Extraction and Separation of Se, Zr, Pd, and Cs Including Long-Lived Radionuclides

Yuji SASAKI1*, Keisuke MORITA1, Shinichi SUZUKI1, Hideaki SHIWAKU1, Keisuke ITO1, Yuya TAKAHASHI2 and Masaaki KANEKO2

1Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan; 2Toshiba Corporation, 4-1, Ukishima-cho, Kawasaki-ku, Kawasaki, 210-0862, Japan

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The solvent extraction of Se(IV), Zr(IV), Pd(II), and Cs(I) from nitric acid into 1-octanol (OC), or 1-octanol and n-dodecane has been performed. These elements include long-lived radionuclides in spent nuclear fuels, so a simple separation method is indispensable for the development of the treatment of high-level liquid radioactive waste. It was found that Se can be extracted using phenylenediamine, Zr(IV) can be extracted using tetraoctyl diglycolamide and di-2-ethylhexyl phosphoric acid, and Pd can be extracted using (methylimino)bis(N,N,N',N'-hexaoctylnitrilotriacetamide. These elements can be recovered in over 90% yield by these extractants from nitric acid into OC. A distribution ratio of Cs(I) of greater than 1 can be obtained using di-t-butyldibenzo-18-crown-6. It is clear that 90% recovery of Cs(I) can be achieved using an extraction solvent with ten times the volume of the aqueous phase.

1. Introduction

In addition to actinides, various types of fission products are dissolved in high-level radioactive waste (HLW), which is HNO₃-based liquid waste generated from the plutonium–uranium redox extraction (PUREX) process. The raffinate solution, which is the aqueous phase after the PUREX process, contains several long-lived radionuclides, such as Se, Zr, Pd, and Cs. These elements have radioisotopes with a half-life ($T_{1/2}$) of over $10^4$ y, i.e., Se-79 ($T_{1/2} = 3.27 \times 10^5$ y), Zr-93 ($T_{1/2} = 1.64 \times 10^6$ y), Pd-107 ($T_{1/2} = 6.5 \times 10^6$ y), and Cs-135 ($T_{1/2} = 2.3 \times 10^6$ y) [1]. These are also elements that need to be recovered from HLW and transmuted for reducing the long-term environmental burden. An overall study, including the development of a chemical recovery method as well as its transmutation, has commenced. The name of this program is Impulsing PAradigm Change through disruptive Technologies (ImPACT) [2-3]. This current study is closely related to this program.

All the above mentioned elements exhibit different chemical behavior, so different conditions have to be established for their recovery. Namely, Zr(IV) is a hard acid metal, Pd(II) is a soft acid metal, Se(IV) forms oxyanions, and Cs(I) is an extremely strong hard acid metal [4]. Therefore, it is necessary to employ different chemical methods in order to recover these elements. Solvent extraction is a useful technique for recovering metals in the industrial field and is flexible in terms of the recovery of metals that exhibit different chemical behavior. This method is simple and available for reducing radioactive waste.

In this study, the extraction and the separation of these four elements was performed. The extractants
used were (methylimino)bis(N,N-dioctylacetamide) (MIDOA) and $N,N,N',N''$-hexaoctylnitrilotriacetamide (NTAamide) for extracting Pd(II) [5-6], tetraoctyl diglycolamide (TODGA) and di-2-ethylhexyl phosphoric acid (HDEHP) for extracting Zr(IV) [7-8] phenylenediamine derivatives (phenylenediamine (PDA) and dimethylphenylenediamine (DMePDA)) for Se(IV) in order to form an extractable piazselenol [9-10], and crown ether compounds (di-$t$-butyldibenzo-18-crown-6 (DtBuDB18C6) and dicyclohexyl-18C6 (DCH18C6)) for extracting Cs(I) [11-12]. The structures of all eight extractants are shown in Figure 1. Using these extractants, the basic results and extraction properties were investigated. A recovery rate of greater than 90% is one of the purposes of this program, so the experimental conditions for attaining this performance were determined. Here, the reasons for the use of these extractants are as follows; MIDOA and NTAamide show very high $D(Pd)$ values from nitric acid and can be gasified by combustion due to their composition. TODGA and HDEHP have high $D(Zr)$ values from nitric acid, TODGA can be gasified by combustion and HDEHP shows less extractability for lanthanides, whose concentrations in HLW are very high. Zr(IV) can be extracted by TBP and MIBK but only from HCl media. Although less information on Se(IV) extraction from nitric acid is available, PDA and DMePDA form extractable piazselenol complex with Se(IV). DtBuDB18C6 and DCH18C6 can be dissolved in 1-octanol, which can be used under the process conditions. However, DB18C6 cannot be used.

