

SESSION III

PARTITIONING

J.P. Glatz (ITU) – J. Laidler (ANL)

SESSION III
PARTITIONING

SUB-SESSION III-A:
AQUEOUS REPROCESSING

PARTITIONING-SEPARATION OF METAL IONS USING HETEROCYCLIC LIGANDS

Michael J. Hudson¹, Michael G.B. Drew¹, Peter B. Iveson¹, Charles Madic², Mark L. Russell¹

¹Department of Chemistry, University of Reading

Box 224, Whiteknights, Reading, RG6 6AD, United Kingdom

²Commissariat à l'Énergie Atomique, B 171, Bagnols-sur-Cèze, 30207 France

Abstract

Some guidelines are proposed for the effective design of heterocyclic ligands for partitioning because there is no doubt that the correct design of a molecular extractant is required for the effective separation of metal ions such as actinides(III) from lanthanides(III). Heterocyclic ligands with aromatic ring systems have a rich chemistry, which is only now becoming sufficiently well understood in relation to the partitioning process. The synthesis, characterisation and structures of some chosen molecules will be introduced in order to illustrate some important features. For example, the molecule N-carboxybutyl-2-amino-4,6-di (2-pyridyl)-1,3,5-triazine (BADPTZ), which is an effective solvent extraction reagent for actinides and lanthanides, has been synthesised, characterised and its interaction with lanthanide ions studied. The interesting and important features of this molecule will be compared with those of other heterocyclic molecules such as 2,6-bis(5-butyl-1,2,4-triazol-3-yl) pyridine (DBTZP), which is a candidate molecule for the commercial separation of actinides and lanthanide elements.

Primary co-ordination sphere

One of the most critical features concerning whether a molecule is a suitable extraction reagent is the nature of the binding and co-ordination in the primary coordination sphere of the metal. The resultant effects for partitioning will be considered briefly for selected heterocyclic molecules. It will be shown how the structural types change as the complete lanthanide series is traversed from lanthanum to lutetium. For effective solvent extraction, the ligand(s) should be able completely to occupy the primary co-ordination sphere of the metal ion to be extracted. Interactions in the secondary co-ordination sphere are of less importance.

Inter-complex (Hydrogen Bonding) interactions

Another feature that will be briefly considered is the intermolecular binding between ligands when bound to the metal ion. Thus the intermolecular structures between complex molecules will be considered where these have relevance to the extraction process. For effective separations, the intermolecular interactions should be minimised such that there are only weak van der Waals interactions arising from the hydrophobic exteriors of the complexes.

Implications for partitioning

The effectiveness of the above heterocyclic reagents will be considered in relation to the interactions in the primary co-ordination sphere of the metal and the intermolecular interactions.

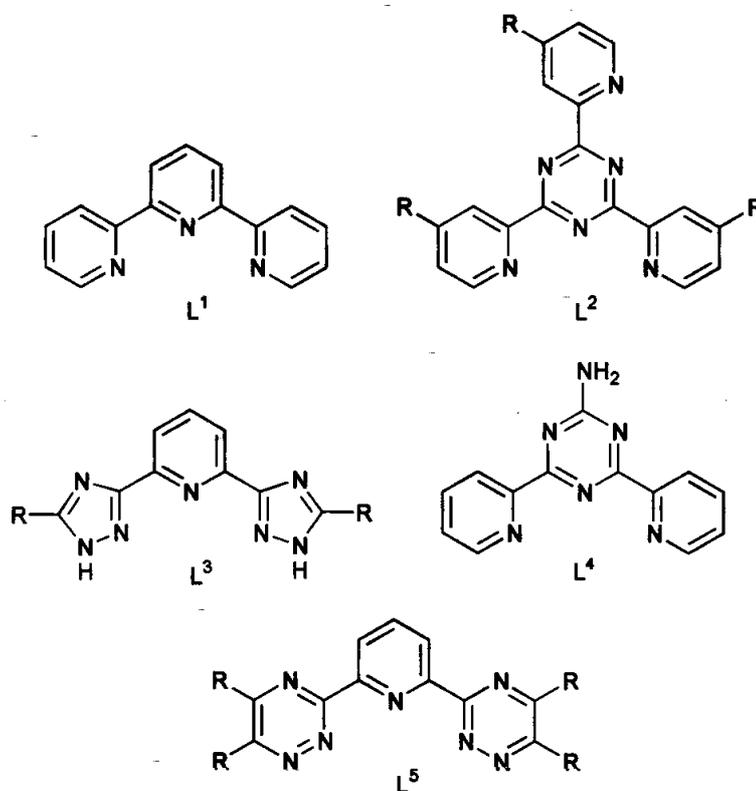
1. Introduction

There is no doubt that the correct design of a molecule is required for the effective separation of metal ions such as actinides(III) from lanthanides using solvent extraction reagents. Recent attention has been directed towards malonamides for coextraction but heterocyclic ligands with aromatic ring systems have a rich chemistry, which is only now becoming sufficiently well understood in relation to the partitioning process for the selective extraction of the actinides [1].

A future goal in nuclear fuel reprocessing may be the conversion or transmutation of the long-lived radioisotopes of minor actinides, such as americium, into short-lived isotopes by irradiation with neutrons [1]. In order to achieve this transmutation, it is necessary to separate the trivalent minor actinides from the trivalent lanthanides by solvent extraction, otherwise the lanthanides absorb neutrons too effectively and hence limit neutron capture by the transmutable actinides. Solvent extraction using ligands containing only carbon, hydrogen, nitrogen and oxygen atoms is desirable because they are completely incinerable and thus the final volume of waste is minimised [2]. Nitric acid is used in the extraction experiments because it is envisaged that the An(III)/Ln(III) separation process could take place after the existing PUREX process. For the ensuing discussion the heterocyclic ligands are considered as free bases but in practice one or more of the nitrogen atoms will be protonated – this should not influence the overall discussion since co-ordination to metal ion dominates over protonation particularly in the chelating molecules under consideration.

There is clearly a need to study future processes such as SANEX in which the minor actinides are selectively separated from the lanthanides. For the reasons outlined below, the solvent extraction reagents depicted in Figure 1 have been evaluated.

Figure 1. The ligands L^1 , L^2 , L^3 , L^4 and L^5



The terpyridyl reagent (ligand L^1) has been extensively studied previously [3]. With common ligands such as L^1 and 2,4,6-tri(2-pyridyl)-1,3,5-triazine (L^2), Am(III)/Eu(III) separation factors between 7 and 12 have been obtained when 2-bromohexanoic acid is used as a synergistic reagent [4]. The alkyl derivatives of tripyridyl-*s*-triazines (L^2) may well be good candidates for future studies but difficulties of synthesis has limited the availability of these reagents. The design of molecules such as the 2,6-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-pyridines (BTPs) (L^5) has lead to improved separation factors [5] without the requirement for reagents such as 2-bromohexanoic acid, which is required with most other heterocyclic reagents. The evaluation of the structures of complexes formed by L^4 with some trivalent metal ions has enabled the co-ordination of these ligands with the entire range of lanthanides to be evaluated. This has meant that the limitations on co-ordination caused by the lanthanide contraction are now better understood.

We have studied the molecule N-carboxybutyl-2-amino-4,6-di(2-pyridyl)-1,3,5-triazine (BADPTZ), which is an effective solvent extraction reagent for actinides and lanthanides. This molecule co-ordinates to the metal ions to L^4 but has improved Am(III)/Eu(III) separation factors of over 10. Thus it will shortly be possible to correlated precise solvent extraction data with known metal-ligand interactions.

2. Guidelines

One of the most important features concerning whether or not a molecule is a suitable extraction reagent is the nature of the binding and co-ordination in the primary and secondary co-ordination spheres of the metal ion. Thus it is possible to formulate some general guiding suggestions (not rules) for the purposeful design of ligands:

- The extractant molecules (ligands) should be designed so as to exploit the differences in the co-ordination chemistries (including ion-pair formation) of the ions to be separated.
- For effective solvent extraction, the ligand molecule(s) should be able completely to occupy the primary co-ordination sphere of the metal ion to be extracted.
- Interactions in the secondary co-ordination sphere are of less importance even though the counter-ions are in the secondary co-ordination sphere.
- There should be limited intermolecular interactions between the extracted species – preferably only van der Waals interactions such that even hydrogen bonding is minimised.
- There should only be a single species that is extracted.
- The chemical bonds within the primary co-ordination sphere should be strong but not so strong as to prevent subsequent bond breaking for the subsequent stripping process.
- There should be acceptable resistance to radiolysis.
- The likely decomposition products should have minimal interference with the solvent extraction process.

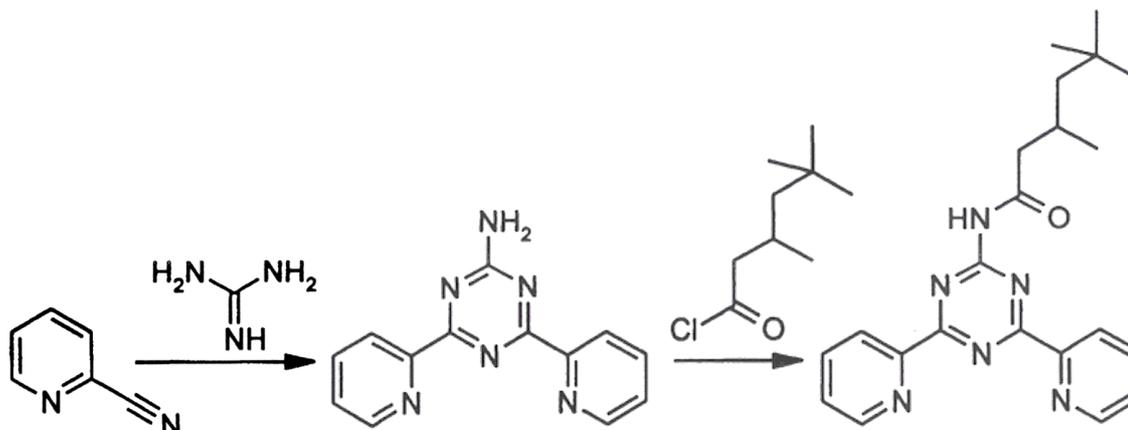
2.1 Primary co-ordination sphere

The primary co-ordination sphere of the metal ion is defined by the covalent binding between the metal atom and the immediate ligand atoms and the stereochemical arrangement of the ligands (or solvent extraction reagents). For lanthanides and minor actinides, metal-ligand binding is considered

to be much more ionic than is the case with the trivalent transition metals for which Crystal Field Effects play an important thermodynamic part. Thus the ligands are much more loosely bound in many cases – such that the metal-ligand bonds are broken and reformed much more readily than is the case with the transition metals or with the major actinides prior to Am. The design of polydentate nitrogen ligands, which complex minor actinides such as Am(III) preferentially to lanthanides, has proved to be challenging because the chemistries are so similar. Such differences that can be identified include the marginally enhanced selectivity of “soft” nitrogens in a heteraromatic ring for Am(III) than for Eu(III). Moreover, there is a body of evidence to suggest that the polydentate ligands are more firmly bound to the metal than is the case with monodentate ligands. Accordingly, we have been varying the nature of the donor nitrogen ligands in order to enhance these small differences so that they are manifested in increased separation factors (Am(III)/Ln(III) [2,3].

In order to do this, however, it is essential to understand the fundamental chemistries involved and to evaluate the structural types that are formed with different stereochemistries and bound ligand atoms. For example, the molecule N-carboxybutyl-2-amino-4,6-di-(2-pyridyl)-1,3,5-triazine (BADPTZ), which is an effective solvent extraction reagent for actinides and lanthanides, has been synthesised, characterised and its interaction with metal ions studied – see Figure 2. A low pressure cyclisation route has proved to be particularly useful in the synthesis of these reagents and has enabled a wide range to be prepared. In particular, the ligand ADPTZ (L^4) in which there are no alkyl groups on the amide group, has enabled the study of the range of structures that are manifest across the whole lanthanide series [6]. There are five structure types, which can be broadly divided into two equal groups. The larger lanthanides from La to Sm form structure types in which the co-ordination numbers are 11 and 10. La is the only lanthanide to form an 11-coordinate complex $La(ADPTZ)(NO_3)(H_2O)_2$ in which the ligand is tridentate and the nitrates are all bidentate. The La cation is too large to fit into the tridentate cavity of the ligand and sits outside. One general feature of the lanthanide complexes and the minor actinides is that there is rather rich co-ordination chemistry and several complexes have been identified for the same metal and ligands. For example, Nd and Sm both form two different 10-coordinate complexes. The first, $M(ADPTZ)(NO_3)_3(H_2O)$ is neutral with three bidentate nitrates and one water molecule. The second, $[M(ADPTZ)(NO_3)_2(H_2O)_3]^+$ is a cation with two bidentate nitrates and three water molecules. For the smaller lanthanides, there are two structure types, each of which is nine co-ordinate. One of these structures, $[LnL^4(NO_3)_2(H_2O)_2](NO_3)$, is rather unusual in that a dication is formed together with two nitrate anions. The complex $[Yb(ADPTZ)(NO_3)_3(H_2O)]$ is unusual in that it contains a monodentate nitrate anion. Without exception, the structures show intermolecular hydrogen bonding between the amine group of the metal complexes or solvent molecules. Such an observation is contrary to Guideline 4 but the inclusion of an alkyl or other hydrophobic group on the amine group greatly restricts the intermolecular hydrogen bonding so that BADTPTZ remains a candidate molecule for partitioning [7].

Figure 2. The synthesis of ADTPTZ and then BADTPTZ

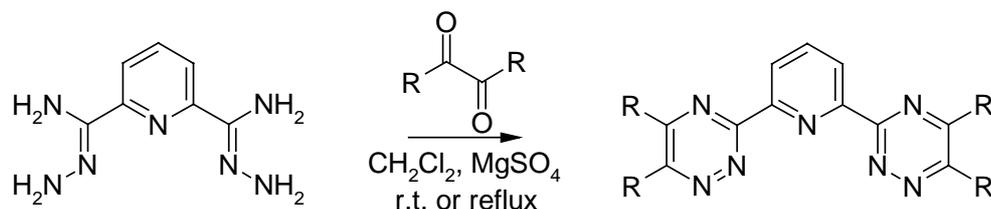


Thus, it can be seen even from this limited account of structures formed in the solid state that there is a wide range of structural types to be found with the lanthanides (and minor actinides). Probably the same also holds true for the actinides in that there is a wide range of structures for a given ligand plus nitrate and water. EXAFS studies have shown that structures to be found in the solid state are also present in the liquid phase. The principal implication for solvent extraction, however, is that there are several possible candidate species that may move across the aqueous and organic solvent interface during extraction or stripping [8]. In each of the above structures the metal is bound to ligand molecules (solvent extraction reagent) but in addition there are nitrate anions and/or water molecules. However, since these species have high rates of self exchange compared with polydentate groups, there is the possibility that a wide range of structural types are formed during solvent extraction. Therefore, the above Guideline 4 is pertinent throughout partitioning studies – particularly so if the species may have very different rates of transfer across the aqueous/organic interface.

2.2 Partitioning – enclosing the primary co-ordination sphere with only the ligand molecules

When the metal cation is completely surrounded by the ligand molecule(s) the rates of self-exchange of the ligands are minimised because the more mobile ligands such as water and nitrate are excluded from the co-ordination sphere of the metal. Thus it might be expected that there are enhanced solvent extraction properties when this is the case. BTPs are reagents in which the co-ordination sites of the metals may be satisfied by only the ligand. These reagents include 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine and one general method of synthesis of these reagents is shown in Figure 3. For R = propyl, the ligand gave D_{Am} values of between 22 and 45 and $SF_{Am/Eu}$ of 131-143 when 0.034 M of the ligand in modified TPH was used to extract from 0.9 -0.3 M HNO_3 and different amounts of NH_4NO_3 [5]. Other BTPs give separation factors between 50 and 150, which values are also far in excess of those obtained with many other ligands containing just carbon, hydrogen, nitrogen and oxygen atoms [5,6]. In addition, these BTP ligands do not require the use of a synergist such as 2-bromodecanoic acid, which is frequently necessary when extractions are carried out with other nitrogen heterocycles.

Figure 3. One method of the synthesis of BTP-type reagents



The initial solvent extraction studies indicated that the formula of the extracting species for Eu was possibly $ML_3(NO_3)_3 \cdot HNO_3$. The co-ordination of three tridentate heterocyclic aza-aromatic ligands to an actinide (III) or a lanthanide (III) ion in the presence of a co-ordinating anion such as nitrate was unprecedented and we initiated structural studies in order to verify the composition of the complexes formed with the 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-pyridines. Whereas for the larger lanthanides (La-Sm), centrosymmetric dimers of the form $[M_2L_6(NO_3)_6]$ were confirmed for the smaller lanthanides (Sm-Lu) $[ML_3]^{3+}$ cations were found with a variety of complex anions. These results contrast markedly with the types of complexes formed by lanthanum nitrates with other tridentate nitrogen ligands. For example, we have recently studied complexes formed between the lanthanide nitrates and the ligand 2,6-bis(5-methyl-1,2,4-triazol-3-yl) pyridine [8] and those formed with the terpyridyl ligand. The terpyridyl ligand also forms 1:1 complexes of several formulations but with excess ligand it is possible to form complexes with two ligands e.g. $[M(NO_3)_2(terpy)_2]$ $[M(NO_3)_4(terpy)]$, where M = La, Nd, Sm, Tb and Dy. Our work with other tridentate ligands has established similar structural features where the majority of complexes showed M:L ratios of 1:1 but for the larger lanthanides M:L ratios of 1:2 were occasionally observed.

The structure of $[Yb(L)_3]^{3+}$ where L is the BTP molecule with propyl groups is shown in Figure 4. Thus, we can conclude that our structural studies provide the first solid state evidence for the unique type of complex, which is involved in the extraction process using these new solvent extraction reagents. This structure is also to be found in the with the elements from Sm-Lu and include the complex cation $[Eu(L)_3]^{3+}$ cation. The structure shows that the nitrogen atoms in the tridentate cavity are bound to the central metal cation. Thus the co-ordination sphere, which results in a co-ordination number nine is completely satisfied by the ligand molecules with no nitrate or water in the primary co-ordination sphere (Guidelines 2 and 4). The rates of exchange of the ligand(s) are minimised so that as far as possible there is one extracted species.

