from complexing agent-bearing solutions set a limit on the process. The TPE recovery could be excluded by allowing the TRE concentrate to stand until organic constituents are completely decomposed.

The basic diagram of the Talspeak-process is unaffected by one or other type of POA.

Extraction chromatography and TVEX processes are useful for selective partitioning of TPE and REE but extractant capacity limitations are much more dramatic in this case.

The solvent chromatography involving a free liquid phase has the advantage of combining a complete exhaustion of extractants with efficient chromatographic partition.

Cation chromatography has its greatist impact in partitioning individual constituents

Use of dry methods partitioning HLW is of interest for use of physical methods separation - electrolysis , distillation, not requiring introduction chemical reactants. In too time at the stage of gas cleaning there is the essential accumulation secondary waste of processing. An opportunity of use of physical methods partitioning HLW is unsufficiently investigated at processing raffinate of Purex-process. First of all it concerns to an opportunity fractional crystallization in process evaporation HLW at modify of concentration of a nitric acid and salts.

The inclusion of processes partitioning HLW and transmutation actinides and fission products in the nuclear fuel cycle requires accent on problems of safety, protection of an environment and non-distribution [32]. Processing the most active products (up to 1000 Ku/l), containing extremely toxic radionuclides, requires as much as possible reliable technology.

The perfection of processes partitioning HLW is connected to development new selective reactants and methods of organization of multistep processes:

·   Perfection of existing processes with the purpose of minimization secondary waste and increase of safety of processing HLW;

        seeking for stereoselective polydentate compounds containing carbonyl, amid and phosphoryl groups for selective partitioning of TPE and REE;

        development of the equipment for realization of multistep processes of separation radionuclides, in particular liquid chromatography with a free liquid phase.

·   Use of physical methods of recovery and separation radionuclides for minimization total accumulation HLW.

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DEVELOPMENT OF PYROMETALLURGICAL PARTITIONING TECHNOLOGY OF LONG-LIVED NUCLIDES
- DEVELOPMENT OF SALT WASTES TREATMENT TECHNOLOGY -

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In order to stabilize chloride wastes generated by the pyrometallurgical partitioning process of TRU, a process to vitrify chlorides is being developed. In the process, chlorides are reduced to metals by molten salt electrolysis and the metals are oxidized by air and then vitrified, when lithium metal and chlorine gas are recycled. The behaviors of lithium and other elements during molten salt electrolysis were studied as a function of composition of salt and cathode materials. It was shown that every metal can be recovered into liquid lead cathode by electrolysis, and that liquid cadmium and solid cathode are suitable for recovering lithium and sodium metal, respectively. Consequently, the flow sheet for the salt wastes treatment process was demonstrated.

INTRODUCTION

The pyrometallurgical partitioning technology to recover transuranium elements (TRU) from high level radioactive wastes (HLW) generated by PUREX reprocessing is being developed by CRIEPI[1][2]. The flow diagram for the pyrometallurgical partitioning process is shown in Fig.1. HLW are denitrated to oxides by microwave heating and the oxides are converted to chlorides by chlorine gas and carbon. Then in a molten chlorides/liquid cadmium system noble metals, TRU and most of rare earth elements are reduced by addition of lithium metal and extracted into liquid cadmium. Alkali and alkaline earth metal chlorides such as CsCl and $SrCl_2$ remain in the molten chlorides. Finally TRU are separated from the liquid cadmium by electrorefining and/or multistage extraction in LiCl-KCl eutectic salt.

Two types of salt which should be treated for disposal are generated by the pyrometallurgical partitioning process. One is mixed chloride consisting of LiCl, NaCl, $RbCl,CsCl$, $SrCl_2$, $BaCl_2$, $SmCl_2$ and $EuCl_2$ from reductive extraction step. The other is LiCl-KCl eutectic salt containing rare earth trichlorides from electrorefining and/or multistage extraction step.

Since chlorides are easily soluble in water, they must be converted to stable waste form suitable for geologic disposal. So a vitrification process for chlorides is being developed. In the process chlorides are decomposed into metals and chlorine gas by molten salt electrolysis. Then the metals are converted to oxides with air and are vitrified. It is desirable that lithium metal, chlorine gas and LiCl-KCl eutectic salt are recycled in the TRU partitioning process to reduce secondary wastes. In order to demonstrate this vitrification process, behaviors of elements during molten salt electrolysis were studied experimentally and the process flow sheet was discussed.