![Figure 1. Structures of extractants.](image)

### 2. Experimental

#### 2.1 Reagents

TODGA, MIDOA, NTAamide, HDEHP, DtBuDB18C6, DCH18C6, PDA, and DMePDA, used as extractants in this study, were purchased from Wako Pure Chemical Industries. Synthetic methods for TODGA, MIDOA, and NTAamide are reported elsewhere [5,13-14]. Extractants having greater than 98% purity were used for solvent extraction. The other extractants in Figure 1 and the reagents employed for the back-extraction, thiourea and oxalic acid, were obtained as commercial products. Standard solutions containing 1000 ppm of Se, Zr, Pd, and Cs (Wako Pure Chemical Industries) were used for solvent extraction. Other reagents, such as n-dodecane, 1-octanol, and nitric acid, were of analytical grade.
2.2 Solvent extraction methodology

The extraction procedure was as follows: each extractant was dissolved in n-dodecane or 1-octanol (OC) at room temperature. Aliquots of a standard solution of each element were evaporated using an infrared heat lamp, and the residues were dissolved using HNO₃ at the appropriate concentration. The organic or aqueous phases containing a certain concentration of extractant, (1-200 mM) or element (200 ppm), were mixed and shaken mechanically at 1500 strokes per min for 30 min at 25 ± 0.1 °C. After centrifugation, the concentrations of the elements extracted from the aqueous phase were measured by inductively coupled plasma optical emission spectrometry (ICP-OES, SPS 3100; Seiko Instruments, Inc.). The concentrations of the elements in the organic phase were determined by subtracting the final concentration in the aqueous phase from the initial concentration. The values of the distribution ratio (D) were defined as the ratio of the concentration of the element ([M]) in the organic phase to [M] in the aqueous phase.

The back-extraction experiments were performed as follows: the organic phases containing metal ions were used. After forward-extraction, the aqueous phase was removed carefully from the organic phase. The fresh aqueous phase, thiourea for Pd(II), oxalic acid for Zr(IV), concentrated acid for Se(IV) or diluted HNO₃ for Cs(I), was put in the extraction tube with the organic phase and shaken. After centrifugation, the metal concentration in the aqueous phase was measured by ICP-OES in order to determine the efficiency of the back extraction.

3. Results and Discussion

3.1 Extraction of Pd

Pd(II) is generally extracted using an extractant containing sulfur and nitrogen donor atoms. In this study, we must focus on the recovery of Pd(II) from HLW, so nitrogen donor atoms are more useful than sulfur with respect to the production of a vitrified product [15]. In accordance with the details described above, MIDOA and NTAamide were used for the extraction of Pd(II), and the extraction results are shown in Figure 2. Both extractants can be dissolved in n-dodecane and OC, so the values of D for these diluents are shown in Figure 2. Figure 2(a) shows the dependence of \( D(Pd) \) on the HNO₃ concentration, whereas Figure 2(b) shows the dependence of \( D(Pd) \) on the extractant concentration.