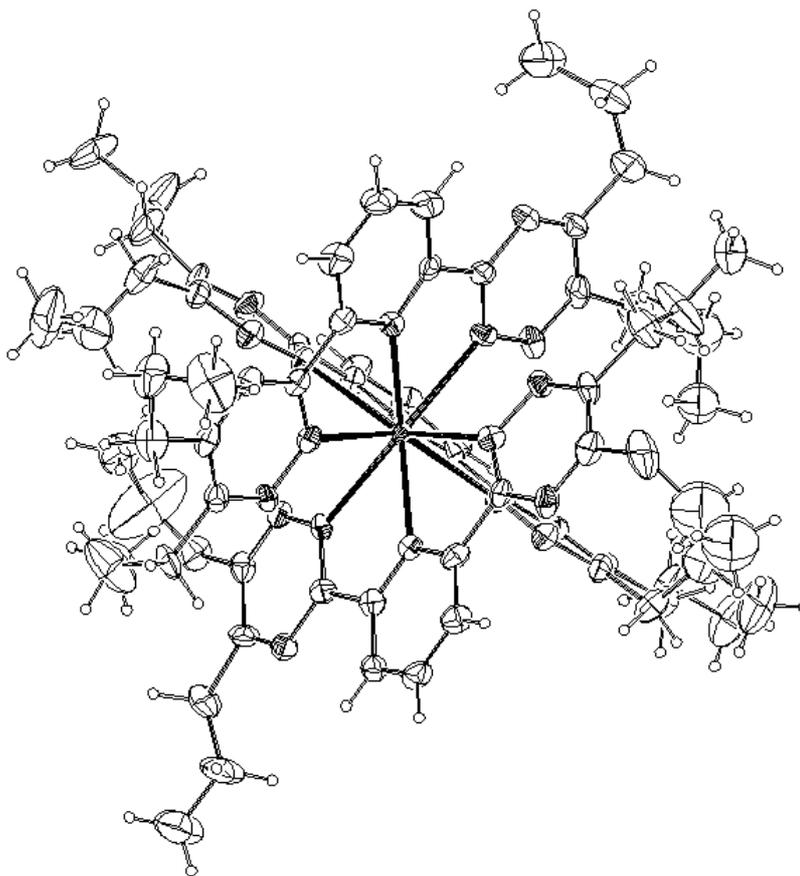
2.3 Intermolecular interactions

When the ligand or solvent extraction reagent is bound to the metal ion, there is the possibility to have a hydrophilic or hydrophobic "external" surface presented to the solvent. In the case where there is extensive hydrogen bonding, the interaction between the neighbouring extracted species may be too high. For the $[Yb(L)_3]^{3+}$ cation, the counter anion may be nitrate or a complex anionic species. In spite of this, the intermolecular interactions are minimised owing to the hydrophobic nature of the outer regions of the ligand. These would be further minimised if a neutral species could be extracted. Perhaps anionic groups could be built into the ligand.

2.4 Implications for partitioning

The above guidelines are able to provide general ideas for the design and implementation of new solvent extraction reagents with enhanced properties. Of course, in one way the guidelines may be called a “wish-list” of desirable properties. Consideration of the guidelines does, however, indicate that there is still a lack of fundamental knowledge particularly with respect to the comparison between the chemistries of the lanthanides and the actinides.

Figure 4. **The structure of $[\text{Yb}(\text{L})_3]^{3+}$ where L is the BTP molecule with propyl groups [9]**
(Note how the ligands completely occupy the co-ordination sphere of the metal ion with Yb-N distances ranging from 2.450(11) to 2.499(11)Å)



Acknowledgements

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SEPARATION OF MINOR ACTINIDES FROM A GENUINE MA/LN FRACTION

B. Sätmark, O. Courson, R. Malmbeck, G. Pagliosa, K. Römer, J.P. Glatz
European Commission, Joint Research Centre, Institute for Transuranium Elements
Hot Cell Technology, Postfach 2340, 76125 Karlsruhe, Germany

Abstract

Separation of the trivalent Minor Actinides (MA), Am and Cm, has been performed from a genuine MA(III) + Ln(III) solution using BisTriazinePyridine (BTP) as organic extractant. The representative MA/Ln fraction was obtained from a dissolved commercial LWR fuel (45.2 GWd/tM) submitted subsequently to a PUREX process followed by a DIAMEX process. A centrifugal extractor set-up (16-stages), working in a continuous counter-current mode, was used for the liquid-liquid separation.

In the *n*Pr-BTP process, feed decontamination factors for Am and Cm above 96 and 65, respectively were achieved. The back-extraction was more efficient for Am (99.1% recovery) than for Cm (97.5%).

This experiment, using the BisTriazinePyridine molecule is the first successful demonstration of the separation of MA from lanthanides in a genuine MA/Ln fraction with a nitric acid concentration of ca. 1M. It represents an important break through in the difficult field of minor actinide partitioning of high level liquid waste.

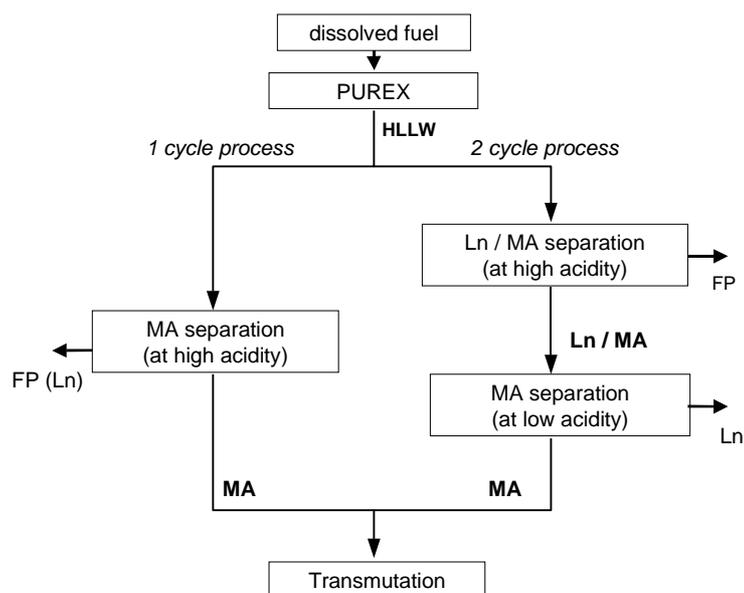
1. Introduction

Radioactive by-products are unavoidably generated during normal reactor operation. Some of these by-products are very long-lived and radiotoxic elements which must be separated from the biosphere for a very long time. The potential harmfulness of the wastes generated by reprocessing are primarily due to the presence of Minor Actinides (MA) and they are of special concern regarding partitioning and transmutation.

Current reprocessing technology is based on the aqueous PUREX process in which uranium and plutonium are recovered. The technique can also be extended for the recovery of neptunium, but americium and curium cannot be separated directly in this process. The partitioning of MA is instead done by advanced reprocessing of High Level Liquid Waste (HLLW) generated by the PUREX process, and different systems based on liquid-liquid extraction have been proposed world-wide.

Due to the difficult separation of trivalent MA from trivalent lanthanides (Ln) especially at high acidities, two step processes are at present considered. In the first step, at high acidity, a group separation of MA and lanthanides is carried out, followed by a separation of MA from lanthanides at lower acidity, see Figure 1.

Figure 1. Main routes for the separation of MA from HLLW



In the French DIAMEX (DIAMide EXtraction) process the minor actinides are directly extracted from the PUREX raffinate together with fission lanthanides using the completely combustible DiMethyl-DiButyl-TetraDecyl MalonAmide (DMDBDMA). The MA(III)+Ln(III) mixture generated after this first step is low-acidic to facilitate the second process, the SANEX process, which concerns the separation of the MA from the lanthanides. This process is based on the BTP, which belongs to a new family of extractants, the Bis-Triazinyl-Pyridine developed by Z. Kolarik et al, and is very efficient for a selective extraction of MA(III) at high acidity [1] and shows good capabilities in centrifugal extractors.

In the present work, the 2,6-Bis(5,6-alkyl-1,2,4-Triazin-3-yl)Pyridine (*n*Pr-BTP) process has been tested in continuous counter-current extraction experiments, using a centrifugal extractor battery

installed in a hot cell. The feed was a genuine MA(III)+Ln(III) mixture obtained from small scale PUREX/DIAMEX reprocessing of commercial LWR fuel (45.2 GWd/tM) [2].

2. Experimental

2.1 Reagents

The *n*Pr-BTP compound was obtained from CEA Marcoule [3]. It was dissolved, using an ultrasonic bath, in Hydrogenated TetraPropene (TPH) and 30vol% of octanol obtained from PANCHIM (France) and MERCK (Germany), respectively. The solvent with a final concentration of 0.04M *n*Pr-BTP was directly used as organic phase in the centrifugal extractor experiment.

All reagents and chemicals were of the analytical reagent grade. MQ grade water (18 M Ω /cm) was used for all dilutions.

2.2 Continuous experiments using a genuine MA/Ln fraction

The centrifugal extractor equipment installed in the hot cells, see Figure 2, is described elsewhere [4,5]. For the *n*Pr-BTP process, 16 extractors were used, with 5 extraction stages, 3 acid scrubbing stages and 8 strip stages. The continuous counter-current centrifugal extraction scheme is shown in Figure 3. This flow-sheet was optimised on the basis of preliminary data obtained from batch tests with spiked solutions [6]. The genuine MA/Ln solution obtained as a product in the DIAMEX process was used as feed solution and adjusted to 1 M HNO₃ with concentrated nitric acid.

Figure 2. **Photograph showing the 16 stage continuous counter-current extractor battery installed in the hot cell**

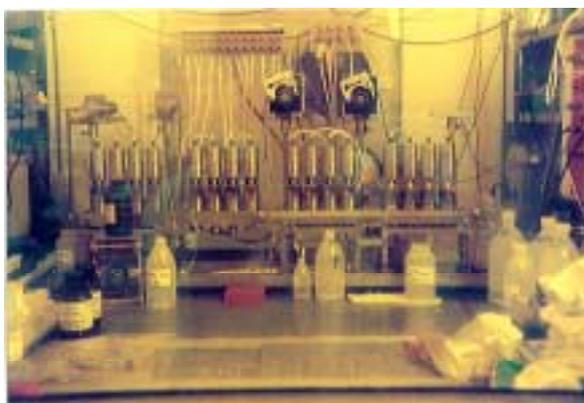
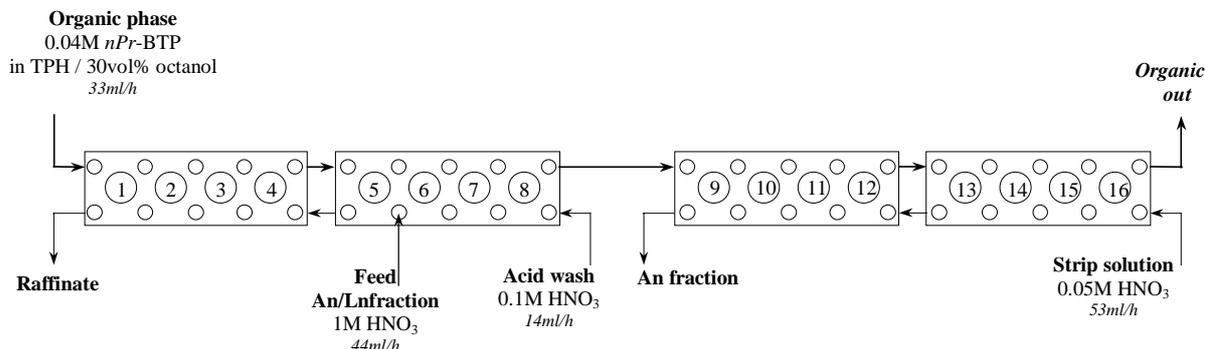


Figure 3. Flowsheet for the hot experiment using the *n*Pr-BTP and centrifugal extractors



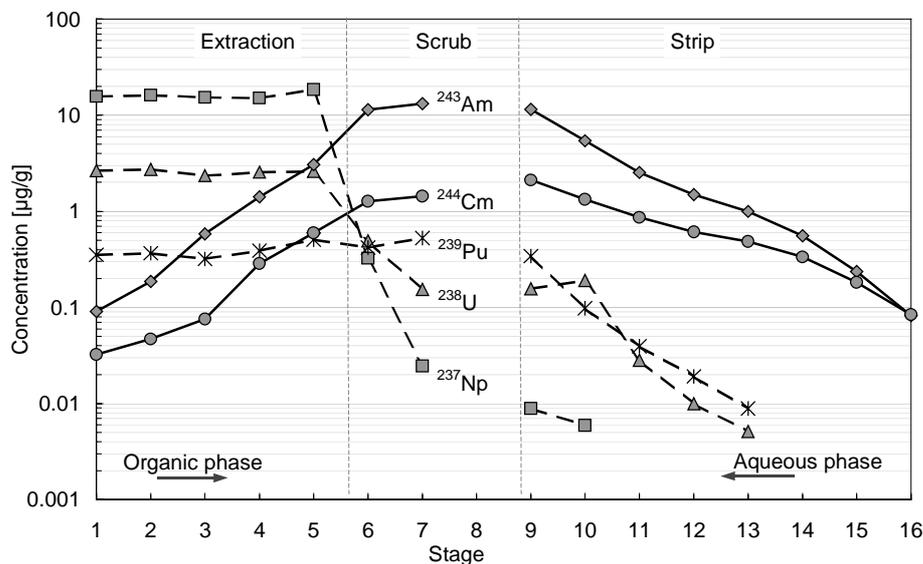
After the system reached steady-state conditions (ca. 3 h), the outgoing fractions were collected for about 30 min. At the end of the experiment the centrifuges and the pumps were switched off simultaneously and samples were taken from mixing chambers (well sampling) of each centrifuge.

All concentrations in the aqueous samples were determined using a quadrupole ICP-MS (Perkin-Elmer, ELAN250).

3. Results and discussion

The aqueous concentration profiles of actinides (Np, U, Pu, Am and Cm) in μg of isotope per g of solution are shown in Figure 4.

Figure 4. Aqueous profiles of actinides in the wells

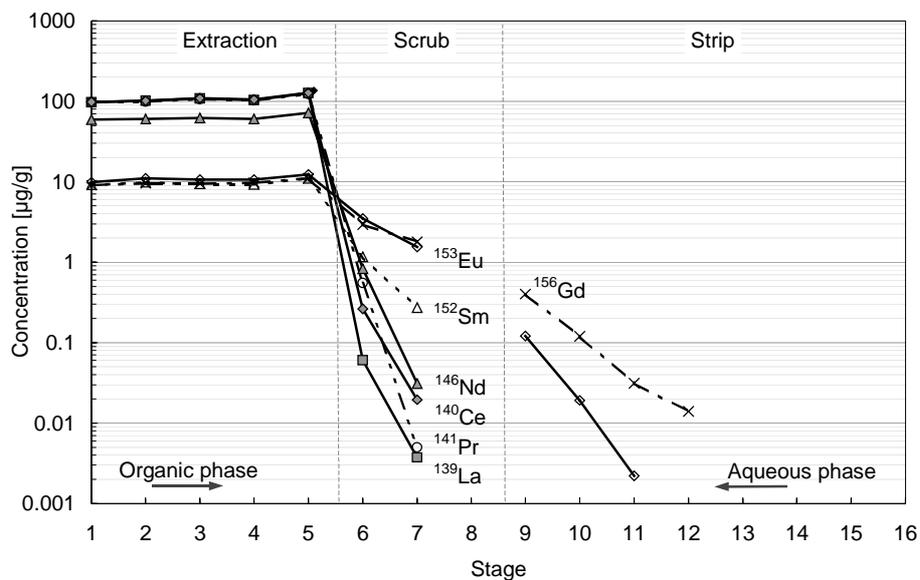


Similar extraction behaviour of Am and Cm is observed and the concentrations of those elements decrease by several orders of magnitude. Np and U are efficiently washed out in the scrubbing section but Pu is co-extracted. In the strip section all actinides are back-extracted. It should be mentioned that

the concentrations of U, Pu and Np in a MA/Ln feed originating from optimised PUREX/DIAMEX process schemes will be insignificant.

In Figure 5 the aqueous concentration profiles of lanthanides are shown.

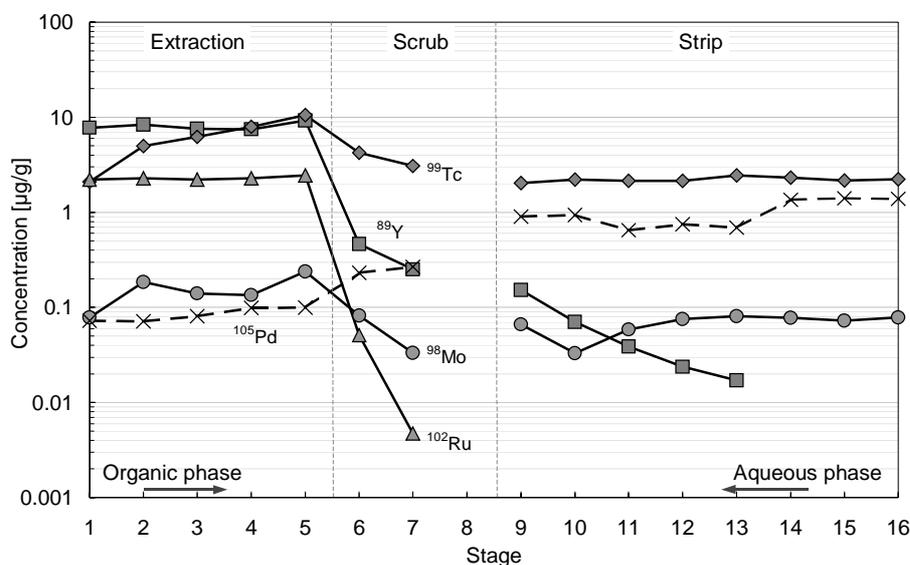
Figure 5. Aqueous profiles of lanthanides in the wells



As expected, the lanthanides are not extracted and the acid scrubbing efficiently reduces the co-extraction. However, the scrubbing efficiency significantly decreases with the increase of the element number. Higher lanthanides (Eu, Gd) are to some extent transported to the organic phase and efficiently back-extracted together with the MA. This co-extraction can be prevented by addition of more scrubbing stages.

The aqueous concentration profiles of some lighter fission products are shown in Figure 6.

Figure 6. Aqueous profiles of fission products in the wells



Extraction can be seen for Tc, Pd and Mo. The acid scrubbing efficiently removes Ru and Y from the organic phase, especially Ru is almost completely washed-out. For Tc the number of scrubbing steps is not enough, and Pd is even extracted in the scrubbing section. In the strip section only Y is well back-extracted. The other elements Tc, Mo and Pd are accumulated in the organic phase.