EXPERIMENTAL

Experiments of molten salt electrolysis were carried out by use of various composition of salt with
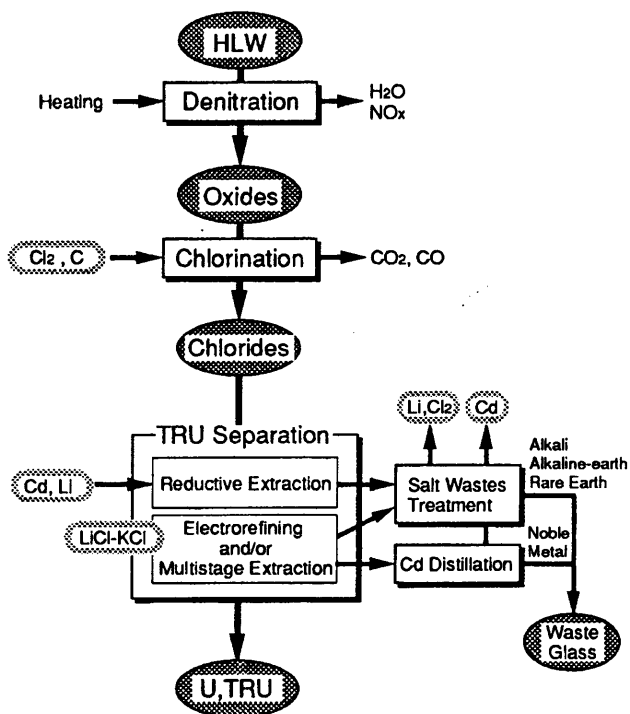

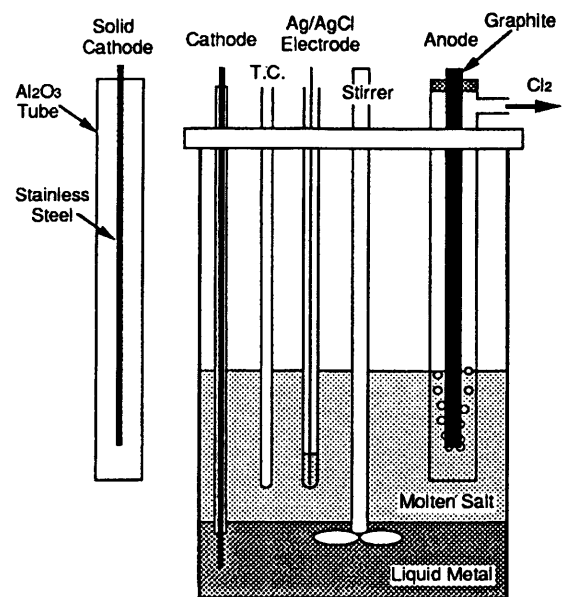Fig. 1 Schematic flow diagram for TRU pyrometallurgical partitioning from high level wastes.

Fig. 2 Experimental cell for molten salt electrolysis.

three types of electrode which are liquid cadmium, liquid lead and solid cathode. The experimental cell is shown schematically in Fig.2. There were a graphite anode, a lead for liquid metal cathode, an Ag/AgCl reference electrode, a thermocouple and a stirrer in an alumina crucible containing molten chloride and liquid metal. Cadmium or lead was used as liquid cathode. In some experiments a solid cathode made of stainless steel was used instead of liquid metal cathode. The solid cathode was surrounded by an alumina tube to prevent metal deposit dispersing. At graphite anode chlorine gas was generated during electrolysis. The cell was located in a stainless steel thermowell attached to the floor of a glove box. The atmosphere in the glove box was high purity argon. The well was heated externally with a electric furnace. Salt and liquid metal samples were taken with pyrex glass tube and dissolved in nitric acid. The content of each element in the solutions was determined by ICP-AES or atomic absorption spectrometry.

RESULTS

A typical result for a electrolysis with liquid metal cathode is shown in Fig.3. Initial salt consisted of 68mol% of LiCl, 29mol% of NaCl, and small amount of $CsCl, BaCl_2$ and $SmCl_3$. As electrolysis proceeded, concentrations of all elements except cesium in liquid lead increased and samarium concentration in the salt decreased. Concentrations of lithium and sodium in liquid lead were high because of those in salt were high. To evaluate which element can be reduced easily, distribution coefficients were calculated. Distribution coefficient D is defined by equation [1].