From Figure 2(a), a gradual decrease in \( D(Pd) \) on increasing the HNO₃ concentration can be observed, because of the protonation of the N donor atoms in the extractants. A competition reaction between Pd(II) and the protons occurred at high concentrations of HNO₃ [6]. Consequently, the values of D decreased. The effective extraction of Pd can be achieved when using dilute HNO₃ as the aqueous phase. On comparing the two diluents, the value of D for n-dodecane (DD) is clearly higher than that for OC, the reason for is not understood. However, similar result, in which greater values for D in n-dodecane can be seen in a previous study [16]. Figure 2(b) shows the linear relation of \( \log D \) vs. \( \log [\text{extractant}] \); the slopes indicate the molar ratio of [M]:[extractant]. The values of the slopes are 1 – 2 (MIDOA/DD: 0.96, MIDOA/OC: 1.32, NTAamide/DD: 1.14, and NTAamide/OC: 1.89), so one or two molecules of MIDOA or NTAamide can react with Pd. From these results, both MIDOA and NTAamide can quantitatively extract Pd(II) from HNO₃.
Figure 2. Pd extraction using (methylimino)bis(N,N-dioctylacetamide) (MIDOA) and \(N,N,N',N'',N''',N''''\)-hexaoctylnitritoltriacetamide (NTAamide). (a) Dependence of \(D(Pd)\) on the HNO\(_3\) concentration (0.1 M MIDOA or NTAamide/1-octanol (OC) or \(n\)-dodecane); (b) Dependence of \(D(Pd)\) on the extractant concentration (HNO\(_3\): 2–3 M).

As a 90% decrease of extraction corresponds to \(D(M) = 10\), \(D = 10\) is one of the indications that 90% extraction has been achieved. Using dodecane as a diluent may provide appropriate conditions for extracting Pd(II) using MIDOA and NTAamide. However, \(n\)-dodecane generally exhibits low solubility for any organic compound, such as the extractants used in this study. On the other hand, OC has a high dielectric constant and can dissolve various organic materials. As shown in Figure 2, extraction into OC results in low \(D\) values, particularly using MIDOA. As a result, using NTAamide/OC as the extraction solvent is promising and has the potential to extract Pd(II). The conditions for attaining 90% extraction of Pd(II) are 0.2 M NTAamide/OC and a HNO\(_3\) concentration of less than 2 M.

With regard to stripping of Pd(II) from the organic phase, the use of thiourea is well-known [17]. Thiourea, 10 mM in 0.2 M HNO\(_3\), is used for the back-extraction of Pd(II). From the present work, one hundred % recovery of Pd(II) from 0.2 M NTAamide/OC can be achieved.

### 3.2 Extraction of Cs

The most widely used extractant for Cs(I) is a crown ether. The majority of crown ethers exhibit less lipophilic properties, so these compounds require substitution with alkyl groups or phenyl groups in order to obtain high solubility in the organic phase. The most well-known functional groups for binding to crown ethers are cyclohexyl or phenyl groups [11,12]. DCH18C6 and DB18C6 are commercially available; however, these materials also have insufficient solubility in the organic phase. In this study, we used DtBuDB18C6 (Figure 1) as well as DCH18C6 for extracting Cs(I). This compound can also be purchased and is soluble in OC.
The results for extracting alkali and alkaline-earth metals using DtBuDB18C6 are shown in Figure 3. Figure 3(a) shows the dependence of $D(M)$ on the HNO$_3$ concentration, whereas Figure 3(b) shows the dependence of $D(M)$ on the extractant concentration. Here, M denotes alkali and alkaline-earth metals. All results indicate a gradual increase in $D(M)$ with the HNO$_3$ concentration (Figure 3(a)), suggesting the ion-pair extraction of metals using DtBuDB18C6 is accompanied by nitrate anions. From this figure, the trend in the extractability of metals by this crown ether is K(I) > Cs(I) > Na(I) > Rb(I) > Ba(II) > Li(I) > Sr(II), indicating better extraction of alkali metals than that of alkaline-earth metals. A study suggests that the phenyl groups in DtBuDB18C6 play a role in extracting Cs(I), due to a probable effect of electron density [12]. The relation between log $D$ and log [extractant] indicates a nearly linear relation with a slope of $1 - 2$ (Na: 1.1, K: 1.1, Rb: 1.2, Cs: 1.7), suggesting that a metal–ligand complex with a 1:1 or 1:2 molar ratio is formed in the organic phase.