In Table 1 the process decontamination factors, DF, is shown. They were calculated according to Equation 1, where **C** and **V** are aqueous component mass concentration ($\mu\text{g/g}$) and total volume (mL), respectively.

$$DF = \frac{C_{\text{feed}} \cdot V_{\text{feed}}}{C_{\text{raff}} \cdot V_{\text{raff}}} \quad (1)$$

Table 1. Decontamination factors of the feed (in $\mu\text{g/g}$)

	DF		DF		DF		DF
^{89}Y	1.02	^{105}Pd	300	^{144}Nd	1.00	^{237}Np	1.00
^{98}Mo	13	^{139}La	1.00	^{152}Sm	1.00	^{243}Am	122
^{99}Tc	11	^{140}Ce	1.00	^{153}Eu	1.01	^{244}Cm	64
^{101}Ru	1.00	^{141}Pr	1.00	^{156}Gd	1.04		

In spite of the high acidity of the process (1M HNO_3) high decontamination factor is achieved for the MA elements. Lanthanides are not extracted except for Eu and Gd showing DF of 1.01 and 1.04, respectively. In parallel the DF of Eu, Cm and Am were also determined by α and γ spectrometry to be 1.01, 151 and 112 respectively.

Table 2 shows the recovery in the raffinate and in the MA fraction obtained after 3.5 hours of experiment. The small amounts of co-extracted lanthanides are efficiently back-extracted in the scrubbing section, as can be seen in Figures 5 and 6. To decrease the amount of co-separated higher lanthanides the number of scrubbing stages has to be increased. This is also the case for some lighter fission products such as Y, Mo and Tc.

Table 2. Recovery (% feed)

	Raffinate	MA fraction		Raffinate	MA fraction		Raffinate	MA fraction
Y	98.2	1.8	Ce	>99.99	–	Np	99.9	0.05
Mo	7.5	6.0	Pr	>99.99	–	Pu	52	48
Tc	9.2	8.5	Nd	>99.9	–	Am	0.8	99.1
Ru	99.8	0.2	Sm	99.9	0.1	Cm	1.6	97.5
Pd	0.3	3.9	Eu	99.9	0.1			
La	>99.99	–	Gd	96	4			

4. Conclusion

The process reported, using the BisTriazinePyridine molecule, is the first successful demonstration of MA separation from lanthanides in a genuine MA/Ln fraction with a nitric acid concentration ~1 M. In the experiment, carried out in a centrifugal continuous counter-current set-up, a MA fraction almost free of lanthanides was obtained. Due to an efficient MA extraction and back-extraction a reasonably good recovery of Am was achieved. However, the process scheme has to be improved to increase the recovery of Cm, to decrease the co-extraction of lanthanides, and to prevent the Pd accumulation in the organic phase. Nevertheless, this result represents an important break through in the difficult field of minor actinide partitioning of high level liquid waste.

Acknowledgements

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PARTITIONING ANIONIC AGENTS BASED ON 7,8-DICARBA-NIDO-UNDECABORATE FOR THE REMEDIATION OF NUCLEAR WASTES

Clara Viñas, Isabel Rojo, Francesc Teixidor
Institut de Ciència de Materials de Barcelona, CSIC,
Campus UAB, Bellaterra 08193, Spain

Abstract

$[3,3'-M(1,2-C_2B_9H_{11})_2]^-$ ($M = Co^{3+}, Fe^{3+}, Ni^{3+}$) anionic compounds perform similarly in PVC membranes as Cs^+ sensors in ion selective electrodes. Their behaviour is very similar, but the higher stability of $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ makes it the more interesting for extraction at low pH's. Species $[1,1'-(PPh_2)_2-3,3'-Co(1,2-C_2B_9H_{11})_2]^-$, **[2]**, $[1,1'-(OPPh_2)_2-3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ **[3]**, $[3,3'-Co(1-CH_3-2-(CH_2)_nOR-1,2-C_2B_9H_9)_2]^-$ (**[4]**: $n = 3$, $R = -CH_2CH_3$; **[5]**: $n = 3$, $R = -(CH_2)_2OCH_3$; **[6]**: $n = 3$, $R = -(CH_2)_3CH_3$; and **[7]**: $n = 6$, $R = -(CH_2)_3CH_3$), were tested for ^{137}Cs , ^{90}Sr and ^{152}Eu in extraction. Permeability tests on Supported Liquid Membranes with H**[6]**, and H**[7]** have shown that these compounds present the highest values reported so far for this sort of radionuclides transport experiments.

1. Introduction

Nuclear waste reprocessing operations produce both high level and medium level activity liquid wastes (HLW/MLW). The major nuclides in these radioactive wastes are those with long half-lives, mainly β/γ emitters or α emitters such as transuranium elements. This is why great efforts have been devoted throughout the world to propose harmless storage of these wastes. The burial of vitrified reprocessed HLWs (containing fission products and α emitters) has been considered as the safest method for their permanent disposal, whereas MLWs are treated by evaporation in order to concentrate their radioactivity into the smallest possible volume. This treatment nevertheless leads to large volumes of concentrates composed of active and inactive salts (mainly: NaNO_3 , 4 mol.l^{-1} and HNO_3 , 1 mol.l^{-1} as the matrix). The greater part of these concentrates has to be disposed off in geological formations after embedding due to their activity in long-lived radionuclides (actinides, strontium, caesium, etc.). Therefore it would be desirable to remove these long-lived radionuclides from the contaminated liquid wastes before embedding. These would allow a large part of these wastes to be directed to a subsurface repository, and a very small part containing most of the long-lived radionuclides to be disposed off, after conditioning, in geological formation [1].

The field of metallocarborane chemistry was initiated by Hawthorne in 1965 [2]. Since that time, metallocarboranes from all areas of the periodic table have been prepared using the dicarbollide ligand [3] $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ (Figure 1). These derivatives have become of increasing interest with regard to their solubility [4], isolation, separation and characterisation of organic bases, radiometal carriers [5], electron acceptor molecules [6], among other areas. One of these organometallic complexes, $[\text{3,3}'\text{-Co}(\text{1,2-}\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ (**1**), has attracted the most attention because of its robustness, its stability in the presence of strong acid (HNO_3), at relatively high temperatures and under a very high radiation [7]. This stability allows it to be considered for nuclear waste remediation. Its hexachloro protected analogue, $[\text{1-Cl}_6]^-$, is remarkable as an extractant (Figure 2). The large size to charge ratio and the hydrophobic nature of **1** and $[\text{1-Cl}_6]^-$ allows extraction of caesium and strontium ions from an aqueous phase to an organic phase, leaving other alkaline and higher-valent metals behind [4,7,8]. The ions ^{137}Cs and ^{90}Sr are used for thermoelectric generators and sterilisation of medical equipment, among other areas, making the possibility of recycling them very attractive [9].

Figure 1

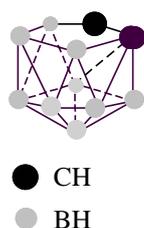
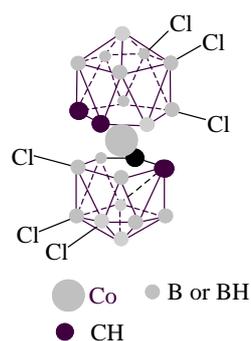


Figure 2. $[\text{1-Cl}_6]^-$



The $[\text{3,3}'\text{-Co}(\text{1,2-}\text{C}_2\text{B}_9\text{H}_{11})_2]^-$, **1** anion, has been used as a highly selective ^{137}Cs sequestering agent in extraction processes, in the presence of Na^+ , with nitrobenzene [4] as the receiving phase. However, nitrobenzene is an ecologically unacceptable solvent, so that other receiving phases are required for environmental applications. Thus, other solvents are needed. On the other hand, additional metallocarboranes similar to **1** are available, namely these with Fe^{3+} , and Ni^{3+} . In an effort to decide

which of these, the Co^{3+} , Fe^{3+} and Ni^{3+} metallacarboranes was the most adequate, their Cs^+ salts were implemented in ion selective electrodes (ISE's). As the potentiometric performance of an ISE can be viewed to be similar to the transport process in one membrane their study as Cs^+ sensors would provide reliable and important information on the stability and extracting capacity of these metallacarboranes, hence permitting to decide which one was more adequate. The study was also intended to discern which of the three anions was more selective towards Cs^+ , in order to choose one for the subsequent studies. The results obtained, however, indicated that the three anions $[\text{3,3}'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{11})_2]^-$, $[\text{3,3}'\text{-Fe(1,2-C}_2\text{B}_9\text{H}_{11})_2]^-$, and $[\text{3,3}'\text{-Ni(1,2-C}_2\text{B}_9\text{H}_{11})_2]^-$ were comparable in their behaviour in ISE's [10]. Since the Co^{3+} complex provides easier synthetic routes, higher yield and higher stability, it was chosen for the studies on the extraction of radionuclides.

Organic compounds incorporating oxygen in the molecule mainly as ethers, and phosphine oxide derivatives have been also tested for this kind of radionuclides waste removal [11]. Accordingly several ether C-substituted cobaltacarboranes [12,13] were prepared and great effort has been dedicated more recently to phosphine oxides, and fluorinated compounds in order to improve the efficiency showed by $[\mathbf{1}]^-$ and $[\mathbf{1-Cl}_6]^-$.

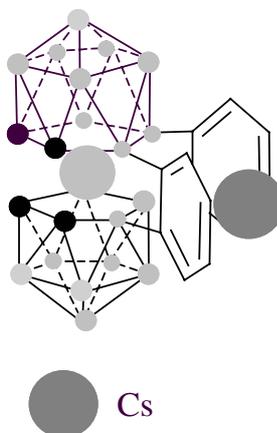
In this paper we report on the synthesis and extracting possibilities offered by these C-substituted cobaltabisdicarbollide species, along with some comments on the B-substitution.

2. Discussion

2.1 *What benefits can be expected from the polyhedral anions?*

Anions with low nucleophilicity, good solubility and weak coordination capacity have recently experienced great interest in areas of major commercial importance such as olefin polymerization [14], lithium battery technology [15], and the radionuclides extraction mentioned above. In 1986 the carborane anion $\text{CB}_{11}\text{H}_{12}^-$ was introduced as a candidate for the least co-ordinating anion [16]. Paradoxically, carboranes combine a versatile functionalization chemistry with unparalleled inertness. One of their main characteristics, which is relevant to this work, is the delocalization of the anionic charge throughout its volume, thus producing the anions with lowest charge density. It has been demonstrated [17] that the delocalized charge on these large anions tends to make them nearly ideal spectator ions with little opportunity to perturb the structure of the cation. In addition to the 12-vertex ions, $\text{CB}_{11}\text{H}_{12}^-$ and $\text{B}_{12}\text{H}_{12}^{2-}$ there are related classes of anions based on the 10-vertex $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{CB}_9\text{H}_{10}^-$ ion, as well as the above mentioned M^{3+} bisdicarbollides. The cobaltabisdicarbollide anion, whose hexachloroderivative molecular structure is depicted in Figure 2 consists of a Co(III) ion sandwiched by two dicarbollide moieties. Each dicarbollide $(\text{C}_2\text{B}_9\text{H}_{11})^{2-}$ bears two negative charges, overall producing a mononegative species. This anion presents a great chemical resistance, e.g. it withstands in HNO_3 2M and in concentrated HCl for several days without apparent decomposition. Thus, these anions do not encounter a parallel in current inorganic or organic areas of chemistry. They are very relevant and can hardly be replaced by other anions. They offer other possibilities derived from their elemental nature as neutron scavengers or glass forming elements, both important for nuclear waste remediation.

Figure 3



2.2 Possibilities of modification

As can be seen from Figure 2, two different sort of reacting points are possible in $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$, the BH's and the CH's. Not all BH's sites are equally reactive, those that have permitted substitution by Cl are the more reactive. This matter has been developed by the Boron Chemistry group at Rez near Prague, and their results shall be attributed to S. Hermaneck, J. Plesek and B. Grüner [18]. One excellent example for extraction of Cs^+ is given by bisphecosan represented in Figure 3. Excellent recent results derive from the dioxane substituted $\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2^-$ complex, $8\text{-C}_4\text{H}_8\text{O}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})$ ($1',2'\text{-C}_2\text{B}_9\text{H}_{11}$). This is neutral and strongly susceptible to nucleophilic attack by anionic nucleophiles, being a precious and highly versatile starting material to produce a rich variety of anionic extracting agents for actinides, the result being only limited to the availability of anionic nucleophiles. These results have been produced in the frame of contract IC15-CT98-0221 and shall be attributed to the same authors from Rez plus Dr. J. Baca.

2.3 Synthesis of C-substituted derivatives of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$

A general approach to the synthesis of C-substituted derivatives of cobalt bis(1,2-dicarbollide) consists in the preparation of the corresponding substituted *o*-carboranes, their degradation into the nido-7,8-dicarborenes, followed by deprotonation and reaction with cobalt(II) chloride [19]. This synthesis is extremely time consuming and always shall produce $[3,3'\text{-Co}(1\text{-R-}1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ derivatives with identical substituents in each dicarbollide moiety.

However, a more versatile method starting from $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ was needed as it would permit a more rapid way to produce derivatives at carbon. A recent approach by Chamberlain *et al.*, to $[3,3'\text{-Co}(1\text{-R-}1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ ($1,2\text{-C}_2\text{B}_9\text{H}_{10}$) anionic mono-derivatives consists in the treatment of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ with *n*-butyllithium followed by the reaction with alkyl halides [20].

This procedure was a good alternative as $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ was a readily available starting material. Some years before we had attempted the same procedure but we had got no conclusive results [21]. According to Chamberlain *et al.* the synthetic procedure is straightforward. A violet colour due to the deprotonated $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^{2-}$ dianion is produced upon the addition of 1 equivalent of BuLi to the orange initial solution of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$, in THF.

This dianionic species must be extremely basic, thus very reactive towards weak acids. We had abandoned this reaction in 1994 since following an equal procedure, the product always reverted to the orange colour of the cobalt bis(1,2-dicarbollide). However, the interesting report [20] from Los Alamos National Laboratory, brought back the possibility of this, otherwise, extremely interesting reaction.

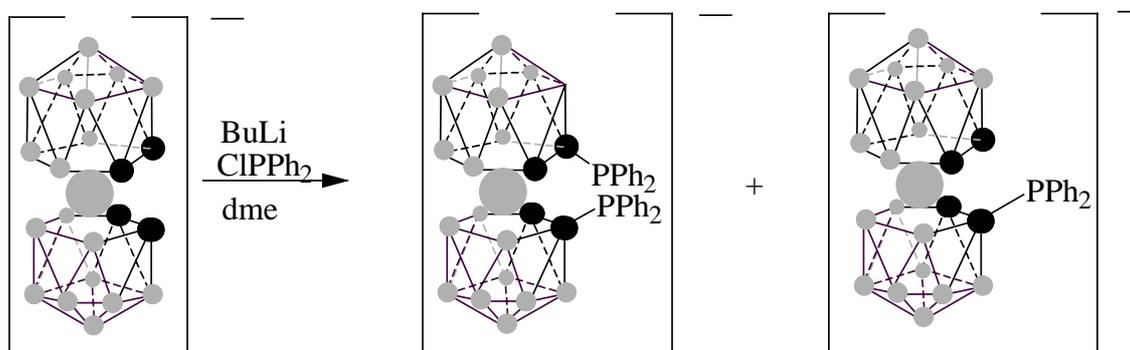
The reaction is very tricky and does not proceed precisely, in our hands, as the authors say. By using the same reagents as they did we were able to get partial conversion, usually of the order of 30-40%. The rest was unreacted $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$. Now, after having reinvestigated this reaction we believe that this “unreacted $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ ” is in fact a “reverted $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ ”.

3. Preliminary results

The solvent initially used was dimethoxyethane, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$, however after noticing the strong basicity of the deprotonated $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^{2-}$, this was replaced by THF. The initial reagents used were $\text{Cl}(\text{CH}_2)_3\text{Br}$ and ClPPh_2 . For this last one, a minor product was obtained which suggested that some reaction, although in very low extension, had taken place. The rest was $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$. This led us to think that $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^{2-}$ was a strong base but a weak nucleophile. Thus, TMDA was added to the reaction pot, (TMDA = $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$), as it is known that butyllithium aggregates show a marked increase in the reactivity when co-ordinating solvents or reagents are added. This explains the initial use of dimethoxyethane. However, neither at room temperature nor under refluxing conditions the result did improve.

Other reagents were $\text{BrCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$, alone or in the presence of AgBF_4 . The result was unsuccessful as previously. The low nucleophilicity of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^{2-}$ had to be overcome by a good leaving group on the second reagent, as was obvious when using $\text{Cl}(\text{CH}_2)_6\text{I}$. In this case the $^{11}\text{B}\{^1\text{H}\}$ NMR of the reaction crude indicated that there was something else besides $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$, but this ended up to be a mixture of several compounds with very similar properties which did not permit an adequate separation, but the interesting point was that it seemed to be necessary the existence of a good leaving group in the reagent.

Figure 4



Although results seemed to be improving the method was not convenient as cumbersome separation procedures were needed. However from the data we had gathered the following conclusions could be inferred: 1) The existence of weakly acidic hydrogens in the reagent was responsible for the

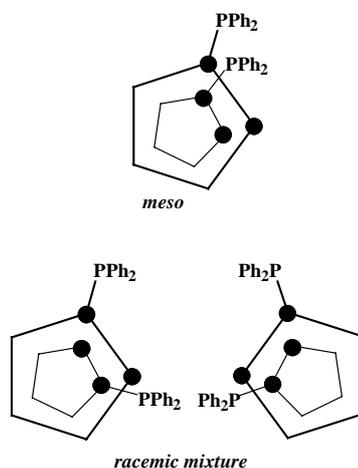
protonation of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^{2-}$, thus reverting to $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$; 2) Good leaving groups are necessary to facilitate attack by $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^{2-}$; and 3) A high excess of reagent is convenient to lower the ratio of reverted $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$.

Considering these points it was initially decided that I_2 was a very good candidate. It did not carry any hydrogen, is susceptible to nucleophilic attack and it can be removed from the flask reaction by sublimation at room temperature. As it was described in the introduction, I_2 has been adequate to produce electrophilic substitution on boron atoms in $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$. Contrarily, in this project, the formation of a C-I bond is sought as a versatile candidate for C-C bond formation, by using appropriate Grignard reagents for coupling reactions.

4. Synthesis of diphenylphosphine cobaltabisdicarbollide derivatives

The reaction is schematised in Figure 4. Reaction of $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ with BuLi in dimethoxyethane followed by chlorodiphenylphosphine yields the disubstituted species $[2]^-$ and only minor amounts of the monophosphine. Concerning the disubstituted species, a mixture of isomers could be possible: the *meso* form (C_s symmetry) and a *racemic* mixture (C_2 symmetry). The first contains a mirror plane (σ_h) while the second contains a C_2 axis. These possible species are schematically represented in Figure 5. The ^{13}C -, and ^1H -NMR confirms the existence of only one of the two possible species. To determine which one of the two had been obtained, crystals suitable for X-ray diffraction were grown [22]. The structure demonstrated that the racemic form was the one produced. These phosphine compounds are basic as a consequence of the negative charge, and of the phosphines themselves. These should not be compatible with the strong acid conditions found in the radioactive waste. The phosphine oxides would be more convenient for the purposes of this project.

