Solvent Extraction of Selenium in Nitric Acid: Evaluation of Multiple Extractants and Proposal of a Novel Separation Process

K.T.M. Ito*[1, 2], T. Kawakami[1], C. Kato[1], S. Fukutani[3], T. Matsumura[4], T. Fujii[1]

1 Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

2 Geochemical Research Center, The University of Tokyo, Hongo 7-3-1, Bunkyo, Tokyo 113-0033, Japan

3 Institute for Integrated Radiation and Nuclear Science, Kyoto University, 2-1010 Asashiro Nishi, Kumatori, Sennan, Osaka 590-0494, Japan

4 Nuclear Science Research Institute, Japan Atomic Energy Agency, Shirakata 2-4, Tokai, Ibaraki 319-1195, Japan

***Corresponding author**: Tel: +81-3-5841-8376, e-mail address: kito@g.ecc.u-tokyo.ac.jp

Abstract

Solvent extraction behaviors of Se (VI) from nitric acid solutions were investigated with multiple extractants used for uranium, plutonium, minor actinides, and rare earth elements separation processes from high-level liquid waste. During the processes, Se remained in the residual aqueous solutions, as all extractants showed distribution ratios < 1. In contrast, Se showed distribution ratios > 1 with *o*-phenylenediamine in dilute nitric acid (< 2 M

HNO_3), octanol as the organic phase, and concentrated nitric acid (8 M HNO_3) for back extraction, suggesting a potential new single separation process and recovery of Se.

Keywords

Selenium-79, Selenium, Solvent extraction, nitric acid, octanol, o-phenylenediamine

Introduction

The treatment and disposal of radioactive waste is a major issue in countries dealing with nuclear power. Research on the separation and transmutation of long-lived nuclides contained in high-level liquid waste is progressing, which is expected to reduce the environmental impact of the geological disposal and to make some of the useful elements available as resources [1]. The SELECT process developed by Japan Atomic Energy Agency [2, 3] is a reprocessing process composed of separation of uranium and plutonium from spent nuclear fuel (Step 1), recovery of minor actinides (MAs) and rare earth elements (REs) from high-level radioactive waste (Step 2) and its separation (Step 3), and separation of americium from MAs (Step 4). *N,N,N′,N′*-tetradodecyl-diglycolamide (TDdDGA), *N,N,N′,N′,N″,N″*-hexaoctyl-nitrilotriacetamide (HONTA), and *N,N,N′,N″,N″*-tetra-2 ethylhexyl-damideamine (ADAAM) are novel extractants utilized in Step 2, 3, 4, respectively. The advantages of the SELECT process over other separation processes are the low cost of the used extractant and the possibility of complete incineration since it is phosphorus- and sulfur-free and composed of CHON.

Selenium is contained in spent fuel, and the radioisotope ^{79}Se is one of the long-lived fission products (LLFP) with a half-life of 327,000 years [4]. Due to its determinant of radiation exposure over 10^4–10^5 years, ^{79}Se presents a significant concern in long-term environmental burden and its recovery from spent fuel and transmutation to short-lived or nonradioactive nuclides are being emerged [5, 6]. Selenium is widely used as a chemical catalyst in the field of organic chemistry [7], indicating its potential as a valuable resource. Given this context, the isolation of Se from high-level radioactive waste is highly desirable.

However, while the separation of uranium and plutonium from spent fuel for reuse as energy has been widely investigated, the separation and transmutation of LLFP is not well known. For Se, there are few reports on its solvent extraction properties [8–10], and its distribution behavior is still unclear in nitric acid solutions.

In this study, we aimed to clarify the distribution behavior of Se from nitric acid solutions, and we investigated the distribution behavior of Se using TDdDGA, HONTA, ADAAM, which are used in the SELECT process. Additionally, we also investigated the Se extraction behaviors of existing extractants used in the separation process, tributyl phosphate (TBP) and n-Octyl(phenyl)*N,N'*-diisobutyl-carbaomoylmethyl-phosphineOxide (CMPO). TBP is used in PUREX (Plutonium/Uranium Redox EXtraction), a current reprocessing process, and CMPO is used in TRUEX (TRansUranium EXtraction) for the extraction of transuranium elements. In order to isolate Se, its solvent extraction properties are evaluated using phenylenediamine derivatives [*m*-phenylenediamine (N-PDA), *o*-phenylenediamine (*o*-PDA), and 4,5-dimethyl-1,2-phenylenediamine (DMePDA)], which are known to form extractable piazselenol [11, 12].