As DCH18C6 can dissolve in OC, we also examined the extraction of alkali and alkaline-earth metals from HNO$_3$ into OC using DCH18C6. The results are shown in Figure 4. Figure 4(a) shows the dependence of $D(M)$ on the HNO$_3$ concentration, whereas Figure 4(b) shows the dependence of $D(M)$ on the extractant concentration. Similar to the results in Figure 3(a), $D(M)$ increases with the HNO$_3$ concentration. The trend in the extraction of metals is different, namely, K(I) ≥ Sr(II) > Ba(II) > Rb(I) > Na(I) > Li(I) ~ Cs(I), indicating that both alkali and alkaline-earth metals can be extracted by this crown ether [18] that provides very low-level extraction of Cs(I). Nearly straight lines can be seen in Figure 4(b), wherein the values of the slopes are 0.99 for K(I), 0.99 for Rb(I), 0.43 for Sr(II), and 0.28 for Ba(II). It seems that there is a low level of metal complex formation with DCH18C6.
A 90% level of extraction of Cs is difficult to attain, as seen from Figures 3 and 4, because these conditions result in a maximum value of $D(\text{Cs}) = 1$, namely, an extraction level of approximately 50%. To increase the extraction percentage of Cs(I), the volume ratio of the organic/aqueous phases was changed. The results for the extraction percentage of Cs(I) in this experiment are shown in Figure 5. Figure 5 also shows the changes in the extraction percentage of Cs(I) with different volume ratios of the two phases. Here, the experimental conditions used were 0.1 M DtBuDB18C6/OC and 3 M HNO₃. From Figure 5, a gradual increase in the extraction percentage of Cs(I) with an increase in the volume ratio of the organic phase can be observed, and an extraction level of 90% can be achieved if the volume of the organic phase is 10 times that of the aqueous phase. Changing the volume ratio means using different flow rates of the organic and aqueous phases during the operation of the separation process.
These conditions are easy to provide via mixer-settler conditions.

The back-extraction of Cs(I) is achieved using diluted HNO₃ because $D$(Cs) decrease with dilution of HNO₃ (Figure 3). Here, 0.01 M HNO₃ is employed for the back-extraction of Cs(I) from the organic phase of 0.1 M DtBuDB18C6/OC resulted in recovery of 91.2 %. This is a good recovery of Cs(I) from the organic phase.

3.3 Extraction of Zr

Two extractants were employed for the extraction of Zr(IV), namely, HDEHP and TODGA (Figure 1). TODGA and HDEHP can be dissolved in $n$-dodecane and OC, so both diluents were used for the organic phase. The results are shown in Figure 6. Figure 6(a) shows the dependence of $D$(Zr) on the HNO₃ concentration, whereas Figure 6(b) shows the dependence of $D$(Zr) on the extractant concentration.

![Figure 6](image-url)

Figure 6. Extraction of Zr using tetraoctyl diglycolamide (TODGA) and di-2-ethylhexyl phosphoric acid (HDEHP). (a) Dependence of $D$(Zr) on the HNO₃ concentration (100 mM TODGA, 1 mM – 100 mM HDEHP/OC or $n$-dodecane); (b) Dependence of $D$(Zr) on the extractant concentration (HNO₃: 3 M).

Figure 6(a) shows that a high value of $D$(Zr) can be observed even at high HNO₃ concentrations using these extractants, especially $D$(Zr) for HDEHP in $n$-dodecane shows an extremely high value, so 1 mM HDEHP concentration was employed in order to determine the acid concentration dependence on $D$. TODGA exhibits ion-pair extraction with an increase in the extraction percentage with HNO₃ concentration. Although HDEHP is an acidic extractant that should display a decrease in performance with an increase in the HNO₃ concentration, the $D$(Zr) for both diluents increased with acid concentration. From Figure 6(a), TODGA and HDEHP can quantitatively extract Zr(IV) into the organic phase. Figure 6(b) indicates a linear relation between log $D$ and log [extractant], and the values of the slope seem to be low in OC (TODGA/DD: 3.45, TODGA/ORC: 1.27, HDEHP/DD: 2.13, and HDEHP/ORC: 2.1). OC is a polar organic solvent, and a metal-ligand complex that is low in the order of formation is still stable in such a solvent,
leading to a low molar ratio of metal–ligand complexation [19]. A 90% degree of extraction of Zr(IV) can be easily achieved with TODGA and HDEHP. As shown in these figures, OC seems to exhibit a low value of $D(\text{Zr})$ compared with $n$-dodecane. When 0.1 M TODGA or HDEHP in OC and 2 – 3 M HNO$_3$ are used, a $D(\text{Zr})$ value greater than 10 is achieved.