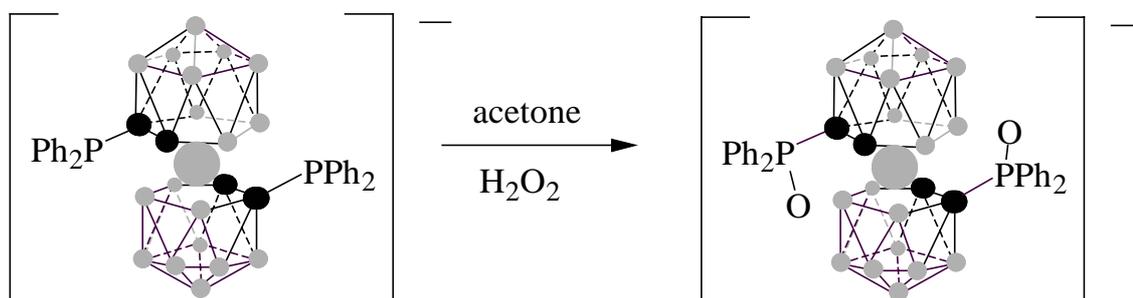
Figure 5



5. Synthesis of diphenylphosphine oxide cobaltabisdicarbollide derivatives

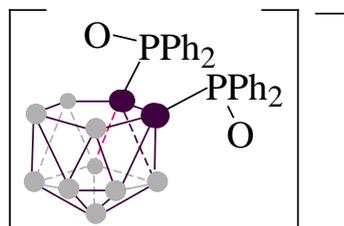
The reaction is schematised in Figure 6. Reaction of $[1,1'\text{-(PPh}_2)_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$, $[2]^-$ with H_2O_2 in acetone yields the expected phosphine oxide.

Figure 6



As the initial diphosphine was in the racemic form, upon oxidation, it was required that the resulting phosphine oxide maintained this isomerism. Indeed this is what happened. This was fully confirmed by the X-ray structural determination of suitable crystals. The acid stability of both $[1,1'-(\text{PPh}_2)_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ and $[1,1'-(\text{OPPh}_2)_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ [**3**] was studied by dissolving the Cs^+ salts of these two species in 3M HNO_3 and HCl . The resulting solutions were then neutralized with 3M NaOH . The possible modifications were then followed by ^{31}P -NMR. It was found that the oxide was recovered fully, while the initial phosphine could be recovered in a 80%. These results demonstrated the stability of the phosphine oxides versus the starting phosphines. The $[1,1'-(\text{OPPh}_2)_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ oxide is one cluster anion bearing two OPPh_2^- units, similar to the anion shown in Figure 7. This would allow to study the role of the cluster. Both are monoanionic species and both contain two OPPh_2^- units.

Figure 7

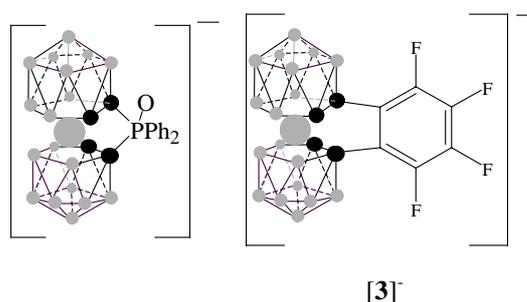


6. Introducing bridging fragments

C,C' bridged species could be relevant as they hinder rotation of the two halves of the molecule. Interestingly, extraction results found in the former project CIPA-CT93-0133 (EUR 18217 EN) by the IIC-, NRI (Rez) and CEA (Cadache) upon derivatives of $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ bridged at the 8,8'- positions, both being boron positions, e.g. PHECOSAN stimulated research on these species. Similarly, bridged $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ on the carbon atoms, have been produced now. Contrarily to those described formerly, the bridge in these cases would be between carbon atoms.

Syntheses have been performed as described in Figure 4. Cl_2PPh and perfluorinated benzene have been used as reagents. The bridging phosphine has been oxidized following the $\text{H}_2\text{O}_2/\text{acetone}$ procedure shown in Figure 6.

Figure 8



6.1 Protecting the cluster with halogen groups

It was long reported that hexachlorinated $[\text{Co}(\text{C}_2\text{B}_9\text{H}_5\text{Cl}_6)_2]^-$ and dibrominated $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{10}\text{Br}_2)_2]^-$ derivatives of $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ withstand acid conditions better than the parent compound. The fact that the hexachloro and the dibromo protected species had a comparable stability in acid conditions indicated that the crucial point was substitution on 8,8'- as these are the only common protected positions in both compounds. Considering that the low performance of these and other previously reported $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ derivatives at $[\text{H}^+] > 0.1 \text{ M}$ in Eu, Sr, and actinides had to be due to the reactivity of BH's at the 8,8'- positions, a project leading to protect these positions is under way.

This may be addressed starting from the already protected 8,8'- positions either with halogen or carbon atoms. A second alternative would be to protect the phosphine or phosphine oxide product. Results have shown that starting from the $[8,8'-\text{Cl}_2-\text{Co}(\text{C}_2\text{B}_9\text{H}_{19})_2]^-$ is better than starting from $[\text{Cl}_6-\text{Co}(\text{C}_2\text{B}_9\text{H}_8)_2]^-$. This may have to do with steric hindrance.

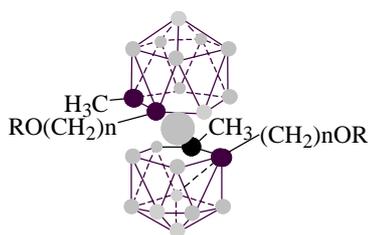
On the other hand, when the protection reaction was performed on the $[1,1'-(\text{PPh}_2)_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ anion, results concerning halogen substitution at boron atoms were unsuccessful. Reaction with Br_2 in glacial acetic acid led to borates.

More encouraging seem to be the results obtained from the phosphine oxide $[1,1'-(\text{OPPh}_2)_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$. Reactions have been directed to get 8,8'- disubstitution (protection) as these seem to be sufficient to improve the stability of the cluster in acid media.

7. Extractants derived from $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$

The series of compounds derivatives of $[3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ derivatives incorporating ether groups, $[3,3'-\text{Co}(1-\text{CH}_3-2-(\text{CH}_2)_n\text{OR}-1,2-\text{C}_2\text{B}_9\text{H}_9)_2]^-$, which are presented graphically in Figure 9 ([4]: $n = 3$, $\text{R} = -\text{CH}_2\text{CH}_3$; [5]: $n = 3$, $\text{R} = -(\text{CH}_2)_2\text{OCH}_3$; [6]: $n = 3$, $\text{R} = -(\text{CH}_2)_3\text{CH}_3$; [7]: $n = 6$, $\text{R} = -(\text{CH}_2)_3\text{CH}_3$) [12,13] have been studied following the general approach indicated in "Synthesis of C-Substituted Derivatives of $[3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ ".

Figure 9



- [4]⁻ n=3, R= CH₂CH₃
 [5]⁻ n=3, R= (CH₂)₂OCH₃
 [6]⁻ n=3, R= (CH₂)₃CH₃
 [7]⁻ n=6, R= (CH₂)₃CH₃

The bis(dicarbollide) derivatives [4]⁻, [5]⁻, [6]⁻, [7]⁻, have been tested in the liquid-liquid extraction of ¹³⁷Cs, ⁹⁰Sr and ¹⁵²Eu from the aqueous HNO₃ phase to the organic nitrophenyl hexyl ether.

For the extraction of ¹³⁷Cs, the polyether substituted compounds show a very high extraction efficiency at pH 3 (D>100) regardless of the nature of the exocluster chain. This efficiency is expected to be lower if the acidity of the medium is increased. This behaviour is displayed by [4]⁻, whose D value decreases from >100 to 3, just by varying the pH value from 3 to 1. However, [6]⁻, which is very similar to [4]⁻, but with the longest alkyl chain next to the oxygen atom, maintains an excellent efficiency for the extraction of ¹³⁷Cs even at pH 1. Anion [6]⁻ shows again the best performance for the extraction of ⁹⁰Sr but the D value decreases strongly with decreasing pH. For the extraction of ¹⁵²Eu, it seems that the larger the exocluster chain the better the performance of the extracting agent. Therefore, [7]⁻ shows the best performance in the extraction of ¹⁵²Eu. The lower efficiency in the extraction of ⁹⁰Sr and ¹⁵²Eu shown by compound [6]⁻ and the excellent results obtained in the extraction of ¹³⁷Cs, should permit a selective extraction of Cs⁺ from a mixture containing all the radionuclides in solution. This result led us to perform some transport experiments at CEA (Cadarahe) by using Supported Liquid Membranes (S.L.M.) with NPHE (nitrophenylhexyl ether) as the membrane solvent. Preliminary results carried out with compounds H[4], H[5], H[6] and H[7] showed that the best transport performance was for compound H[6]. Compound [7]⁻, displaying the best efficiency in the extraction of ¹⁵²Eu, was used for its transport studies.

At pH 3, transport of ¹³⁷Cs was very efficient with compound [6]⁻, and a permeability of 30.6 cm/h was obtained. An extraction of 93% of Cs⁺ in 1 hour was achieved.

In the case of the transport of europium, transport with compound H[7] is very rapid at pH 3, showing a permeability of 8.9 cm/h, i. e. an extraction of 31.2% after 1 hour or 91.3 after 3.5 h. For comparison, permeabilities ranging from 1 to 4 cm/h have been measured for several "carriers" such as calix[4]arenes crown 6, CMPO (carbamoylmethylphosphine oxides) or diphosphine dioxides under comparable conditions. Improved permeabilities were achieved with calixarenes incorporating CMPO moieties (4-7 cm/h) [23]. Thus, generally speaking, the cobalt(dicarbollide) carriers are considerably faster transport agents than others well-recognised as doing this job, such as those indicated above [12,13].

As expected H[2] does not display a good extracting capacity at 3≥pH due to the basicity of the phosphine groups, enhanced by the negative charge of the anion. This extracting capacity is very much improved when the phosphine oxides are utilised, however it diminishes abruptly at pH = 1. It is

remarkable the Sr affinity of the fluorinated bridged species shown in Figure 8. The existence of the bridging monophosphine oxide does not influence favourably the extraction.

8. Conclusion

Metallacarborane complexes of formula $[3,3'\text{-M}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ (M = Co, Fe, No) have been tested as Cs sensors. The results have demonstrated a similar behavior, however due to the large stability of the Co complex and the better yield this seem to be the anion to be studied.

Synthesis of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ derivatives can be made from the *o*-carborane, producing the wanted substitution, removing the boron connected to both carbon atoms, and the proton. The dianion, thus formed, is reacted with anhydrous cobalt chloride. An alternative is to start directly from $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$. In this paper compounds obtained by both ways are prepared, however the second provides a more accessible route to these extracting agents.

The largest drawback that these anions suffer is the lost of activity at low pH, specially below 1. This will require protection at the boron 8,8'- positions. The phosphine oxide extracting agents seem to be adequate for radioactive waste treatment once the pH dependence problem is solved.

On the other hand the anionic character and low charge density of these extracting agents along with the high boron contents and specially the results already obtained by us and other groups participating in the EU project make them extremely suitable candidates to solve the present problem of partitioning.

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SESSION III
PARTITIONING

SUB-SESSION III-B:
DRY REPROCESSING

PYROCHEMICAL PROCESSING OF IRRADIATED TRANSMUTER FUEL

James J. Laidler

Argonne National Laboratory
9700 South Cass Avenue, Argonne, Illinois 60439-4837, USA

James C. Bresee

US Department of Energy,
NE-20, Forrestal Building, 1000 Independence Avenue, SW, Washington, D.C. 20585, USA

Abstract

The US accelerator transmutation of waste program is directed toward the destruction of transuranic elements and long-lived fission products present in spent light water reactor fuel. Initial separation of these materials from the light water reactor spent fuel will be accomplished by conventional aqueous processing methods. The transuranic elements will be incorporated in blanket fuel assemblies that will be irradiated to burn-ups in the range of 30 atom percent, and the fuel assemblies will be processed to recover and recycle unburned transuranic elements and newly-generated long-lived fission products. The accelerator driven transmutation system will use a fuel type much different from light water reactor fuel, however, and the fuels under consideration are amenable to pyrochemical processing. Two different pyrochemical processing methods are described in this paper, both involving an initial chlorination of the irradiated transmuter fuel.

1. Introduction

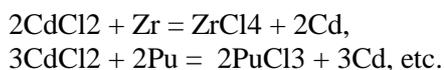
The present concept for partitioning and transmutation of selected radionuclides in the US accelerator transmutation of waste (ATW) program calls for the extraction of transuranic elements and certain long-lived fission products from spent light water reactor (LWR) fuel and their subsequent destruction in an accelerator-driven sub-critical system. Transmutation will be carried out in an accelerator-driven sub-critical assembly, providing an intense flux of high-energy neutrons produced by spallation reactions resulting from the impingement of high-energy protons on a liquid metal target. The technology development roadmap [1] for this program called for approximately 1 450 tons of spent LWR fuel to be treated per year, corresponding to some 14 tons of transuranics per year. The form of the targets to be used for long-lived fission product (i.e. ^{99}Tc and ^{129}I) transmutation is tentatively set as metallic technetium and sodium iodide, and the selection of the form of the transuranic-bearing blanket fuel elements seems to be converging on a design that comprises a dispersion of metallic transuranic elements in a metallic zirconium matrix. Uranium is excluded from the fuel in order to preclude the formation of additional transuranic elements by neutron absorption. The initial version of the fuel contains 23 weight percent transuranics and 77 weight percent zirconium. More recent studies suggest that a 50-50 composition may be preferred. An alternative to the metal dispersion/metal matrix fuel is a dispersion of transuranic nitrides or oxides in an inert matrix such as molybdenum, stainless steel, or zirconium nitride. Regardless of fuel type selected, the burn-up target for the transmuter blanket fuel is on the order of 300 MWd/kgHM, or approximately 30 atom percent burn-up of the TRU elements; the fuel must thus be processed to extract the significant concentrations of newly-generated fission products and to recover the unfissioned transuranics (as well as iodine and technetium) for recycle to the transmuter system. At this burn-up level, throughput requirements for the processing of the transmuter blanket fuel are in the range 4-35 tons (heavy metal) per year, depending on the fuel composition, transmuter operating cycle, and plant deployment scheme ultimately chosen.

2. Process selection

In the case of the metal dispersion/metal matrix fuel, the low throughput rate and the large concentration of zirconium in the fuel material, combined with a desire to minimize the generation of high-level radioactive wastes and secondary wastes, favor the use of a non-aqueous processing method. Conventional electrorefining methods, as applied to metallic fast reactor fuels, were considered inappropriate in this application because the high zirconium concentration would tend to reduce throughput to an unacceptably low level and require extensive replication of equipment to achieve throughput goals. The focus of process development has thus been on volatility processes, specifically chloride volatility processes that retain the non-volatile transuranic elements in a chloride salt that can be dealt with by means already developed for actinide extraction.

3. Primary chloride volatility process

The process concept under study, shown in Figure 1, involves the chopping of irradiated fuel elements, followed by chlorination of the constituents of the fuel in a salt bath containing added cadmium chloride that is formed by sparging chlorine gas through the liquid metal. The cadmium chloride reacts with the metallic constituents of the fuel by reactions such as:



The metallic cadmium product of the chlorination reaction drops back to the bottom of the chlorination vessel for subsequent reaction with chlorine. The temperature of the chlorination vessel is then increased to volatilize $ZrCl_4$. The primary purpose of the volatilization step is to remove the matrix zirconium, in order to facilitate the subsequent extraction of the transuranic elements. Experiments have shown the ready volatilization of $ZrCl_4$ at modest operating temperatures (500-700°C) whilst transuranic elements and the noble metal fission products are retained in the salt. Initial tests with a LiCl-KCl salt were not successful because the $ZrCl_4$ tended to complex with KCl, forming a non-volatile K_2ZrCl_6 compound. Removing the KCl from the bath resulted in full volatilization of the zirconium without loss of any of the transuranic elements. The recovered $ZrCl_4$ can be reduced to form zirconium metal, which can then be recycled to the fuel fabrication process.

The liquid cadmium at the bottom of the chlorination vessel contains the noble metal fission products (NMFP). The cadmium can be separated from the residual salt by freezing the metal and drawing off the salt bearing the transuranic chlorides and other fission product chlorides. Cadmium can then be recovered for recycle by distillation, sending the noble metal fission products to an extraction step where technetium is selectively removed and sent to transmutation target fabrication. The other noble metal fission products are immobilized by alloying with zirconium and iron to produce a highly durable metal waste form. This waste form will effectively immobilize technetium as well, should it prove disadvantageous to extract and transmute technetium.

The residual salt containing the transuranic chlorides, strontium and caesium chlorides and lanthanide chlorides is transferred to an electrowinning vessel, where the transuranic elements are extracted by electrowinning. It appears that the iodine can also be extracted by electrowinning, but that step has yet to be proven. The transuranic elements are sent to the fuel fabrication step, and the iodine to transmutation target fabrication after converting it to sodium iodide. The recovery of TRU elements has been demonstrated and it is planned to conduct experiments with iodine extraction during the year 2001.

Because the thermodynamic properties of technetium are not well known, it is not clear that the technetium will be volatilized along with the zirconium, but the expectation is that it will remain in the salt. Experiments are necessary to validate this assumption. The fate of iodine in this process is also not clear, and there may be multiple routes for recovery of iodine for subsequent transmutation. Testing of the complete flow-sheet in 2001 will serve to answer many of these questions.

4. Alternative fuel processing

Figure 2 shows a schematic flow-sheet for a process to treat those alternative transmuter blanket fuels incorporating an inert matrix material that will not form a volatile chloride. This process would be applicable to oxide or nitride fuel dispersions, with the added restriction in the case of nitride fuels that the nitrogen may be fully enriched in ^{15}N , to preclude the formation of excessive amounts of ^{14}C by the (n,p) reaction with the more common isotope of nitrogen, ^{14}N . This necessitates recovery and recycle of the enriched nitrogen. The process would also be useful in treating LWR fuels designed with inert matrices for burning plutonium. The initial part of the flow-sheet is much the same as that for treatment of TRU-Zr alloy fuel described above, with the exception that no species are volatilized in the course of the chlorination step. The noble metal fission products will not be chlorinated, and they will be sent to the metal waste form along with the inert matrix material (molybdenum or stainless steel), which will also not be chlorinated by $CdCl_2$. The transuranic chlorides, rare earth fission product chlorides, strontium and caesium chlorides, and the LiCl-KCl carrier salt are then contacted with a dilute alloy of lithium in cadmium in a series of centrifugal contactors operating well above the melting temperature of the salt mixture. By appropriate control of the lithium activity, the

transuranics will be reduced to the metallic state and transferred into the cadmium phase, while the fission product chlorides remain in the salt phase. The fission product bearing salt is directed to the ceramic waste form production process, resulting in a glass/sodalite composite waste form that has been shown to be highly resistant to leaching by groundwater.