Experimental

We conducted two series of experiments: experiment A to evaluate the solvent extraction behaviors of Se with 5 extractants (TBP, CMPO, TDdDGA, HONTA, ADAAM), and experiment B to efficiently separate Se from high level radioactive waste. In experiment A, the distribution ratios of Se (D_{Se} = ($[Se(VI)]_{org}$)/($[Se(VI)]_{aq}$)) were investigated as a function of nitric acid concentration and extractant concentration. Nitric acid was used as the aqueous phase and *n*-dodecane was used as the organic phase. For the nitric acid concentration dependence, 1 mM Se solutions were prepared in 0.5, 1, 2, 3, 4, 5, 6, 7 mol dm^{-3} (M) HNO_3, and additionally, more dilute nitric acids (0.04, 0.05, 0.08, 0.1 M) are only prepared for HONTA. Furthermore, investigating D_{Se} in the coexistence of other elements, Eu was added to the aqueous phase at a concentration of 10 mM when using TDdDGA, where the nitric acid concentration was 1 and 3M. Extractants (0.05 M for HONTA, ADAAM, and 1 M for TBP, 0.2 M for CMPO in addition to 1 M for TBP, and

0.1 M for TDdDGA) dissolved in *n*-dodecane were used as extraction solvents. For TDdDGA, the precipitation is reduced by using octanol as an organic phase [13], hence the dependence of D_{Se} on nitric acid concentration were determined using two types of solutions: *n*-dodecane solution with 20% octanol and pure *n*-dodecane solution. We conducted D_{Se} analyses when the octanol concentration was varied from 0 to 20% at 5% intervals. Additionally, the dependence of D_{Se} on extractant concentration (0.005–0.8 M) was investigated to determine the stoichiometry of extractant and Se during the extraction.

In experiment B, D_{Se} for N-PDA, *o*-PDA, and DMePDA were investigated as a function of nitric acid concentration, organic phase, and nitric acid concentration in the back-extraction. The used nitric acid concentration is same as an experiment A, and three different organic solvents (*n*-dodecane, octanol, and nitrobenzene) were used as organic phases. Back-extraction was performed with nitric acid concentrations of 0.1 M and 8 M, respectively. Furthermore, as a simulation of high-level radioactive liquid waste, extraction experiments of Se was conducted under coexisting La, Dy, Gd, Pd, Sr, and Cs in nitric acid with the highest D_{Se} condition. The concentrations were 15 mM (Cs), 10mM (La, Pd), 2.5 mM (Sr), 1 mM (Se, Dy, Gd) in 0.5−7 M nitric acids, respectively. The separation factor (SF) for a metal and Se was calculated from D(Se)/D(Metal).

The aqueous and organic phases were set in vials at a volume ratio of 1:1, and the vials were stirred for 30 minutes at room temperature, 25 ℃. All the organic phases were pre-equilibrated with fresh nitric acids prior to the experiments. After the stirring, the two phases were separated by centrifugation at 2000 rpm for 2 minutes, and the Se in aqueous phases were extracted. The Se in organic phases were back-extracted with 0.01 or 0.1 M dilute nitric acid in experiment A and 0.1 or 8 M nitric acid in experiment B after 30 minutes stirring, centrifugation at 2000 rpm for 2 minutes. The Se concentrations in aqueous and organic phases were determined by ICP-AES (iCAP6300 Duo, Thermo Fisher Scientific) or ICP-MS (Plasma Quant MS, Analytik Jena) to determine the distribution ratios. The error is propagated to the D value from the three times measurement during the ICP-AES/MS analysis, with an analytical error of 2SD being ~ 20% of D. Detailed error

information is in a Supplementary Table.