The back-extraction of Zr was studied using oxalic acid [8] dissolved in water. Both organic phases (0.1 M TODGA/OC and 0.1 M HDEHP/OC) including Zr(IV) were used for the back-extraction tests and the results are shown in Table 1. From this table, the back-extraction efficiency of Zr(IV) increases with oxalic acid concentration, and over 90 % recovery can be reached by using 500 mM oxalic acid, which is in good agreement with the results from a previous paper [8].

Table 1. Back-extraction of Zr using oxalic acid from TODGA/OC and HDEHP/OC.

| [Oxalic acid]/ mM | back-extraction efficiency/ % |
|------------------|-------------------------------|
| 10               | 67                            |
| 50               | 78                            |
| 100              | 85                            |
| 500              | 98                            |

- Zr from 0.1 M TODGA/OC

| [Oxalic acid]/ mM | back-extraction efficiency/ % |
|------------------|-------------------------------|
| 10               | 64                            |
| 20               | 67                            |
| 50               | 71                            |
| 100              | 74                            |
| 200              | 77                            |
| 500              | 90                            |

- Zr from 0.1 M HDEHP/OC

3.3 Extraction of Se

Se may form oxyanions, of which the stable ions are SeO$_3^{2–}$ and SeO$_4^{2–}$. Previous studies suggest that these oxyanions can be extracted using N-donor extractants [5,6,16]. In this study, we used two types of phenylenediamines (PDA and DMePDA, Figure 1) as complexants to form an extractable piazselenol, and the results are shown in Figure 7. Figure 7(a) shows the dependence of $D(\text{Se})$ on the HNO$_3$ concentration, whereas Figure 7(b) shows the dependence of $D(\text{Se})$ on the extractant concentration. Here, Figure 7(a) shows the results for both Se(IV) as well as Se(VI). From Figure 7(a), Se(IV) can be extracted using PDA and DMePDA; however, Se(VI) is hardly extracted at all using these extractants. Therefore, only Se(IV) can form a piazselenol as the extractable complex [20]. For the extraction of Se(IV), a gradual decrease in $D(\text{Se})$ with an increase in the HNO$_3$ concentration is observed. Comparing both extractants, PDA provides a good extraction performance for Se(IV) over a range of HNO$_3$ concentrations; therefore, this extractant is more useful than DMePDA. Figure 7(b) shows the relation between log $D$ and log [extractant]. The values of the slopes (PDA/OC: 1.75, DMePDA/OC: 1.7) indicate that a Se–phenylenediamine complex with a ratio of 1:2 was formed. A 90% level of extraction of Se can be obtained using both PDA and DMePDA. In addition, PDA exhibits a value of $D(\text{Se})$ of greater than 10 over a wide range of HNO$_3$ concentrations, so PDA is more promising than DMePDA. The conditions for obtaining 90% extraction of Se(IV) comprise 0.1 M PDA/OC and a HNO$_3$ concentration of less than 2 M.

The back-extraction of Se was studied using two methods, one was to oxidize Se(IV) to Se(VI). The other method was to use concentrated acid as suggested by the results in Figure 7. The former method using an oxidizing agent was not successful. An aqueous phase containing 0.3 M Ce(IV) was tested for the
stripping of Se(IV) from the organic phase. The efficiency using 0.3 M Ce(IV) was under 40 %, which is not a satisfactory result. Therefore, concentrated acids, 8 M HNO₃, HCl, HClO₄ and H₂SO₄ were tested, instead of the oxidizing method. The efficiency of the back-extraction of Se is as follows, 8 M HNO₃: 37 %, 8 M HCl: 115 %, 8 M HClO₄: 109 % and 8 M H₂SO₄: over 100 %, so these conditions, except for HNO₃, are sufficient to strip Se(IV) quantitatively.

Figure 7. Extraction of Se using phenylenediamines (PDAs). (a) Dependence of $D(Se)$ on the HNO₃ concentration (0.01 – 0.1 M PDA or dimethyl PDA/OC); (b) Dependence of $D(Se)$ on the extractant concentration (HNO₃: 0.2–1 M).