The transuranic elements in the cadmium phase are oxidized by sparging chlorine through the melt, and the resultant transuranic chlorides (together with a trace amount of rare earth chlorides formed from the small amount of rare earth fission products that extract with the transuranics in the reductive extraction step) are separated from the metal phase. They are then placed in a LiCl-KCl salt bath, where the transuranics are reduced with metallic lithium and recovered as metals. The metallic transuranic elements are then sent to the fuel fabrication process for recycle to the transmuter. The trace amount of rare earth contamination of the transuranics will not cause any neutronics problems in the high neutron energy spectrum of the transmuter.

Figure 1. Schematic flow-sheet for the chloride volatility process for treatment of irradiated transmuter blanket fuel of the general composition 30-50% TRU, 70-50% Zr

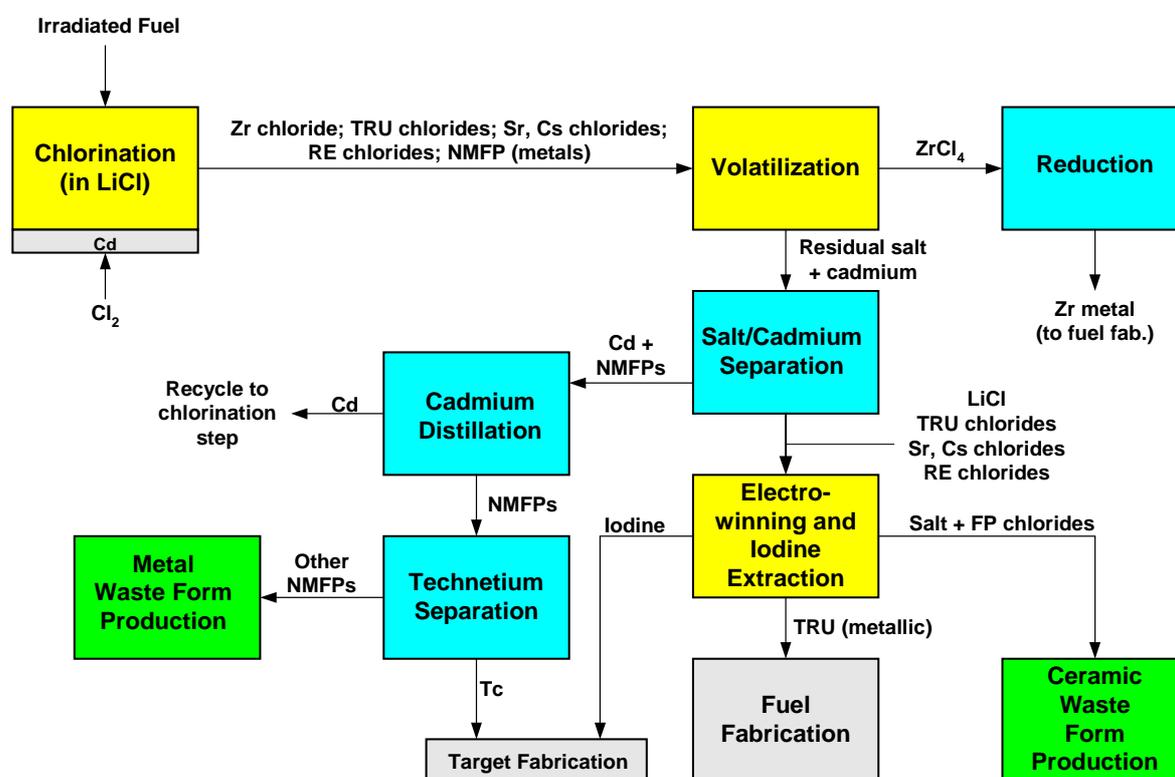
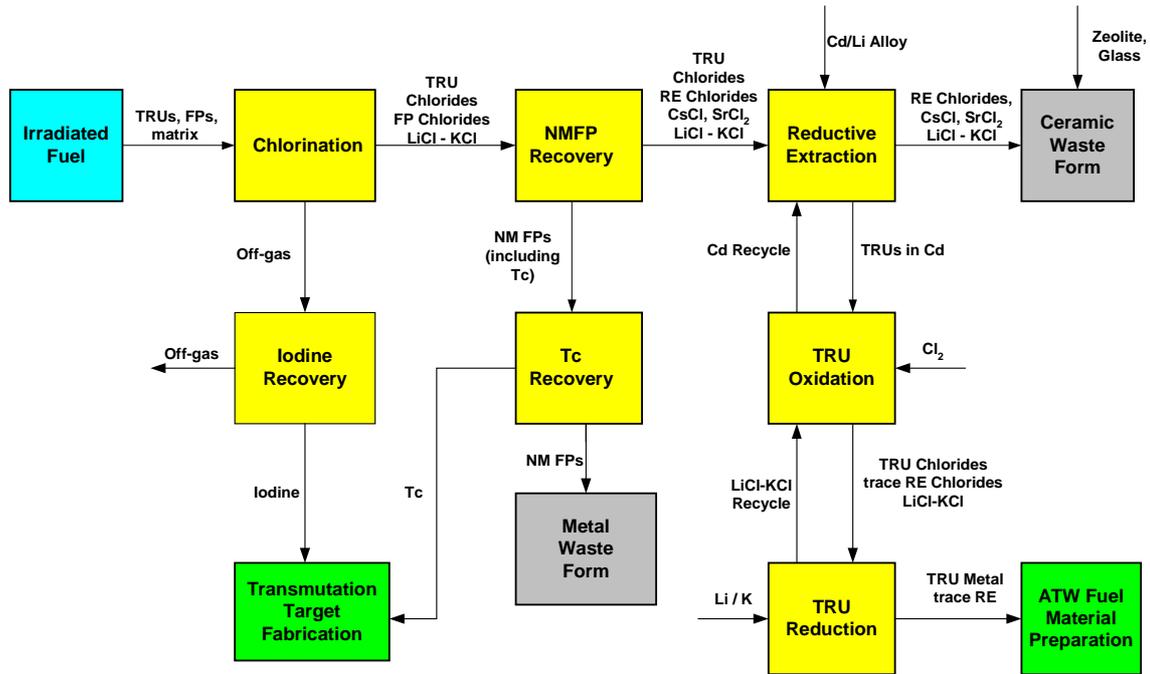


Figure 2. Schematic flow-sheet for the chlorination process for treatment of irradiated transmuter blanket fuel containing inert matrix material that will not form a volatile chloride. This process could be used for treatment of fuels with, for example, stainless steel or ceramic matrices.



5. State of process development

Both processes described here have been demonstrated with simulated irradiated fuel containing representative transuranic elements and non-radioactive fission product elements. The recovery of technetium and iodine has not, however, been shown, and remains to be accomplished with the next year. Experiments with irradiated fuels are necessary for final validation of process chemistry, but; the absence of an operating fast reactor test facility in the United States imposes a delay on access to irradiated fuel samples. In the meantime, tests will be conducted with fuel samples irradiated in thermal reactors. Even though the burn-up levels in thermal reactors will be somewhat less than would be achieved with fast reactor irradiations, the initial experiments will comprise a reasonable test of process designs and should be adequate for flow-sheet adjustment and discrimination among competing processes. Scale-up to prototype equipment sizes will occur within the next three to five years, with initial tests to be performed with simulated irradiated fuel.

Acknowledgements

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R&D OF PYROCHEMICAL PARTITIONING IN THE CZECH REPUBLIC

Jan Uhlir

Nuclear Research Institute Řež plc
250 68 - Řež, Czech Republic

Abstract

The Czech national research and development programme in the area of “Pyrochemical Partitioning” is directed primarily on the development of the “front-end” part of the fuel cycle technology for the molten salt reactor systems with a liquid fuel based on fluoride melts. The present research is directed particularly on the development of suitable fluoride separation technology based on “fluoride volatility method” the target of which is the removal of the uranium component from spent nuclear fuel and on the research of the electroseparation procedures and further on the development of appropriate construction materials and equipment for the fluoride molten salt technologies.

1. Introduction

Nuclear waste, especially spent fuel from nuclear reactors containing long-lived radionuclides represented mainly by actinides and long-lived fission products, presents a common problem for all countries operating nuclear power plants. Satisfactory solution of this problem is a factor limiting to a considerable extent the further nuclear power industry development, namely in developed countries. The present technical and technological sum of knowledge indicates that this problem could be largely resolved by using the transmutation technology so that the nuclear power industry may become widely acceptable for the public.

The use of transmutation reactors with fluoride salts based liquid fuel might be one of the possible answers. In the near future, these systems might be conceived as critical ones and successively as sub-critical accelerator driven reactor systems. In addition to the nuclear burning of plutonium and minor actinides produced in the U-Pu cycle these reactor systems might consecutively operate within the U-Th cycle as well.

The advantage of the molten salt transmutation reactors (MSTR) demonstrates itself above all in connection with a continuous or at least quasi-continuous chemical separation process.

For such a compact coupling of MSTR with chemical reprocessing it will be very appropriate to keep fuel in one chemical form, as far as possible, in the course of the entire fuel cycle. Accordingly, if the MSTR fuel will be based on fluoride melt then the separation processes should also be based on separation techniques from fluoride melt media. Pyrochemical and pyrometallurgical technologies comply generally with this requirement [1].

2. Czech research and development programme

The Czech research and development programme in the field of pyrochemical and pyrometallurgical separation is based first of all on the experience acquired in the past in the development and realisation of a pilot-plant fluoride technology for the reprocessing of spent fuel from the Russian BOR-60 fast reactor [2]. At present, this experience is utilised for the development of suitable separation processes and technologies for the fluoride based MSTR fuel cycle.

Experimental and theoretical studies in the field of pyrochemical technology development for the MSTR fuel cycle are oriented in particular to the following areas:

- Technological research in the field of the “Fluoride volatility” method directed at the suitability verification of a technology for thermal or fast reactor spent fuel reprocessing, which may result in a product the form and composition of which might be applicable as a starting material for the production of liquid fluoride fuel for MSTR. Consequently, the objective is a separation of a maximum fraction of uranium component from Pu, minor actinides and fission products. Integral part of this research also is the flowsheeting research – working out a proposal for a suitable technological flowsheet for treating spent fuel into a form fitted for MSTR including the separation procedures before transmutation (front-end) and separation processes after passage of fuel through the transmutor (back-end).
- Research on material and equipment for fluoride salts media connected with the experimental programme on ADETTE technological loops. Objective of the programme is verification of the new developed construction material for fluoride melts, development of selected devices

(first of all pumps) for fluoride melts and acquirement of practice in fluoride melts handling and manipulation in greater amounts.

- Laboratory research on electro-separation methods in fluoride melts media in relation to the study of their properties. The effort in this field is aimed first of all to the determination of optimum conditions for uranium and fission product separations and to the selection of suitable electrolyte composition based on fluoride salt mixture.

At present, the greatest attention is aimed to the realisation of the pilot-plant technology for the separation of the uranium component from other spent fuels components by the modified “Fluoride volatility” method. The other two areas mentioned are also intensively studied.

3. Technological research in the area of “fluoride volatility” method

Technological research of the “fluoride volatility” method can be ranked into the “front-end” area within the MSTR fuel cycle. It is a separation process for reprocessing spent fuel from thermal or fast reactors into a form suitable for the MSTR.

The main operations of this process are:

- Removal of the cladding material from spent fuel.
- Conversion of the fuel into a powder form (oxides) of a granulometric composition suitable for the fluorination reaction.
- Fluorination of the fuel (the purpose of this operation is the separation of the uranium component from plutonium, minor actinides and most of fission products).
- Uranium component purification.

The essential research activities are centred upon the technological verification of items 3 and 4 leading to the removal of the main portion of the uranium component from spent fuel. The proposed technology is based on the spent fuel fluorination with gaseous fluorine in a flame fluorination reactor, where the volatile fluorides are separated from the non-volatile ones, and on the subsequent purification of the component by using technological operations of condensation and distillation and also of sorption. As the fluorination reaction is suggested as a flame reaction, the necessary size of the flame fluorination reactor (Figure 1) is a critical parameter influencing dimensions of the entire experimental technological line.

According to the process design, up to 95-99% of uranium in the form of volatile UF_6 will be removed from the non-volatile fluorides of plutonium (PuF_4), minor actinides and majority of fission products. In this way, the component representing the greatest share of the spent fuel will be removed.

The technological research is closely associated with the “flowsheeting research”, the aim of which is also to act as an unifying framework of the individual research activities, in addition to the working out of the technological flowsheet. In Figure 2 a simplified flowsheet is presented of the designed MSTR fuel cycle, the “front-end” of which is based on the “Fluoride volatility” method.

Figure 1. Experimental flame fluorination reactor

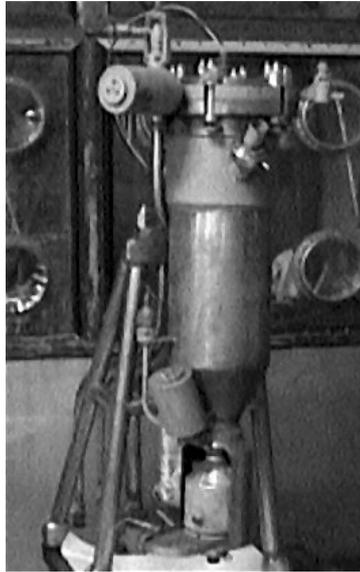
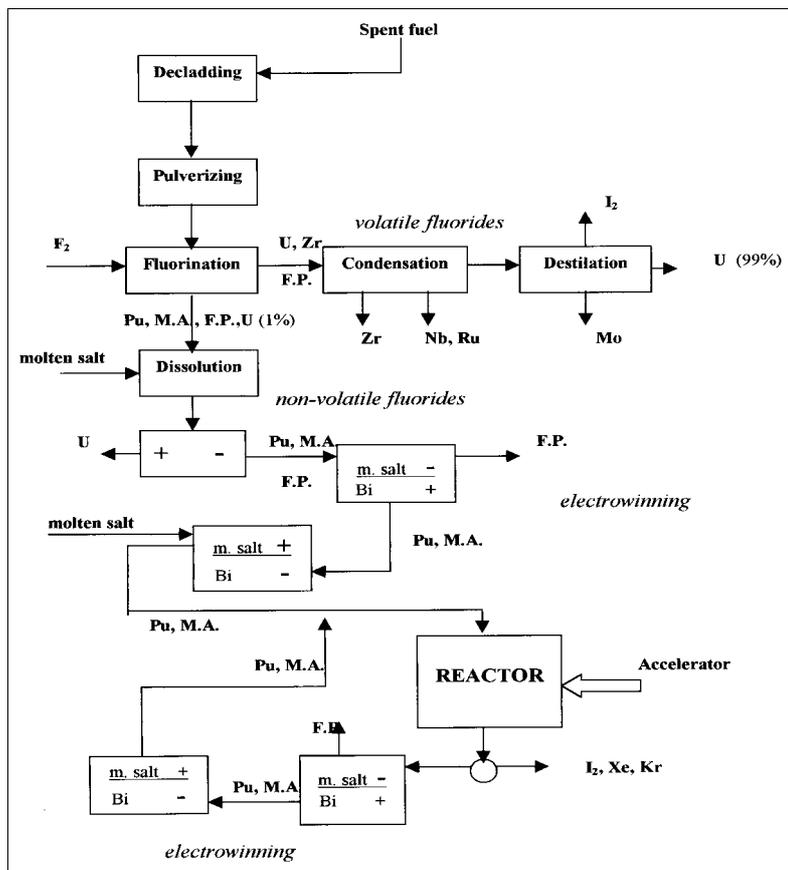


Figure 2. Simplified scheme of fuel cycle of MSTR



4. Research on material and equipment for fluoride technologies

Development of material and equipment for molten fluoride salts based technologies is connected first of all with the ADETTE technological loop programme [3] (Figure 3). The main objectives of the ADETTE loops experiments are:

- Testing of construction materials – corrosion research including the stress corrosion.
- Testing of welds.
- Research of fluoride melts thermohydraulics.
- Testing of pumps and valves for fluoride melt medium.
- Testing of measuring sensors and of the methods of measurement and control.
- Collection of data for the development and design of apparatuses for ADS technology with fluoride melts.

Special attention has been paid to the testing of the new corrosion resistant alloy MONICR SKODA. This high nickel content alloy is designated as a structural material for fluoride experimental loops for the operation temperatures of approx. 700°C.

The MONICR material is also intended for the construction of specific components of the loops like molten salt pump (impeller vertical pump with a flange-mounted electric motor), control and closing valves, molten salt storage tanks, heat exchangers etc.

Figure 3. **Experimental molten salt loop ADETTE-0**



5. Laboratory research on electroseparation methods

Laboratory research in the area of electro-separation methods is directed first of all at the determination of optimum conditions for residual uranium and fission product separation from fluoride melt and further on the selection of a suitable composition of the electrolyte based on fluoride salts mixture. As the fluoride melt should be able to dissolve sufficient amounts of plutonium and minor actinide elements, mixtures of LiF–NaF and LiF–NaF–KF type are in the foreground of interest. The assumed ability of sodium and potassium fluorides to form co-ordination compounds with transuranium element fluorides and so to significantly increase their solubility in the melt was the reason for choosing the mixtures mentioned.

The research programme in this area is further directed to the determination and study of selected physicochemical properties of fluoride melts, particularly to the:

- Solubility of lanthanides in molten fluorides.
- Standard redox potentials of individual elements.
- Melting points of the molten salt mixtures.
- Density and viscosity of the supporting fuel matrices.
- Data on corrosion resistance of structural materials.

6. Conclusion

Research and development in the area of “Pyrochemical Partitioning” is carried out in the Czech Republic as a component of the national P&T programme within the framework of the “Transmutation” consortium. The programme is funded first of all by the Ministry of Industry and Trade and by the Radioactive Waste Repository Agency. The participants of the programme are, in addition to the NRI Řež, SKODA Nuclear Machinery, Energovyzkum Brno, Nuclear Physics Institute of the Czech Academy of Sciences and Faculty of Nuclear Sciences and Physical Engineering of the Czech Technical University Prague.

Experimental research work related to the development of pyrochemical technologies is concentrated mainly in the Fluorine Chemistry Department of the NRI Řež.