Results and discussion

Experiment A: Selenium behavior in nitric acid solutions

Dependence on Nitric Acid Concentration

The calculated distribution ratios of Se, when HONTA, ADAAM, TBP, and TBP + CMPO were used as extractants, are shown in Table 1 and Fig. 1 as functions of [HNO_3] (M). D_{Se} is < 1 in any nitric acid concentration. Therefore, it is difficult to extract Se into the organic phase when using these extractants. D_{Se} systematically decreases with increasing nitric acid concentration. In the high nitric acid concentration, D_{Se} decreased with slope −1, whereas, in the low nitric acid concentration, D_{Se} tends to converge to a constant value, as suggested by the results of HONTA. A comparison of the extractants showed that ADAAM showed 3–5 times higher D_{Se} than HONTA, and TBP + CMPO showed 3 times higher D_{Se} than TBP.

Dependence on Octanol Concentration

D_{Se} using dodecane and octanol mixture was > 10 times higher than that of dodecane in Fig. 2a and the values ranged from 10^{-2} to 10^{-1}. D_{Se} increased gradually with increasing nitric acid concentration, that is different from D_{Se} when using other extractants. It is observed that D_{Se} also increases in proportion to the percentage octanol concentration in the organic phase in Fig. 2b, indicating that Se has solubility in octanol. Therefore, the higher D_{Se} observed with TDdDGA compared to other extractants when using dodecane and octanol indicates that in addition to the extractability of TDdDGA, the effect of dissolution of Se in octanol is taken into account.

Complexation of trivalent f-elements with selenate ions

In the TRUEX solvent system, pertechnetate ions are extracted as the counter-anions of uranium ([14] and references therein). Since Se in highly oxidic solutions forms

a selenate ion, SeO_4^{2-} [15], it may act as a counter-anion during the extraction of trivalent f-elements. The speciation diagram for trivalent f-element selenate was shown in Fig. 3 as a function of acidity. A cationic selenate exists in the high acidic region. Suppose the association reaction of the species with NO_3^- occurs, Se may distribute into the organic phase. As shown in Fig. 2, we demonstrated that the D_{Se} under the coexistence of Eu^{3+} are smaller than those without Eu^{3+}. This suggests that the extraction of Se is not enhanced via the associated reaction between f-element cations and selenate ions.

Dependence on Extractant Concentration

The slope analysis shows that there are two trends in the coordination number of extractants and Se in Fig. 4. For CMPO, the slope is 1, suggesting that the extractant and Se are extracted in one coordination as shown in Eq. (1), whereas for TBP and TDdDGA, the slope is 2, suggesting that these extractants and Se are extracted in two-coordination as shown in Eq. (2).

$$H_2SeO_4 + 1\,extractant \rightleftarrows H_2SeO_4 \cdot 1\,extractant \quad (1)$$

(extractant: CMPO)

$$H_2SeO_4 + 2\,extractant \rightleftarrows H_2SeO_4 \cdot 2\,extractant \quad (2)$$

(extractant: TBP, TDdDGA)

For HONTA and ADAAM, these extractants protonate in the high nitric acid region as shown in Eqs. (3) and (4).

$$extractant + HNO_3 \rightleftarrows extractant\,H^+ \cdot NO_3^- \quad (3)$$

$$H_2SeO_4 + extractant\,H^+ \cdot NO_3^- \rightleftarrows extractant\,H^+ \cdot HSeO_4^- + HNO_3 \quad (4)$$

(extractant: HONTA, ADAAM)

The trend observed in Fig. 1 for D_{Se} to decrease with increasing nitric acid concentration can be attributed to the decrease in coordination to the extractant with increasing nitric acid concentration, based on this equilibrium reaction equation. In conclusion, D_{Se} with TBP, TDdDGA, CMPO, HONTA, and ADAAM were less than 1, indicating that Se remains in the aqueous phase in the SELECT, TRUEX, and PUREX process.