$$D_M = X_{M \, in \, liquid \, metal} / X_{M \, in \, salt} \quad \cdots \quad [1]$$

where $X_{M \, in \, liquid \, metal}$ is mol% of metal in liquid metal and $X_{M \, in \, salt}$ is mol% of metal chloride in salt. The relationship between logarithm of distribution coefficients of elements and that of lithium is shown in Fig.4. The straight lines were fitted by the least squares method. The slopes
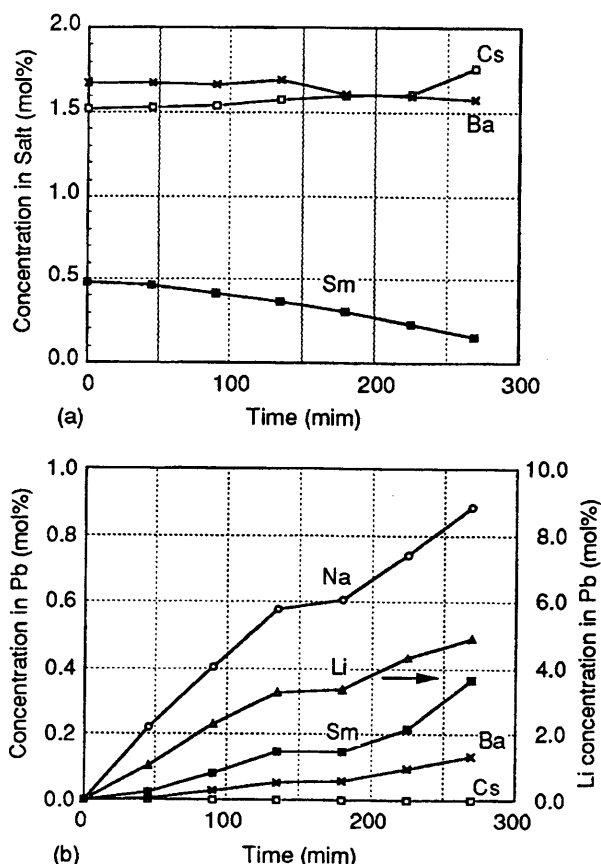
Fig.3 Concentration of elements in molten salt phase (a) and liquid lead phase (b) during constant current electrolysis. Conditions of the electrolysis were as follows: temperature =600°C ; current =3A weight of lead =1030g ; initial weight of salt =353g ; initial composition of salt (mol%) $LiCl:NaCl:CsCl:BaCl_2:SmCl_3$ =67.6:28.7:1.5:1.7:0.5
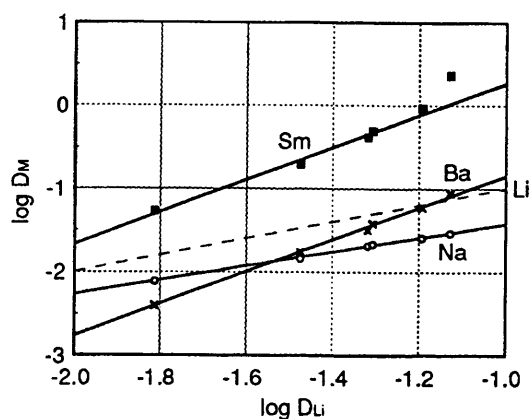
Fig.4 Distribution coefficient of metals against that of lithium during electrolysis. Distribution coefficient, $D_M = (X_{M \, in \, liquid \, metal}) / (X_{M \, in \, salt})$.

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of the lines for samarium, barium and sodium were 1.97, 1.93 and 0.85, respectively. It is explained that as samarium and barium form dichloride in salt, their slopes are near two. As sodium form monochloride, its slope is near one (At equilibrium there is a thermodynamic relationship that $\log D_M = n_M \log D_{Li} + const.$, where n_M is the oxidation state of the element in salt). It is indicated that samarium is more easily reduced than lithium and that lithium is more easily reduced than sodium. Where $\log D_{Li}$ is more than 1.17, barium is more easily reduced than lithium.

Separation factor SF of a element against lithium is defined by equation [2].

$$SF = D_M / D_{Li} \qquad \cdots [2]$$

Separation factors obtained by four electrolysis experiments and one equilibrium experiment [3] are shown in Table 1. These SFs were calculated by extrapolation of the lines to $\log D_{Li} = 0$, which obtained by the least squares method with the slopes of the fitted lines regarded as n_M. The results in Table 1 indicates that (1)trivalent rare earth elements such as yttrium and cerium can be reduced into liquid metal very easily, (2)divalent rare earth elements such as samarium and europium can be reduced into liquid metal easily, (3)alkaline earth elements such as strontium and barium are more easily reduced than lithium where concentration of lithium in liquid metal is higher, (4)sodium is not so much as reduced than lithium, (5)cesium cannot be reduced into liquid metal cathode until concentration of cesium in salt becomes higher, (6)cadmium cathode is more suitable to separate lithium from sodium than lead cathode, and that (7)lead cathode is more suitable to separate lithium from alkaline earth elements than cadmium cathode.