The Czech national conception in the area of P&T research issues from the national power industry programme and from the Czech Power Company intentions of the extensive utilisation of nuclear power in our country. The Czech Republic, as a relatively small country, has an understandable interest in a wide integration into the solution of problems associated with spent nuclear fuel in the international context, first of all in co-operation with the EU member countries. Involvement into the 5th Framework Programme EC is an evidence of it, viz. in the area of “Pyrometallurgical Partitioning” where, for example, the PYROREP project is complementing very well with the research activities within the national programme framework.

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DEMONSTRATION OF PYROMETALLURGICAL PROCESSING FOR METAL FUEL AND HLW

Tadafumi Koyama, Kensuke Kinoshita, Tadashi Inoue
Central Research Institute of Electric Power Industry (CRIEPI)
2-11-1 Iwado-kita, Komae, Tokyo 201-8511, Japan

Michel Ougier, Jean-Paul Glatz, Lothar Koch
European Commission Joint Research Center
Institute for Transuranium Elements (JRC-ITU)
Postfach 2340, 76125 Karlsruhe, Germany

Abstract

CRIEPI and JRC-ITU have started a joint study on pyrometallurgical processing to demonstrate the capability of this type of process for separating actinide elements from spent fuel and HLW. Experiments on pyro-processing of un-irradiated metal alloy fuel (U-Pu-Zr or U-Pu-MA-RE-Zr) by molten salt electrorefining and molten salt/liquid metal extraction will be carried out. The necessary equipment is installed in a new experimental set-up at JRC-ITU. The stainless steel box equipped with telemanipulators is operated under pure Ar atmosphere and prepared for later installation in a hot cell. In first electrorefining tests, U (about 10 g) and Pu (about 5 g) were deposited on a solid and a liquid Cd cathode respectively. Preliminary experiments on molten salt/liquid metal extraction in counter-current batch extraction systems with REs were conducted in CRIEPI. The results showed good separation efficiency in 3 batch extraction stages.

1. Introduction

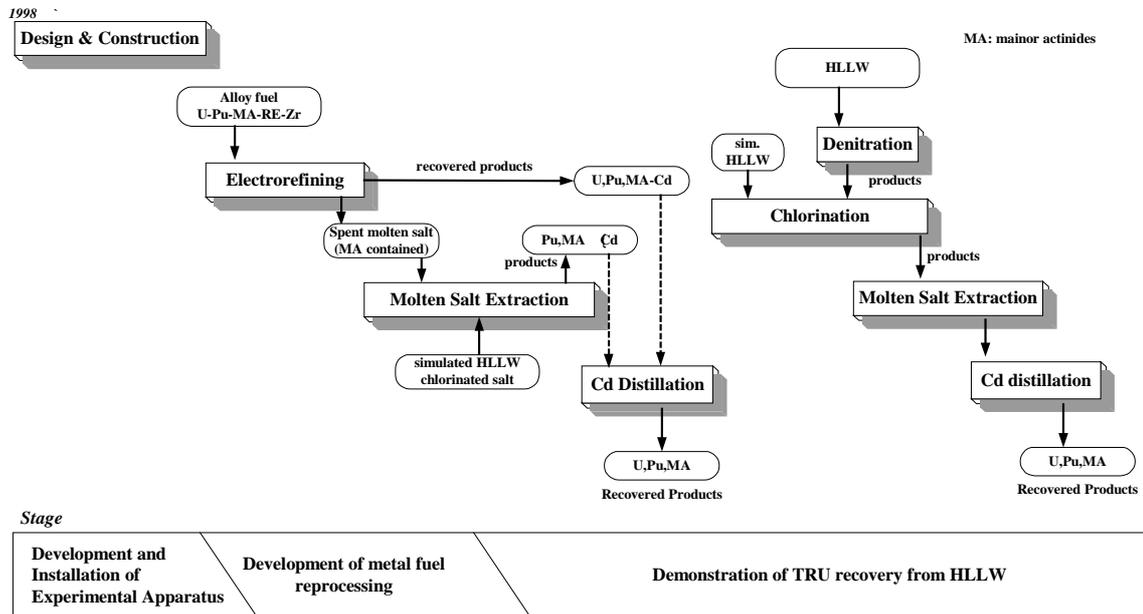
The increasing interest in pyrometallurgy after the selection a few decades ago of oxide fuel and aqueous reprocessing as the fuel cycle reference can be attributed to the drastic change of boundary conditions around the nuclear fuel cycle in the world. The former mission of the fuel cycle was to recover Pu as an important fissile material for the fast breeder reactor, however at present positive credit from recovered Pu can hardly be expected. Today's main emphasis is put on a maximal cost reduction of the fuel cycle. Furthermore recovery of long-lived nuclides becomes a new requirement, since geological disposal of high level waste (or once-through fuel) is facing large difficulties to get public acceptance. Recovery of long-lived nuclides means to use of various reactor systems for transmutation, resulting in new requirements to reprocess different fuel types e.g. MOX, metal fuel, nitride fuel, high burn-up fuel, etc. These new requirements may result in a different choice for future fuel cycle technology. Pyrometallurgical processing is one of the most attractive alternatives to meet these requirements. The requirement for product purity being much less stringent, the recovery of minor actinides (MA: Np, Am, Cm) will take place simultaneously with plutonium due to the thermodynamic properties of molten salt media. The recovery of MA allows the reduction of TRU wastes, and decrease at the same time the risk of nuclear proliferation. The molten salt media also have two important advantageous properties as a solvent material in nuclear processing. The radiation stability of molten salt allows the processing of spent fuels of high radioactivity (e.g. spent fuel with short cooling time) without any increase of solvent waste. Since molten salt is not a neutron moderator such as water is, comparatively large amount of fissile material can be handled in the process equipment, i.e. experimental facilities are compact and economical.

The Central Research Institute of Electric Power Industry (CRIEPI) investigated these promising features in pyroprocessing according to an information exchange with US-EPRI in 1985. The feasibility of pyrometallurgy to separate/recover actinides from spent nuclear fuel or high level waste (HLW) has been started on 1986 [1,2,3]. As a joint study with US-DOE, CRIEPI had participated in the Integral Fast Reactor (IFR) Program of Argonne National Laboratory (ANL) from 1989 to 1995 in order to study the pyrometallurgical technology development [4,5] and to demonstrate the pyroprocess of spent metal fuel [6]. In parallel, the measurement of thermodynamic properties of actinides as well as pyrometallurgical partitioning of TRUs from simulated HLW had been carried out by CRIEPI in collaboration with the Missouri University and Boeing North American [7,8]. In the course of the study, the feasibility of pyrometallurgical processing to recover/separate actinides from spent metal fuel or HLLW was confirmed by the results of experiments with unirradiated TRU materials and theoretical calculations based on measured thermodynamic properties. The demonstration of TRU recovery from spent metal fuel (or even from unirradiated ternary alloy fuel) could however, not be realised because of a sudden cancellation of the IFR program. The Institute for Transuranium Elements (JRC-ITU) has studied since many years the capacities of aqueous processing as for the separation of TRUs from HLW [10]. The CRIEPI and JRC-ITU collaboration to study metal target fuels for the transmutation of TRU [9] has led to a new joint study on pyrometallurgical processing. This study will demonstrate the feasibility of pyrometallurgical processes for separating actinide elements from real spent fuel and HLW, also in view of a rational evaluation of future fuel cycle technology. Furthermore this study has also been included in a project of the European 5th Framework program, where CRIEPI and ITU are a joint partner in an international network. In this paper, the current status as well as the whole test plan of this project will be reported.

2. Experimental plan of the joint study

The first phase of the joint study will be carried out from 1998 to 2004, where three different stages are to be carried out as shown in Figure 1.

Figure 1. Experimental test plan of the joint study



The first stage is *the development and installation of the experimental apparatus*. In this stage, an argon atmosphere hot cell equipped with an electrorefiner dedicated for pyrometallurgical experiments is developed. The second stage is *the development of metal fuel reprocessing*, where recovery of actinides from unirradiated metal alloy fuel such as U-Pu-Zr and U-Pu-MA-RE-Zr are to be carried out. The metal alloy fuel is first submitted to an electrorefining step followed by a reductive extraction process of the molten salt electrolyte to recover residual actinides and to separate them from lanthanides. The recovered TRU-Cd metal will be treated by distillation to separate Cd from TRUs. The third stage is *the demonstration of TRU recovery from HLLW* where pyrometallurgical partitioning is to be demonstrated on actual HLLW. In this stage, reductive extraction, Cd distillation and chlorination are first tested with simulated materials. For the experiments on actual HLLW, the whole system will be moved inside a lead shield. The actual HLLW will be converted into oxide and afterwards into chlorides in a Cl₂ gas flow. The obtained chloride salt mixture will be used for the reductive extraction process described previously. The reprocessing of metal fuel irradiated in the French PHENIX reactor will be carried out in the last phase of the project.

3. Development and installation of the Ar-atmosphere hot cell system

The experimental apparatus was newly designed and fabricated for this study and was conceived for later installation in the hot cell system. The apparatus consists of a stainless steel box to be installed in a 15 cm-thick lead shielding. The stainless steel box was first installed in an alpha laboratory Figure 2.

Figure 2. Stainless steel box with Ar purification unit



The box is operated in a pure Ar gas atmosphere, continuously purified. The airlock system for the introduction or extraction of material is separately flushed by Ar. A so called “La Calhène” container is used for the transport. The box is equipped with a vertical heating well (150 mm in diameter, 600 mm in depth) consisting of an inconel liner and a stainless steel tube. The well sited on the bottom of the box is heated from outside by a cylindrical resistance heater which can be heated up to 1 273 K. Double sleeves with intermediate Ar flushing were employed for the telemanipulators in order to reduce diffusion of oxygen. After many modifications, the stainless steel box is now in an operational condition, with an oxygen and moisture concentration less than 10 ppm.

4. Electrorefining process

4.1 Development of electrorefiner

The electrorefiner is a key part of pyrometallurgical reprocessing, since the fuel dissolution as well as the actinide refining is to be done in this step. An electrorefiner was newly designed and fabricated in CRIEPI based on experience gained in various types of experiments. It should be noted that the design concept of this electrorefiner is to demonstrate the separation yield and recovery yield of metal fuel reprocessing. The electrorefiner consists of three electrodes and a liquid Cd pool covered by a molten LiCl-KCl eutectic mixture. It was shipped to JRC-ITU, and installed in the stainless steel box as shown in Figure 3.

Figure 3. Electrorefiner installed in a stainless steel box (lift-up position)



The electrorefiner cell of 100 mm × 130 mm is hung on a metal flange equipped with cathode, anode, stirrer, reference electrode, sampling etc. Metal alloy fuel previously fabricated at ITU in a joint study with CRIEPI on transmutation of TRU targets is charged into a metal basket working as an anode. The pool of liquid Cd below the molten salt works as an anode, or just as a receiver for the noble elements. The cathode assembly of the electrorefiner uses either a solid iron cathode for U recovery or a liquid metal cathode for TRU recovery. The solid iron cathode ($\varnothing 18\text{mm}$) with a spiral groove can be rotated during electrodeposition to achieve a better recovery [2]. The liquid metal itself will be stirred by means of a ceramic stirrer submerged in the liquid metal cathode (surface area = 8 cm²) in order to avoid formation of U dendrites that will hamper the deposition of Pu [2]. The electrode potentials are monitored by a Ag/AgCl reference electrode known for its reliability. The concentration of relevant elements in each phase will be measured by the chemical analyses.

4.2 Electrorefining experiments with U and Pu

The electrorefiner was loaded with approximately 1 000 g of LiCl-KCl eutectic salt and 500 g of cadmium. The whole system was heated up to the operation temperature of 773 K to melt both phases. Depleted U metal was then charged in the anode basket followed by addition of CdCl₂ to oxidise some U metal to UCl₃, necessary to facilitate the electrotransportation in the molten salt electrolyte. At the concentration of U³⁺ of about 1 wt% in the LiCl-KCl salt, notable polarisation was not observed at a current of 1A. Hence electrodeposition of uranium on the solid iron cathode as carried out at a constant current of 500 mA and 1A, respectively. Figure 4 shows the dendritic uranium deposit obtained at 500 mA.

Figure 4. **U deposit on solid cathode (12g)**



The expected amount of uranium metal calculated from the coulomb passed was 12 g. The amount of U deposited will be determined from the chemical analyses of the metal deposit. The electrodeposition of uranium on the liquid Cd cathode was also carried out at a constant current of 200 mA for 1.5 hours resulting in the deposition of about 1 g U in 80 g Cd. After these experiments, the residual U in the molten salt was recovered by the “drow-down electrorefining” where U^{3+} is reduced to metal form at the cathode while metal Ce is oxidised at the anode. The chemical analysis of the treated salt is still under way, but the colour of molten salt turned from purple (U^{3+} ions) to white after drow-down electrorefining indicating a high efficiency of the reaction.

About 45g of plutonium metal was then charged with new 1 000g LiCl-KCl eutectic salt in the crucible. About 1 mol% of $PuCl_3$ was formed in the salt by adding the equivalent amount of $CdCl_2$. Then electrodeposition of Pu in liquid Cd cathode was carried out at a constant current of 500 mA for 4 hours. About 5 g of Pu was recovered in the liquid Cd cathode of 85 g. Figure 5 shows the liquid Cd cathode just after the electrodeposition.

Figure 5. **Pu deposit in liquid Cd cathode (~5 g)**



The deposit was easily removed from LCC crucible as shown in Figure 6.

Figure 6. Recovered Cd-Pu ingot and AlN crucible



In the next step, unirradiated U-Pu-Zr metal alloy fuels will be charged in the anode basket. Plutonium recovery into liquid Cd cathode will be performed after several fuel treatments to recover only U onto solid iron cathodes. FP simulating elements such as lanthanides will next be added to the system, and electrorefining of U-Pu-MAs-REs-Zr will be performed to simulate the processing of irradiated metal alloy fuel. The TRU recovery into the liquid Cd cathode will then be carried out after U recovery on the solid cathode. The cathode products will be analysed to determine the recovery yields and the decontamination factors. The results will provide data on the up to now unknown behaviour of TRUs during electrorefining as well as the operation sequence to maximise the TRU recovery, that will be crucial for the experiments with real irradiated fuel.

5. Reductive-extraction process

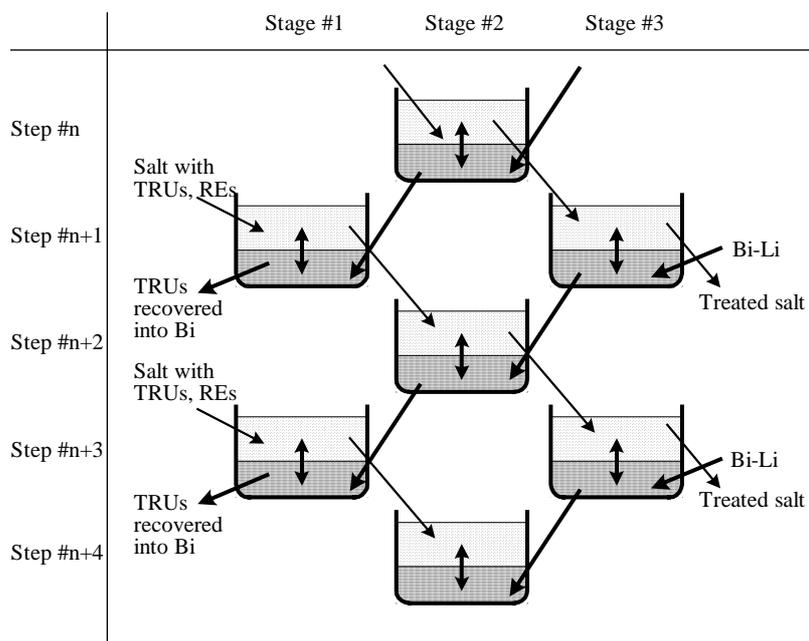
5.1 Process description

In the pyro-partitioning process a reductive-extraction technique in LiCl-KCl/Bi or LiCl-KCl/Cd system is the key step for the recovery and separation of actinides. As explained in the former report [8], a multiple batch extraction experiment was successfully carried out with a high recovery yield of TRUs and high separation efficiency between TRUs and FPs. On the other hand, the separation efficiency by means of the countercurrent extraction will be much higher than that by means of the multiple batch extraction. Hence reductive extraction by means of a counter-current batch method should be tested with TRUs. In this joint research, the reductive-extraction experiments will be carried out after the electrorefining experiments.

5.2 Preliminary experiments with lanthanides

Before starting experiments using TRUs, the experiment of three stages counter-current extraction was carried out by batch system using REs. Ce, Gd and Y were used as substitution elements for U, Am (TRUs) and Nd (REs), because the relationship of distribution coefficients among these three RE in LiCl-KCl/Bi system were roughly similar to that of U, Am and Nd. Figure 7 shows the schematic flow of the counter-current batch extraction method.

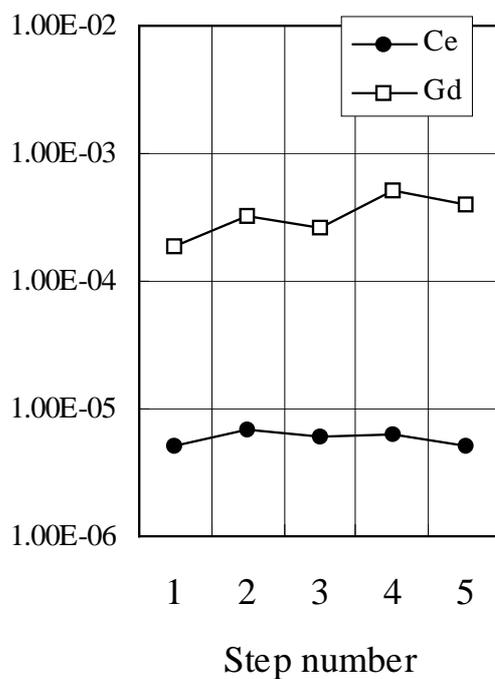
Figure 7. Schematic flow of the countercurrent bath extraction method



An initial salt phase is introduced into stage #1 and recovered as waste from stage #3. The Bi phase with Li is introduced into stage #3 and recovered as product from stage #1.

Figure 8 shows the separation factors of Ce and Gd against Y obtained during three stages at 773K.

Figure 8. Separation factors of Ce and Gd vs. Y



The separation factor (SF(M)) of metal M (Ce or Gd), is defined by:

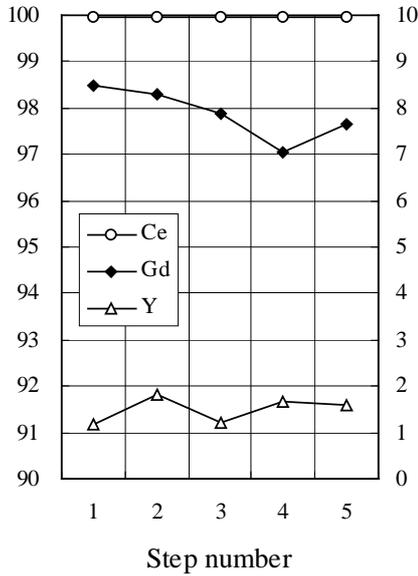
$$SF(M) = \{X(M)/Y(M)\} / \{X(Y)/Y(Y)\}$$

where X(M), X(Y) are the concentrations of MCl_3 and YCl_3 in the salt at stage #3, respectively, and Y(M), Y(Y) are the concentrations of M and Y in Bi at stage #1, respectively.