Experiment B: Separation of Selenium from a high matrix liquid

Effects of organic phases

In this study, D_{Se} was determined using dodecane, octanol, and nitrobenzene as organic phases. For all extractants, D_{Se} is the highest when octanol was used as the organic phase. There are three possible reasons for this behavior. First, as mentioned in the previous section, octanol has the solubility of Se. Therefore, applying octanol as the organic phase, it is likely that the observed D_{Se} is based on the extractant plus the effect of dissolution in octanol. Second, extractants do not dissolve in low polarity organic solvents. As Fig. 4 shows, D_{Se} is expected to increase with increasing extractant concentration. In this experiment, the extractants did not dissolve in dodecane, which is a low polarity organic solvent, < 0.01 M, whereas 0.1 M in octanol. This difference in extractant concentration may have led to the increase in the distribution ratio. Third, to perform back-extraction is difficult when using dodecane and nitrobenzene. The lower mass balance suggests that the complexes of the extractant and Se remained in the organic phase and were not extracted into the aqueous phase. the distribution ratio was larger than that of dodecane, and back-extraction was also easier. For these reasons of the high D_{Se} and easy back extraction, octanol is desirable as the organic solvent to extract Se.

Separation of Selenium using octanol

Since the extraction efficiency of Se is the highest when octanol is used, in the following experiments, octanol is used for the organic phase and the extractants are dissolved in 0.1 M into octanol. All data are shown in Table 2 and Fig. 5 shows the

dependence of D_{Se} on nitric acid concentration when 8 M HNO_3 and 0.1 M HNO_3 were used for back-extraction. Two extractants, *o*-PDA and DMePDA, are described. The figure shows that using dilute nitric acid (< 2 M HNO_3) for the aqueous phase, *o*-PDA as an extractant, and concentrated nitric acid (8 M HNO_3) for back-extraction, $D_{Se} > 1$, indicating that Se was efficiently extracted into the organic phase. This can be due to the easy solubility of the extractant in nitric acid. In other words, it is considered that the extractant was easily extracted into the aqueous phase by using concentrated nitric acid in the back-extraction process, whereas it was partitioned into the organic phase when dilute nitric acid was used in the aqueous phase. The result show that Se can be extracted when *o*-PDA is used as an extractant, and dilute nitric acid is used in the forward extraction and concentrated nitric acid is used in the back extraction.

The distribution behavior and separation factor of Se were investigated in nitric acid solutions containing other matrix elements simulated a high-level radioactive liquid waste. Experiments were performed using *o*-PDA as extractant, octanol as organic phase, and 8 M HNO_3 for back-extraction. As Fig. 6 illustrates, D_{Se} exceeded 1 in the dilute nitric acid range, indicating Se was extracted into the organic phase regardless of the coexistence of other elements. The distribution ratio of lanthanum (D_{La}), used as a representative element for light lanthanides, was generally $D_{La} < 10^{-2}$. D_{La} were low for all nitric acid concentrations. The separation factor of lanthanum from Se was $SF_{Se/La} > 10$ and exceeded 1000 in the low nitric acid region. Dysprosium, which was used as a representative element of heavy lanthanides, also showed low distribution ratios in all nitric acid regions, similar to that of lanthanum. The separation factor of dysprosium from Se was $SF_{Se/Dy} > 100$. The distribution ratio of gadolinium (D_{Gd}), which is intermediate lanthanides, was $D_{Gd} < 10^{-2}$ in all regions, and D_{Gd} did not change much with changing the concentration of nitric acid. The separation factor with Se was found to be $SF_{Se/Gd} > 100$. These results indicate that the separation of Se and lanthanoids is feasible. The distribution ratio of palladium (D_{Pd}), which is classified as a platinum group element among fission products, was $10^{-3} < D_{Pd} < 1$. D_{Pd} and D_{Se} were almost same in the high nitric acid region, but in the low nitric acid region, the separation factor $SF_{Se/Pd} > 100$ was considered sufficient to separate Pd and Se.

The distribution ratio of strontium (D_{Sr}) and cesium (D_{Cs}), which is a common element in high-level radioactive liquid waste, have $10^{-4} < D_{Sr} < 10^{-2}$ and $10^{-3} < D_{Cs} < 10^{-2}$. The separation factor of strontium and cesium from Se was $SF_{Se/Sr} > 100$ and $SF_{Se/Cs} > 1000$ in the low nitric acid region, indicating that the two elements can be separated.The results of this experiment suggest the possibility of the separation of Se from lanthanides, fission products, and other elements contained in high-level radioactive waste. In particular, Se showed high separation factors to all other elements in the low nitric acid region. Therefore, it is desirable to perform the separation in the low nitric acid region for aqueous phase for the single separation of Se.