4. Conclusion

From the present study, the conditions for attaining 90% extraction levels of Pd(II), Cs(I), Zr(IV), and Se(IV) have been studied. These comprise 0.2 M NTAamide/OC and an HNO₃ concentration of less than 2 M for Pd(II), 0.1 M DtBuDB18C₆/OC (with ten times the volume of the aqueous phase) and 3 M HNO₃ for Cs(I), 0.1 M TODGA or 0.1 M HDEHP/OC and an HNO₃ concentration of greater than 2 M for Zr(IV), and 0.1 M PDA/OC and an HNO₃ concentration of less than 2 M for Se(IV). The degree of recovery for Zr(IV) and Cs(I) increase with the HNO₃ concentration owing to ion-pair extraction, whereas those for Se(IV) and Pd(II) decrease with an increase in the HNO₃ concentration owing to the protonation of the extractants (NTAamide and PDA). The back-extraction methods for these metals were confirmed.

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References

1) J. Magill, G. Pfennig, R. Dreher, Z. Soti, Karlsruher nuklidkarte, 9 Auflage 2015, nucleonica.
2) R. Fujita, Available from: http://www.mext.go.jp/b_menu/shingi/gijyutu/gijyutu2/070/shiryo/__icsFiles/afieldfile/2015/11/09/1361284_1_2.pdf
3) L.H. Baetsle, Available from: http://users.ictp.it/~pub_off/lectures/lns012/Baetsle.pdf
4) R.G. Pearson, *J. Am. Chem. Soc.*, 85, 3533-3539 (1963).
5) Y. Sasaki, Y. Tsubata, Y. Kitatsuji, Y. Sugo, N. Shirasu, Y. Morita, T. Kimura, *Solvent Extr. Ion Exch.*, 31, 401-415 (2013).
6) Y. Sasaki, M. Saeki, Y. Sugo, Y. Ikeda, T. Kawasaki, T. Suzuki, A. Ohashi, *Solvent Extr. Res. Dev. Jpn.*, 22, 37-45 (2015).
7) Y. Sasaki, Z.-X. Zhu, Y. Sugo, T. Kimura, *J. Nucl. Sci. Technol.*, 44, 405-409 (2007).
8) Y. Morita, I. Yamagishi, Y. Tsubata, K. Matsumura, K. Sakurai, T. Iijima, *JAERI-Res.*, 2012-031, 2002.
9) A.G. Howard, M.R. Gray, A.J. Waters, A.R. Oromiehie, *Anal. Chim. Acta*, 118, 87-91 (1980).
10) K. Johansson, X.G. Luo, A. Olin, *Talanta*, 42, 1979-1987 (1995).
11) Y. Kikuchi, Y. Sakamoto, *Anal. Chim. Acta*, 403, 325-332 (2000).
12) Y. Takeda, *Bunseki Kagaku*, 51, 515-525 (2002) (in Japanese).
13) Y. Sasaki, Y. Sugo, S. Suzuki, S. Tachimori, *Solvent Extr. Ion Exch.*, 19, 91-103 (2001).
14) Y. Sasaki, S. Tachimori, *Solvent Extr. Ion Exch.*, 20, 21-34 (2002).
15) H.K. Manaktala, Available from: http://www.nrc.gov/docs/ML0336/ML033650021.pdf
16) Y. Sasaki, M. Ozawa, T. Kimura, K. Ohashi, *Solvent Extr. Ion Exch.*, 27, 378-394 (2009).
17) G.-H. Lee, K.-S. Chung, *Anal. Sci.*, 7, 1339-1342 (1991).
18) E. Makrlik, P. Vanura, P. Selucky, *J. Radioanal. Nucl. Chem.*, 281, 633-638 (2009).
19) Y. Sasaki, P. Rapold, M. Arisaka, M. Hirata, T. Kimura, C. Hill, G. Cote, *Solvent Extr. Ion Exch.*, 25, 187-204 (2007).
20) N.Z. Kenduzler, G. Somer, P. Zuman, *Talanta*, 69, 25-31 (2006).