The separation factors of Ce and Gd vs. Y in the single stage extraction previously measured are 1.4×10^{-3} and 1.7×10^{-2} , respectively [12], while those in the counter-current stages obtained here were given as 5.9×10^{-6} and 3.4×10^{-4} , showing far better separation between TRUs and REs.

Figure 9 shows the recovery yield of each RE.

Figure 9. Recovery yields of Ce, Gd and Y



The recovery yield (RCM) of metal M (Ce, Gd or Y), is defined by:

$$R(M) = W_{1,Bi}(M) / \{W_{1,Bi}(M) + W_{3,Salt}(M)\}$$

where $W_{1,Bi}(M)$ is the amount of M recovered in Bi at stage #1 and $W_{3,Salt}(M)$ is the amount of M recovered in salt at stage #3.

The obtained recovery yields R for Ce, Gd and Y were >99.9%, 98% and <2%, respectively. These values agreed well with the target values (>99.9%, >99% and <10%, respectively) [8], suggesting the applicability of a counter-current batch method. The recovery yield of Gd can easily be increased to more than 99% by adding a surplus amount of the reductant, because the obtained separation factor for Gd/Y is much higher than the criterion of partitioning.

6. Conclusions

A new joint study on pyrometallurgical processing between CRIEPI and JRC-ITU has successfully started. This study will demonstrate the capability of this type of process to separate

actinide elements from spent (metallic) fuel and HLW and should provide important data in view of a rational selection of future nuclear options.

A successful installation of the equipment in a new experimental set-up was achieved at JRC-ITU. Electrorefining tests on U and Pu using solid cathodes and a liquid Cd cathode prove the operational capabilities of the facility. The next experiments will be on electrorefining of unirradiated metallic U, Pu, Zr fuels containing MA and REs.

Furthermore reductive extraction of TRUs from molten salt will be demonstrated in counter-current batch extraction systems developed in CRIEPI. The preliminary experiments using Ce, Gd and Y as stand-in elements for U and Am showed good separation efficiency from REs (Nd) in 3 batch extraction stages.

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**DEVELOPMENT OF PLUTONIUM RECOVERY PROCESS
BY MOLTEN SALT ELECTROREFINING WITH LIQUID CADMIUM CATHODE**

Masatoshi Iizuka, Koich Uozumi, Tadashi Inoue
Central Research Institute of Electric Power Industry
2-11-1, Iwado-kita, Komae, Tokyo 201-8511, Japan

Takashi Iwai, Osamu Shirai, Yasuo Arai
Japan Atomic Energy Research Institute
Oarai, Higashi-Ibaraki, Ibaraki 311-1394, Japan

Abstract

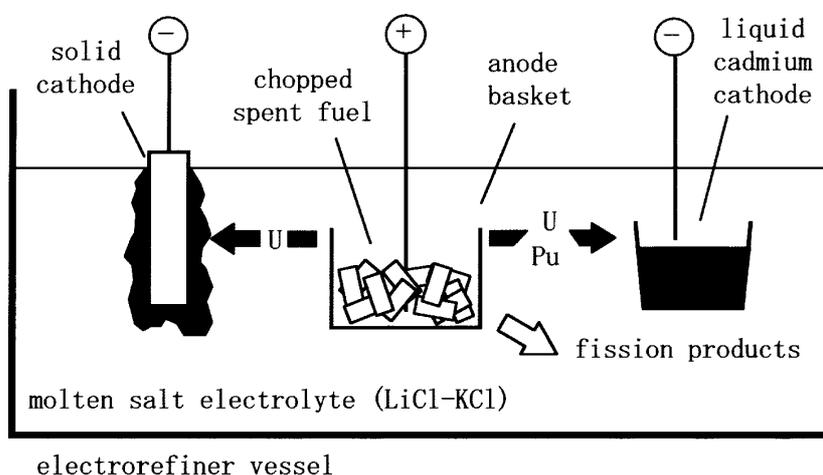
The effects of electrochemical conditions on the behaviour of plutonium and adequate conditions for recovery at liquid cadmium cathode (LCC) used in pyrometallurgical reprocessing were studied with small, not stirred electrodes. Cathodic current density adequate for plutonium collection at LCC was considered to be controlled by diffusion plutonium ion in molten salt and proportional to its concentration. It was shown that plutonium collected at the LCC beyond saturation formed intermetallic compound PuCd_6 and accumulated at the bottom of the LCC. This behaviour of coexisting americium was reasonably explained by the local equilibrium model between plutonium and americium at the surface of the LCC. The plutonium collection rate in practical electrorefining equipment estimated by extrapolation of experimental results was satisfactorily high in designing practical equipment and process.

1. Introduction

Metallic fuel cycle which consists of a metal (U-Zr or U-Pu-Zr) fuelled fast reactor and pyrometallurgical reprocessing has been proposed originally by Argonne National Laboratory (ANL) as an innovative nuclear fuel cycle technology [1]. The metallic fuel cycle has an excellent safety potential aspect originating from high thermal conductivity of the metal fuel [2]. It also has economic advantage because a pyrometallurgical reprocessing plant is estimated to be smaller than conventional aqueous reprocessing plants due to fewer steps and smaller equipments [3].

The main step in the pyrometallurgical process is molten salt electrorefining [4], where the actinide elements are recovered and decontaminated from the fission products. Figure 1 shows a schematic flow of the normal operation of this electrorefining step. The spent fuel is cut into small pieces, loaded in a steel basket, and immersed into molten chloride electrolyte. Almost all of the actinide elements in the spent fuel are anodically dissolved. Noble metal fission products are left in the anode basket by controlling the anode potential. Chemically active fission products such as alkali, alkaline earth, and rare earth metals exchange with the actinide chlorides in the electrolyte and accumulate in the molten salt in the form of their chlorides. Two kinds of cathodes are used to obtain different streams of products. One is a solid cathode made of iron and the other is a liquid cadmium cathode (LCC). At the solid cathode, uranium is selectively collected because the free energy change of chloride formation for uranium is negatively less than those of the other actinide elements. On the other hand, free energy changes of the actinide elements are close to each other at LCC because the transuranium elements (plutonium, neptunium, americium and curium) are stabilised in the LCC due to their very low activity coefficients in liquid cadmium [5,6]. Therefore, transuranium elements can be collected at LCC together with uranium.

Figure 1. Schematic flow of routine operation of the electrorefining step



The use of LCC is the most important technology in the pyrometallurgical process, where plutonium is recovered, roughly separated from uranium, and decontaminated from fission products. Because performance of LCC significantly influences the feasibility of the pyrometallurgical reprocessing, ANL studied plutonium recovery with LCC in depth with laboratory scale equipment [7-10]. Central Research Institute of Electric Power Industry (CRIEPI) has also reported on the LCCs, especially focusing on the formation of dendritic uranium deposit [11,12]. In those studies, it was shown that stirring in cathode cadmium with vertical paddles is effective to restrain growth of the

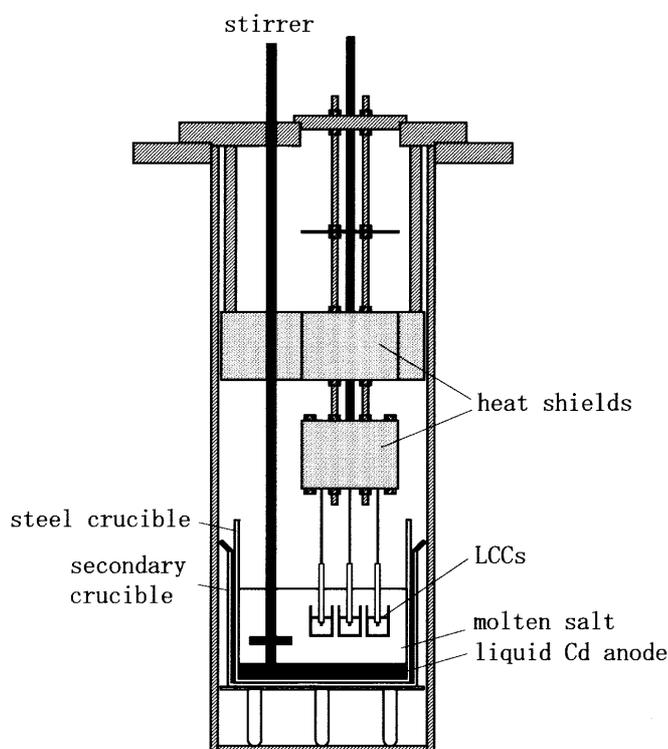
uranium dendrite and that uranium can be collected into LCCs at a cathodic current density of 0.2 A/cm^2 up to about 10 wt% in the cathode without dendrite formation [12]. In addition to the uranium studies, we have launched a joint research program with Japan Atomic Energy Research Institute (JAERI) on pyrometallurgical processes for the actinide elements. In 1999, a plutonium electrorefining apparatus equipped with a LCC assembly was fabricated and installed in a glove box. In this study, fundamental plutonium electrotransport experiments were carried out in order to understand the effects of electrochemical conditions on the behaviour of plutonium at LCC preceding investigation of engineering factors like stirring method.

2. Experiment

2.1 Apparatus

All the experiments were carried out in a high purity argon atmosphere glove box. Both oxygen and moisture levels in the atmosphere were kept less than two ppm during the tests. Figure 2 is a schematic view of the experimental apparatus. Inner diameter and depth of the container for molten salt were 124 mm and 120 mm, respectively. The amount of lithium chloride-potassium chloride (LiCl-KCl) eutectic mixture loaded in this container was about 1 200 grams. Under the molten salt electrolyte, a liquid cadmium layer was placed and used as an anode which supplied plutonium in electrotransport experiments. The amount of the anode cadmium was about 1 400 grams. The salt and anode cadmium were heated with an electric furnace and the temperature of the system was kept to $773 \pm 1 \text{ K}$.

Figure 2. Schematic view of experimental apparatus



The electrorefining apparatus and the cathode assembly were originally designed to accommodate a LCC of 50 mm outer diameter, which would be stirred to facilitate the mass transfer of plutonium. In this study, however, much smaller cathodes were used because the study aimed to understand the effects of fundamental electrochemical conditions on the behaviour of plutonium at LCC proceeding to investigate engineering factors like stirring method. The size of the cathode crucible used in this study was 9 mm in diameter and 16 mm in depth. About 3 to 5 grams of cadmium was loaded in the crucible. A silver-silver chloride (1 wt% AgCl in LiCl-KCl) reference electrode contained in a thin Pyrex glass tube was used as a reference electrode.

2.2 Chemicals

The chlorides (LiCl-KCl, CdCl₂ and AgCl) were purchased from Anderson Physical Laboratory. Because their purity was no less than 99.99% and their moisture content was extremely low, they were used with no additional purification procedure. Cadmium metal of more than 99.9999% purity for the anode and the cathode was purchased from Rare Metallic Corporation. Because the cadmium had been packed under vacuum just after production to avoid oxidation by the air, it was not washed or polished before use. PuO₂ used in this study contained about 2% of americium which was generated by (n, γ) reaction of Pu²³⁹ and β -decay.

PuCl₃ was prepared in the following two steps. (a) carbothermic reduction of PuO₂ to produce PuN [13], and (b) exchange reaction between PuN and cadmium chloride (CdCl₂) in LiCl-KCl. Pu in the liquid cadmium anode layer was prepared by reduction of PuCl₃ by addition of Cd-Li alloy. After these procedures were completed, concentrations of plutonium in the molten salt and in the liquid cadmium anode were 2.28 wt% and 1.72 wt%, respectively.

2.3 Analytical procedures

EG&G Princeton Applied Research potentiostat/galvanostat Model 273A and EG&G 270/250 Research Electrochemistry Software were used for both electrochemical measurement and constant-current electrotransport. The concentrations of plutonium and cadmium in the molten salt were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) of the samples. Cathode products were analysed by scanning electron microscope (SEM) and electron probe microanalyser (EPMA). An X-ray diffract meter (XRD) was also used to determine the chemical form of the cathode deposit.

3. Results and discussion

In order to understand the relationship between the behaviour of plutonium at LCC and its reduction rate, electrotransport experiments were carried out at various cathodic current densities. Major results are summarised in Table 1 with experimental conditions.

Table 1. Conditions and results of Pu electrotransport experiments with LCCs

Run no.	Pu concentration in molten (wt %)	Cathodic current density (mA/cm ²)	Electrotransport-time (s)	Electricity passed in experiment (C)	Initial amount of cathode (g)	Increase of cathode weight (g)	Collection efficiency (%)	Final Pu concentration in cathode (wt %)
1	2.28	33	12 000	240	4.036	0.1983	100	4.68
2	2.11	41	11 870	297	2.918	0.245	105	7.75
3	2.28	50	7 800	234	4.899	0.1555	80.6	3.08
4	2.11	66	6 500	260	3.406	0.0023	1.07	0.07
5	4.6	66	7 200	288	4.0287	N/A	N/A	N/A
6	4.6	82	5 400	270	4.0056	N/A	N/A	N/A
7	4.6	100	5 400	324	4.024	N/A	N/A	N/A

3.1 Time course of LCC potential and plutonium recovery efficiency

Changes of LCC potential in the electrotransport tests at plutonium concentration of about 2 wt% in the molten salt are shown in Figure 3. At cathodic current density of 33 to 41 mA/cm², cathode potential was kept between -1.4 V and -1.55 V after a slight shift to the lower direction at the beginning. In this range of the potential, reduction of plutonium followed by dissolution to liquid cadmium or formation of an intermetallic compound is expected to occur from the result of the CV measurement [14]. The moderate change of the cathode potential indicated that plutonium was smoothly collected in the LCC without abrupt growth of solid phase at the interface. Collection efficiencies for plutonium calculated from increase of cathode weight and electric charge passed between the electrodes were nearly 100% in these conditions. This result supports the above consideration. Figure 4 is a photograph of the cathode cadmium ingot taken out of the crucible in Run 2 where plutonium was collected up to 7.75 wt% in cadmium at cathodic current density of 41 mA/cm². Although there was a little inequality on the surface of the LCC, no growth of dendritic deposit was found.

Figure 3. Change of LCC potential in Pu electro-transport tests

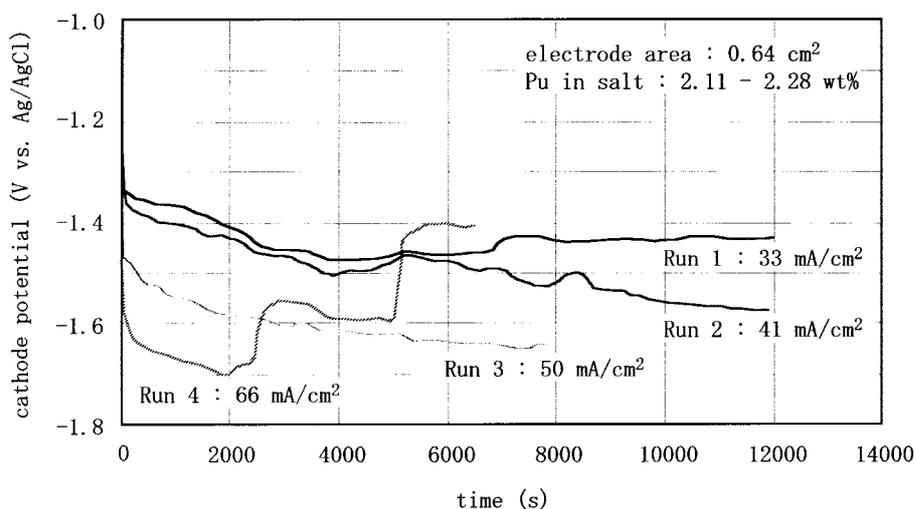
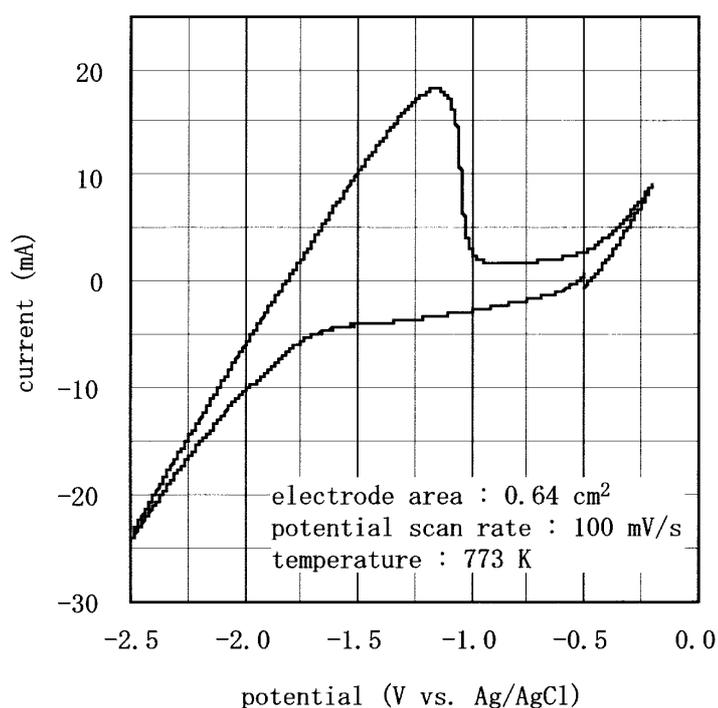


Figure 4. Cathode Cd ingot obtained after Pu electro-transport test at cathodic current density of 41 mA/cm²



Cathode potential went down to -1.65 V at cathodic current density of 50 mA/cm². The solidified salt on the top of the cathode cadmium in Run 3 was white although the bulk salt containing about 2 wt% of plutonium is usually light blue in colour. Collection efficiency for plutonium was about 80%, a little lower than in the preceding case. These results indicate that lithium in the electrolyte was reduced at the LCC at -1.6 V and that the reduced lithium reacted with plutonium tri-chloride near the cathode after the electrotransport. Although lithium forms a very stable chloride which has more than 0.6 V lower standard potential than that of plutonium at an inert electrode, its metal is stabilised in liquid cadmium due to the very low activity coefficient [15]. Figure 5 shows a CV measured for blank LiCl-KCl with a liquid cadmium electrode. It can be seen that reduction current for lithium increases from about -1.6 V, suggesting the validity of the above consideration.