Conclusions

The distribution behaviors of Se using TBP, TDdDGA, CMPO, HONTA and ADAAM, which are new extractants used in the SELECT process, were investigated. The distribution ratios of Se show $D_{Se} < 1$ for all extractants and it indicates that Se remains in the residual aqueous solutions during the SELECT, TRUEX, and PUREX process. As a function of the concentrations of nitric acid, D_{Se} decreased with increasing of the nitric acid concentrations. This dependency was possibly caused by the protonation of extractants in concentrated nitric acids. The extractant concentration dependence indicates that Se is extracted as a 1:1 complex with CMPO, HONTA and ADAAM, and 1:2 complex with TBP and TDdDGA. It was also observed that D_{Se} is high when using dodecane/octanol mixtures instead of dodecane as an organic phase, and D_{Se} increased with the concentration of octanol, indicating that Se preferentially dissolved into octanol than dodecane.

Next, a new single separation method of Se was investigated using N-PDA, DMePDA, and *o*-PDA extractants with variable of nitric acid concentration, the type of organic phase, and the nitric acid concentration in the back-extraction. The highest D_{Se}, which is > 1, was obtained under the condition using *o*-PDA as the extractant, < 2 M dilute nitric acid for the aqueous phase, octanol for the organic phase, and 8 M concentrated nitric acid for the back extraction. On the other hand, in the experiments using N-PDA and DMePDA, all D_{Se} show < 1 and Se could not be separated into the organic phase. For all extractants, use of octanol

as the organic phase gave the ~ 10 times higher D_{Se} relative to the use of dodecane and nitrobenzene, which is due to the dissolution of Se in octanol. Under the highest D_{Se} condition, high separation factors of Se were also obtained, therefore, these results suggest that an extraction system using *o*-PDA, dilute nitric acid as aqueous phase and octanol as organic phase, and 8 M concentrated nitric acid for back-extraction is effective for the isolation of Se.

References

1. Salvatores M, Palmiotti G (2011) Radioactive waste partitioning and transmutation within advanced fuel cycles: Achievements and challenges. Prog Part Nucl Phys. 66(1): 144−166.

2. Ban Y, Suzuki H, Hotoku S, Kawasaki T, Sagawa H, Tsutsui N, Matsumura T (2019) Extraction of trivalent rare earths and minor actinides from nitric acid with *N, N, N', N'*-tetradodecyldiglycolamide (TDdDGA) by using mixer-settler extractors in a hot cell. Solvent Extr Ion Exc. 37(1): 27−37.

3. Ban Y, Suzuki H, Hotoku S, Tsutsui N, Tsubata Y, Matsumura T (2019) Minor actinides separation by *N, N, N', N', N'', N''*-hexaoctyl nitrilotriacetamide (HONTA) using mixer-settler extractors in a hot cell. Solvent Extr Ion Exc. 37(7): 489−499.

4. Jörg G, Bühnemann R, Hollas S, Kivel N, Kossert K, Van Winckel S, Gostomski CLV (2010) Preparation of radiochemically pure ^{79}Se and highly precise determination of its half-life. Appl Radiat Isotopes. 68(12): 2339−2351.

5. Wakabayashi T (2022) Concept of a small fast breeder reactor system capable of transmuting MA and LLFP. Nucl Eng Des. 390, 111700.

6. Sasaki Y, Morita K, Suzuki S, Shiwaku H, Ito K, Takahashi Y, Kaneko M (2017) Extraction and Separation of Se, Zr, Pd, and Cs Including Long-Lived Radionuclides. Solvent Extr. Res. Dev., Jpn. 24(2): 113−122.

7. Freudendahl DM, Santoro S, Shahzad SA, Santi C, Wirth T (2009) Green chemistry with selenium reagents: development of efficient catalytic reactions. Angew. Chem., Int. Ed. 48: 8409−8411.

8. Chowdhury MR, Sanyal S K (1993) Separation by solvent extraction of tellurium (IV) and selenium (IV) with tri-n butyl phosphate: some mechanistic aspects. Hydrometallurgy 32(2): 189−200.