Table 1 Separation factors (SF) in molten chlorides / liquid metal syatems, where (XLi in metal)/(XLi in salt) = 1

Element	Separation Factor (SF)				
	During Electrolysis				Equiliblium
	Li-NaCl/Pb (Li:Na=7:3) 600°C	CsCl/Pb (Cs:96mol%) 700°C	Li-NaCl/Cd (Li:Na=7:3) 600°C	Li-Na-CsCl/Cd (Li:Na:Cs=38:16:45) 600°C	LiCl-KCl/Cd * (Li:K=59:41) 500°C
Li (basis)	1	1	1	1	1
Na	0.42	2.1	0.078	0.26	0.19
K	-	0.25	-	-	2.7×10^{-4}
Cs	ND	0.11	ND	ND	ND
Sr	-	13	-	-	3.7
Ba	15	58	3.0	16	6.7
Y	-	-	10000	-	2.2×10^8
Ce	-	-	10000	-	2.1×10^{10}
Sm	200	-	100	-	680
Eu	-	100	-	-	150

ND : not detected in the liquid metal
* M.Kurata et al. (3)

The result of electrolysis experiment using solid cathode is shown in Table 2. The electrolysis was carried out in molten salt consisting of LiCl, NaCl, CsCl, $BaCl_2$ and $SmCl_2$. During electrolysis the deposit of metal floated at the surface of salt surrounded by alumina shroud, as the density of the metal was less than that of molten salt. Finally 4.4g of the deposit of metal was recovered and it was determined that more than 99% of the metal was sodium. It was demonstrated that sodium metal without lithium is

recovered by electrolysis by using solid cathode.

Table 2 Compositions of initial salt phase and metal deposit for the electrolysis with a solid cathode (stainless steel rod).The conditions of the electrolysis were as follows: temperature =500°C; weight of salt =690g ; current =0.7A ; time for electrolysis =380min ; weight of the deposit of metal recovered =4.4g

Element	Composition (mol%)	
	Initial salt	Metal deposit
Li	43.8	< 1
Na	14.4	> 99
Cs	38.2	< 1
Ba	3.0	< 1
Sm	0.6	< 1

FLOW SHEET FOR SALT TREATMENT PROCESS

The flow sheet of salt wastes treatment shown in Fig.5 is proposed on the basis of experimental results. There are two types of salt waste. One is LiCl-KCl eutectic salt containing rare earth trichloride from TRU/RE separation step. It is not difficult to remove rare earth from LiCl-KCl eutectic salt by molten salt electrolysis with lead cathode. Purified LiCl-KCl eutectic salt is recycled. The other is mixed chloride consisting of alkali (Li,Na,Rb,Cs), alkaline earth (Sr,Ba) and rare earth (Sm,Eu) chlorides. The latter salt is treated by the following procedure: (1)rare earth is recovered in lead cathode; (2)lithium is recovered in cadmium cathode to recycle in TRU separation process; (3)all of elements are recovered in lead cathode; (4)lead alloys containing active metals (alkali, alkaline earth and rare earth metals) are reacted with oxygen in air and active metals are converted to oxide; (5)the oxide is mixed with glass materials and vitrified. The lead metal in which active metals are removed is recycled. Chlorine gas generated at carbon anode during electrolysis is recycled in chlorination step for HLW. Sodium comes from solvent cleaning of PUREX processing. If a large amount of sodium accompanies the recycled lithium, the melting point of salt in reductive extraction step gets higher. Therefore, sodium would be removed by electrolysis with solid cathode so that more lithium metal can be recycled.

The advantage of this salt treatment process is that waste form of glass is familiar and that it is possible to reduce an amount of secondary wastes by recycling lithium metal ,chlorine gas and LiCl-KCl eutectic salt.
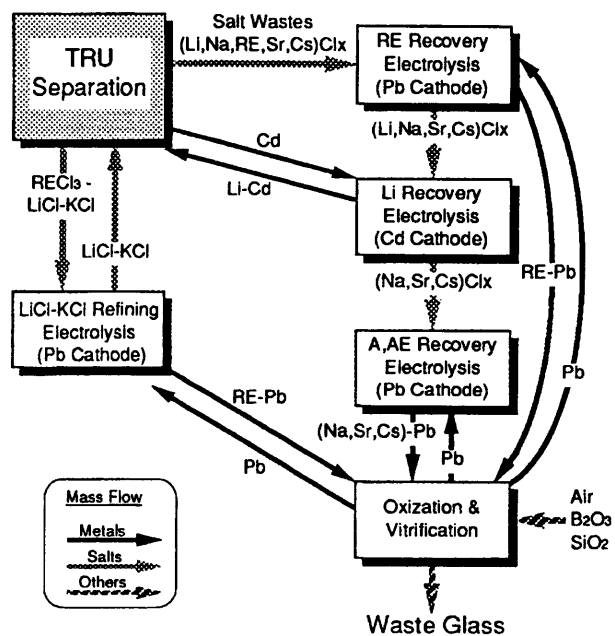

Fig. 5 Schematic flow diagram of salt wastes treatment.

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