Figure 5. Cyclic voltammogram for blank LiCl-KCl with liquid cadmium electrode



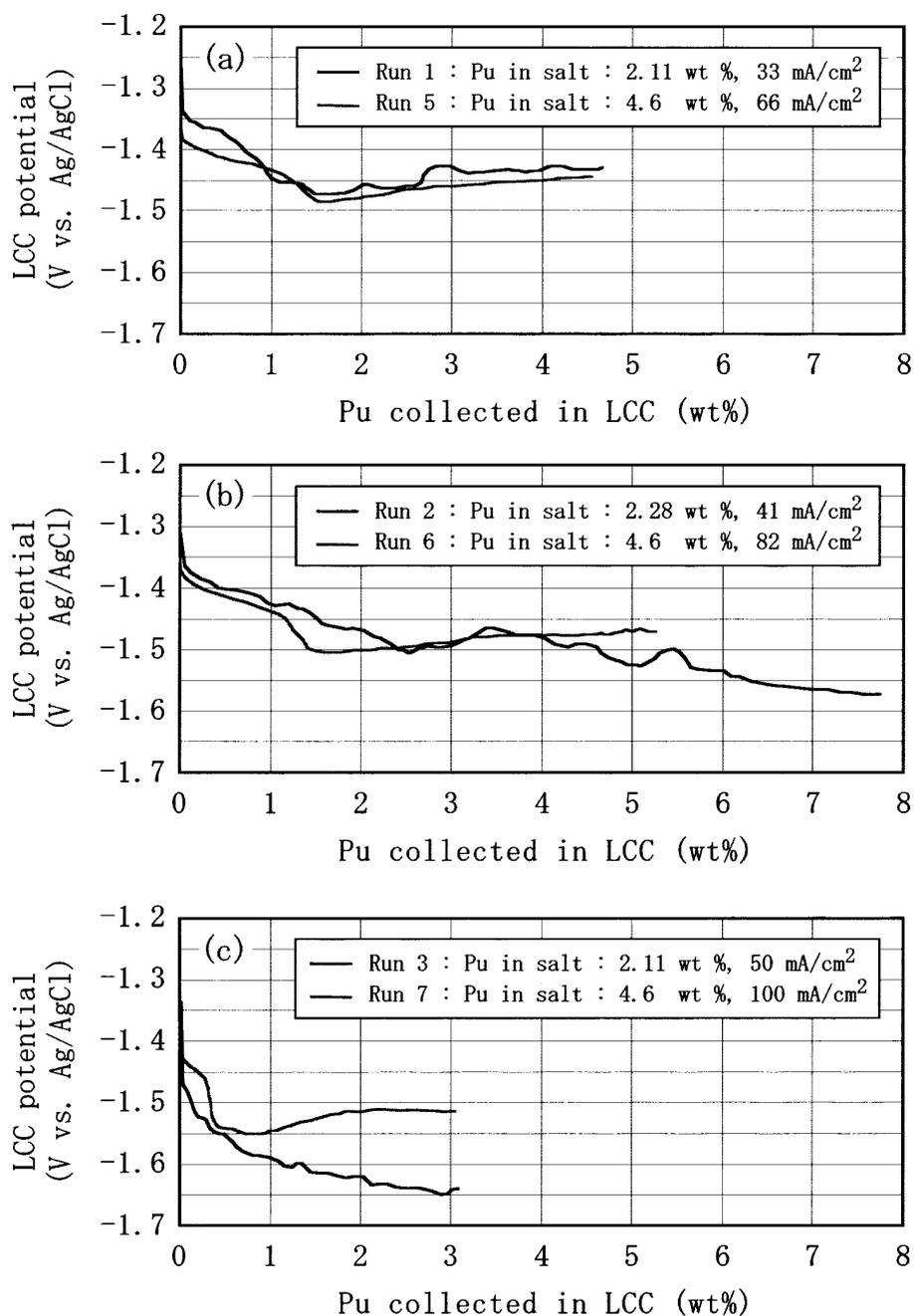
When cathodic current density was increased to 66 mA/cm², cathode potential descended to -1.7 V at first and subsequently ascended in two steps. After the experiment, the cathode was visually inspected. The lower part of the alumina insulator sheath of the electric lead for the LCC had turned black and a deposit with metallic gloss was found on that region. XRD analysis showed that the major portion of this deposit was PuCd₆. At such low potential and higher cathodic current density, it is expected that the reduction rate and the LCC surface concentration of lithium were increased and that the lithium reacted with the alumina sheath. It is very likely that the alumina sheath was wetted much more easily with liquid cadmium due to the reaction with lithium. This is considered the reason why the alumina sheath worked as a thin LCC and PuCd₆ was deposited there. The very low collection efficiency for plutonium (25%) in Run 3 should be due to the PuCd₆ formation out of the LCC.

3.2 Plutonium concentration dependence of optimum cathodic current density

Electrotransport experiments were carried out at higher plutonium concentration in molten salt in order to investigate the effect of plutonium concentration on the reduction behavior of plutonium at LCC. The concentration of plutonium in the molten salt was adjusted to 4.6 wt% by the procedure described above. The results were compared with those at lower concentrations in Figure 6(a) to (c). In Figure 6(a) and (b), it is clear that the overall trends of the charts at approximately same ratio between plutonium concentration in the molten salt and cathodic current density can be closely correlated. It indicates that cathodic current density at which plutonium can be smoothly collected into LCC is proportional to the plutonium concentration in molten salt at least in the range of this study. A distinct difference was found in two charts in Figure 6(c). In Run 3, cathode potential went down to -1.65 V and lithium in the solvent was considered to be reduced. In Run 7, on the other hand, cathode potential was kept higher than -1.55 V at which it was expected that plutonium was selectively reduced at the LCC. As mentioned above, the ratio between cathodic current density and the plutonium concentration in molten salt was a little higher in Run 3 ($24 \text{ mA/cm}^2 \cdot \text{wt}\% \text{-Pu}$) compared to Run 7 ($22 \text{ mA/cm}^2 \cdot \text{wt}\% \text{-Pu}$). It is thought that a limitation in the mass transfer rate of plutonium by diffusion in molten salt in a not stirred system lies between those conditions. Conversely, selective and smooth plutonium reduction at the LCC would be expected at a cathodic current density proportional to the concentration of plutonium in molten salt at a ratio of $22 \text{ mA/cm}^2 \cdot \text{wt}\% \text{-Pu}$ at least.

Throughout the plutonium electrotransport experiments with LCCs in this study, the highest cathodic current density at which plutonium was recovered selectively and stably was 100 mA/cm^2 at plutonium concentration of 4.6 wt% in the molten salt.

Figure 6. Change of LCC potential in electrotransport tests (effect of cathodic current density and Pu concentration in molten salt)



3.4 Behaviour of plutonium and americium in LCC

The LCC ingot recovered after the electrotransport was analysed in order to evaluate the behaviour and distribution of plutonium in the cathode. Figure 7 is a SEM image of the intersection of the LCC ingot obtained in Run 2, where plutonium was collected into the cathode up to 7.75 wt% at cathodic current density of 41 mA/cm². There is a layer near the bottom of the LCC containing a

crystallized phase in high density. Figure 8 is a characteristic X-ray image of plutonium of this layer. It is clearly shown that the crystallised phase in this region contains a high concentration of plutonium and that only a small amount of plutonium exists in the bulk. The plutonium-rich phase was identified to be PuCd_6 by quantitative EPMA analysis.

Figure 7. SEM image of the LCC ingot shown in Figure 4 (near the bottom)

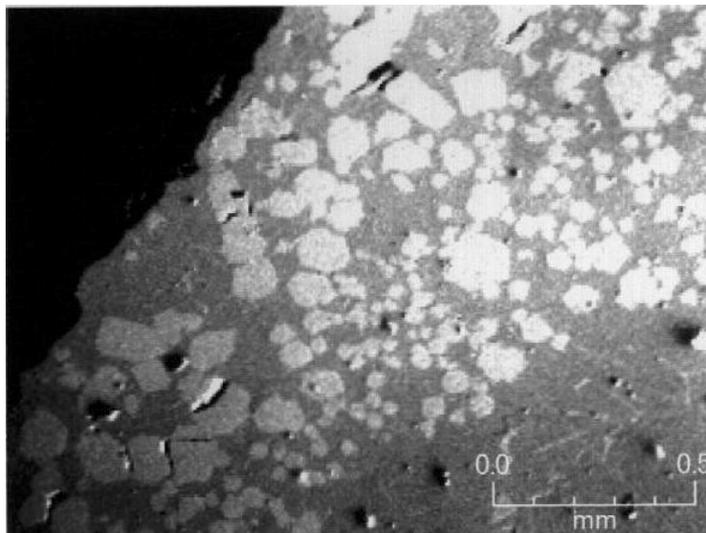
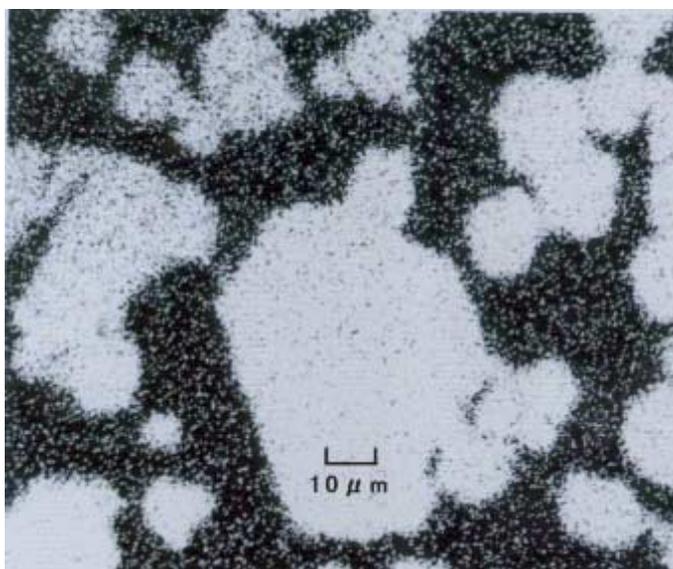
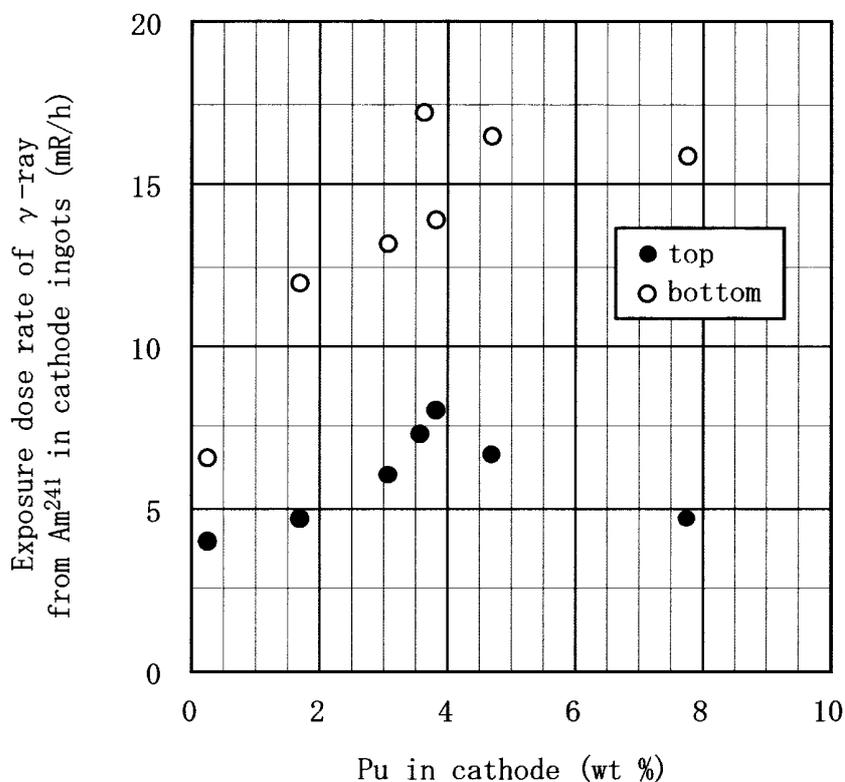


Figure 8. Characteristic X-ray image of Pu at bottom region of LCC ingot



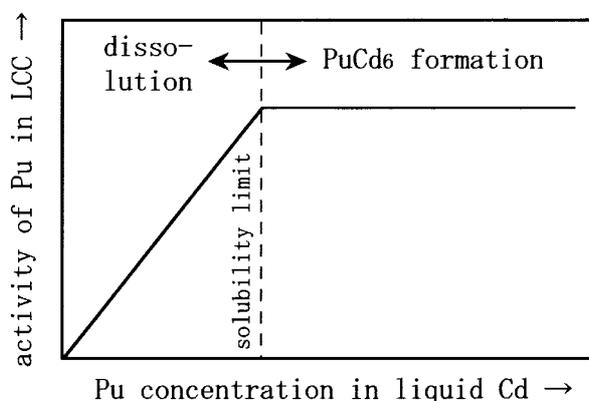
From these results, it seems most likely that plutonium reduced at the LCC beyond its solubility limit in liquid cadmium instantly forms PuCd_6 at the surface of the LCC and settled down to the bottom of the cathode. It is still possible, however, that the segregation of PuCd_6 was caused by vertical temperature gradient in the LCC, because it was cooled very slowly after the experiments. Further tests are needed to elucidate the mechanism of PuCd_6 accumulation at the bottom of the LCC.

Figure 9. Relation between Pu concentration in LCCs and γ -ray from cathode ingots



The exposure dose rate of γ -ray from Am^{241} in the LCC ingots was plotted in Figure 9 versus the concentration of plutonium collected in the cathodes. The dose rate was measured for both top and bottom of the ingots by a GM survey meter placed outside of the glove box at a distance of about 2 mm from the ingots. These plots have a distinctive tendency. At low concentrations of plutonium in the LCCs, the dose rate at either top or bottom of the ingots increased according as the electrotransport proceeded. When the concentration of plutonium in the LCCs reached its solubility limit, however, the increase of the dose rate simultaneously stopped. In our previous LCC study with uranium and lanthanide elements, similar behaviour was observed [16]. While the concentration of uranium in the LCC increased linearly to the electricity, deposition of gadolinium and neodymium stopped before uranium saturation and their concentrations remained almost constant. Such behaviour of americium and lanthanides can be explained by the following consideration based on a local equilibrium model. Assume that electrode reactions of plutonium and americium at the LCC are reversible, that is, a local equilibrium relationship between the two elements at the cathode cadmium/molten salt interface described in equation in Figure 10 is established at every moment. Activity of plutonium in the LCC increases with its concentration before it reaches solubility limit. After saturation, plutonium forms intermetallic compound PuCd_6 . Because PuCd_6 is solid at 773 K, the activity of plutonium in the LCC does not change although a larger amount of plutonium may be collected beyond its solubility limit. Under this condition, deposition of americium would be restrained so that the local equilibrium would be maintained.

Figure 10. Concept of Pu activity change in liquid cadmium and local equilibrium at the surface of LCC



$$\frac{a(\text{AmCl}_3 \text{ salt/Cd})}{a(\text{Am Cd/salt})} = K \frac{a(\text{PuCl}_3 \text{ salt/Cd})}{a(\text{Pu Cd/salt})}$$

where

$a()$ represents activity of each species at the molten salt/LCC interface, and

AmCl₃ salt/Cd : AmCl₃ in molten salt
 Am Cd/salt : Am in LCC
 PuCl₃ salt/Cd : PuCl₃ in molten salt
 Pu Cd/salt : Pu in LCC
 K : equilibrium constant

3.5 Expectation of plutonium recovery rate at a practical electrorefiner

From the results of the electrotransport experiments with LCCs, it was found that lithium was reduced after exhaustion of plutonium in the salt at higher cathodic current densities, and that cathodic current density adequate for smooth plutonium collection is proportional to its concentration in the molten salt at least in the range of this study. Therefore, it is reasonable to assume that plutonium reduction current at the LCC is controlled by diffusion of plutonium ion and is proportional to its concentration in the molten salt. It is also proper to assume that plutonium reduction current is proportional to the surface area of the LCC, although this relationship should be significantly influenced by the geometric design of the electrorefining equipment.

Based on the above consideration, plutonium collection rate at LCC in practical electrorefining equipment was estimated as follows. The sum of the concentrations of all actinides in the molten salt is planned to be adjusted to 2 mol% (about 8 wt%) in the practical operation of electrorefining step [16]. In LCC operation, the plutonium / uranium ratio in molten salt will be set considerably high in order to avoid formation of uranium dendrite. This ratio was assumed to be 7/1 in this calculation. Cathodic current density adequate for smooth plutonium collection was assumed to be proportional to the concentration of plutonium in molten salt at a ratio of 20 mA/cm²·wt%-Pu based on the

consideration described in the preceding section. The inner diameter of a practical scale LCC was supposed to be 30 cm. Consequently, reduction current for plutonium at one LCC was evaluated as:

$$0.02 (\text{A}/\text{cm}^2 \cdot \text{wt}\%) * 7 (\text{wt}\%) * 15^2 \pi (\text{cm}^2) = 99.0 (\text{A})$$

This is equivalent to a collection rate of 294 grams of plutonium per hour. This performance is considered high enough in designing a practical electrorefiner and pyrometallurgical process.

4. Conclusion

Plutonium was smoothly collected into a LCC even without cathode stirring. At plutonium concentration of 2.11 wt% in molten LiCl-KCl and cathodic current density of 41 mA/cm², the collection efficiency of plutonium was nearly 100% and maximum plutonium loading into the LCC was 7.75 wt%. At higher cathodic current densities, lithium and plutonium metals were generated at the surface of the LCC and reacted with ceramic LCC parts. Collection efficiency was decreased due to these reactions.

Cathodic current density adequate for smooth plutonium collection was proportional to its concentration in molten salt at a ratio of about 20 mA/cm²·wt%-Pu at least in the range of this study. At plutonium concentration of 4.6 wt% in molten salt, cathodic current density of 100 mA/cm² was attained without any trouble such as solid deposit growth or descent of cathode potential indicating reduction of lithium.

It was considered that plutonium collected into the LCC after saturation formed intermetallic compound PuCd₆ and accumulated at the bottom of the LCC based on EPMA analysis of the LCC ingot. It is still possible, however, that segregation of PuCd₆ was caused by a vertical temperature gradient in the LCC in the course of the slow cooling process.

Increase of γ -ray count from Am²⁴¹ in the LCC ingots stopped coincident with saturation with plutonium. This behaviour was reasonably explained with the local equilibrium model between plutonium and americium at the surface of the LCC.

Plutonium collection rate in practical electrorefining equipment was estimated to be 294 grams per hour for one LCC based on the assumption that the collection rate is proportional to the plutonium concentration in the molten salt and the surface area of the LCC. This performance is considered sufficient in designing a practical electrorefiner and pyrometallurgical process.

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