9. Mahmoudiani F, Milani SA, Hormozi F, Yadollahi A (2022) Separation of selenium (IV) and tellurium (IV) from nitric acid medium by solvent extraction using CYANEX 301. J. Iran. Chem. Soc., 1−8.

10. Narita H, Maeda M, Tokoro C, Suzuki T, Tanaka M, Shiwaku H, Yaita T (2023) Extraction of Se (IV) and Se (VI) from aqueous HCl solution by using a diamide-containing tertiary amine. RSC Adv 13(25): 17001−17007.

11. Howard AG, Gray MR, Waters AJ, Oromiehie AR (1980) Determination of selenium (IV) by differential pulse polarography of 4-chloro-o-phenylenediamine piazselenol. Anal. Chim. Acta. 118(1): 87−91.

12. Johansson K, Luo X, Olin Å (1995) Rapid one-step derivatization of Se (VI) to a piazselenol for the spectrofluorimetric determination of selenium in biological material. Talanta. 42(12): 1979−1987.

13. Sasaki Y, Sugo Y, Morita K, Nash KL (2015) The effect of alkyl substituents on actinide and lanthanide extraction by diglycolamide compounds. Solvent Extr Ion Exc. 33(7): 625−641.

14. Takeuchi M, Tanaka S, Yamawaki M (1997) Temperature effect on technetium (VII) extraction by CMPO and TBP. J. Nucl. Mater. 247: 203−207.

15. Pourbaix M (1974) Atlas of electrochemical equilibria in aqueous solutions, 2nd edn. Natl Assn of Corrosion Engineers, Houston

16. Lide DR (2008) CRC Handbook of Chemistry and Physics, 89th edn. CRC Press, Boca Raton

17. Treinin A, Wilf J (1970) Electronic spectra of the oxyanions of selenium in solution. J. Phys. Chem. 74(23): 4131−4137.

18. Kolosov IV, Inanov-Emin BN, Korotaeva LG, Khayasi T (1967) Study of the complex formation of scandium with selenate and sulfate ions. Sov. Radiochem. 9: 457−461.

Figure Caption

Figure 1. Dependence of D_{Se} on the HNO_3 concentration

Different extractants, (a) ADAAM, HONTA, and (b) TBP + CMPO, CMPO, are shown (Initial Se: 1 mM, Extractants: (a) ADAAM/HONTA 0.05 M, (b) TBP 1 M, CMPO 0.2 M, Back-extraction 0.1 M HNO_3). As the nitric acid concentration decreases, the D_{Se} increases, whereas the values show <1 in any case. The curves in the figure represent exponential fittings to the obtained data points.

Figure 2. Dependence of D_{Se} on the (a) HNO_3 concentration, organic phase, coexistence of Eu, and (b) octanol concentration using TDdDGA

An increase of D_{Se} was observed when octanol was used as the organic phase. D_{Se} slightly decreases under coexistence of Eu. The curves in the figure represent exponential fittings to the obtained data points.

Figure 3. Speciation Diagram of Selenate Species

Acid dissociation constants have been reported in [16,17]. Formation constants for Sc^{3+} selenates in the literature [18] was adopted to estimate the fraction of trivalent f-elements with the selenate ion.

Figure 4. Dependence of D_{Se} on the extractant concentration

There were two groups with slope of 1 (CMPO, ADAAM, HONTA) and slope of 2 (TBP, TDdDGA). This result suggests that Se and extractant are extracted at a ratio of 1:1 and 1:2, respectively.

Figure 5. Dependence of D_{Se} on the HNO_3 concentration when using PDA derivatives

The highest D_{Se}, which is > 1, was obtained under the condition using *o*-PDA as the extractant, < 2 M dilute nitric acid for the aqueous phase, octanol for the organic phase, and 8 M concentrated nitric acid for the back extraction (BE).

Figure 6. Dependence of D_{Se} on nitric acid concentration in the presence of other matrix elements. In the low nitric acid concentration region, only Se exhibits a distribution ratio > 1, while the other elements show distribution ratios < 1. The curves in the figure represent exponential fittings to the obtained data points.