DECONTAMINATION STUDY OF SOME NOTICEABLE FISSION PRODUCTS IN THE ACTINIDES RECOVERY BY TRUEX PROCESS

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Abstract

Decontamination performance of some noticeable fission products from TRU elements by the TRUEX process was calculated with a multistage extraction simulation code. The batch extraction data of molybdenum, palladium, antimony, and cerium, which have been obtained in our related TRUEX studies, were provided for the calculation. For uranium, plutonium, and americium, literature data were used. A mixed solvent of 0.2 M OϕD[IB]CMPO and 1.0 M TBP in n-dodecane was employed as the TRUEX solvent. The feed and scrub solutions were nitric acid solutions, and the distribution of nitric acid between the organic and aqueous phases was calculated by modified SEPHIS code. The change in the decontamination performance by adding oxalic acid was also evaluated.

Introduction

For establishing actinide recovery by the transuranic elements extraction (TRUEX) process, the distribution behaviour in the TRUEX study has been studied mainly for actinides and lanthanides. However, the extraction behaviour of other FPs is also essential for achieving high decontamination of them from TRUs, because even minor FPs have large neutron capture cross sections and γ-ray emissions affecting the design of fuel fabrication process. In this context, we have studied the extraction behaviour of molybdenum, [1] palladium, [2] and some other FPs [3] by octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (OφD[IB]CMPO, or, simply, CMPO).

In the present study, we present the result of the assessment for the decontamination of FPs from TRUs in the TRUEX process. By using the experimentally determined distribution ratios of FPs as a function of acidity, decontamination performance of FPs from TRUs was calculated with multistage extraction simulation code.

Experimental

Short-lived FPs were produced by neutron irradiation of natural uranium. [3] About 2 mg UO_2 sealed in a quartz tube was irradiated for 20 minutes in a pneumatic irradiation system with a thermal neutron flux $\phi_{th} = 2.75 \times 10^{13}$ n/cm^2 sec in the Kyoto University Research Reactor, Japan. After irradiation, the irradiated UO_2 was dissolved in 7 mol dm^{-3} (M) HNO_3. Insoluble residues were removed by a filter having 0.45 μm pore size. In this paper, the data of ^{143}Ce were provided for the calculation. Radioactive tracers ^{99}Mo, ^{109}Pd, and ^{122}Sb were produced by neutron irradiation of Mo, Pd, and Sb metals. [1-3] The irradiated metals were dissolved in HNO_3. The filtered solution or the supernatant after centrifugation was used for preparing aqueous phase. Portions of these solutions were used and nitric acid solutions of various concentrations were prepared. Nitric acid solutions with 0.023 M $H_2C_2O_4$ were also prepared.

The mixture of 0.2 M OφD[IB]CMPO (Elf Atochem North America, Inc., 95% purity) and 1.0 M TBP diluted with *n*-dodecane was prepared as the TRUEX solvent. The TRUEX solvent was scrubbed twice with 0.5 M Na_2CO_3 solution to remove degradation products of CMPO. The TRUEX solvents were pre-equilibrated with fresh nitric acid solutions

Fifteen mL each of the aqueous solution and the organic solution were contacted by magnetic stirring in a glass centrifuge tube for 20 minutes at room temperature. After separating the two phases by centrifugation, weighed portions of both phases were taken for γ-spectrometric analysis to determine the distribution ratios (*D*). The concentrations of hydrogen ion, [H$^+$], in the equilibrated aqueous phases were determined by a titration using NaOH. All quantifications of the aqueous and organic solutions were performed gravimetrically to avoid the large errors associated with volumetric treatment. The gravimetric concentrations were converted to volumetric concentrations using the density of the solutions. The chemical reagents used were all of analytical grade. The detailed procedure of our TRUEX study can be seen elsewhere. [1-3]

Process flow

Composition of nuclides in the typical PWR spent fuel burned up to 44 000 MWD/t and cooled for 5 years was estimated by the calculation with ORIGEN2. By using this composition, an extraction feed for PUREX HA process containing 250 g/L uranium was set. The recovery of uranium and

plutonium in the PUREX process was set as 99.9%, and volumetric dilution rate through the process was set as 22/25. The composition of the HA raffinate is shown in Table 1. The nitric acid solution containing U, Pu, Am, Ce, Mo, Pd, and Sb with this composition was served as the feed solution of the TRUEX process for the calculation.

Table 1. **Components in HA raffinate**

Nuclides	Concentration g/L
U	0.22
Pu	0.0024
Am	0.13
Ce	0.74
Mo	1.0
Pd	0.44
Sb	0.0066

The process flow diagram of the TRUEX process is shown in Figure 1. The organic solution was 0.2 M CMPO and 1.0 M TBP in *n*-dodecane. The feed solution was the HA raffinate given in Table 1 whose nitric acid concentration was 0.5, 0.8, 1.0, 2.0, 3.0, 4.0, or 5.0 M. The scrub solution was 0.05 M HNO_3.

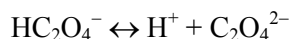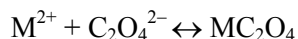Figure 1. **Flowsheet of TRUEX extraction-scrub bank**
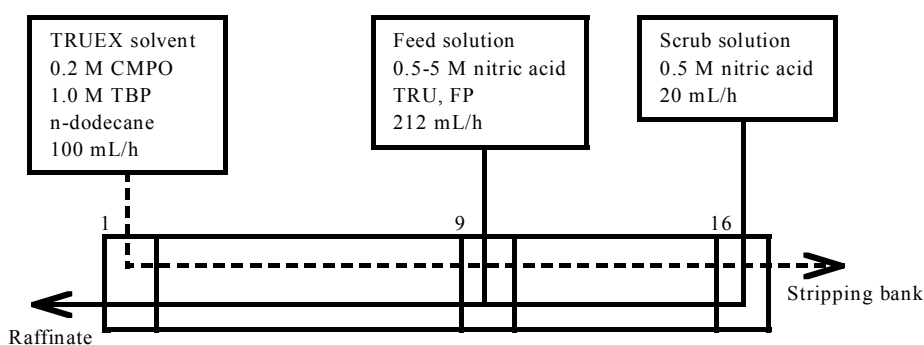
Results and discussion

The experimentally obtained distribution ratios of [99]Mo, [1] [109]Pd, [2] [122]Sb, [3] and [143]Ce [3] are shown in Figure 2. The *log D* values are shown as functions of *log* [HNO_3]. Since the D_{ce} values under the TRUEX condition are close to the reported D_{Am} values, [4,5] the separation of radionuclides from Ce can be regarded as those from Am. As shown in Figure 2, Sb can be well separated from Ce. For Pd, the difference between D_{Pd} and D_{Ce} increases with acidity. Though the separation factor of D_{Ce}/D_{Pd} is large in the high acidic region, this is not preferable for establishing the TRUEX system. It is difficult to separate Mo from Ce (Am) at any acidic conditions.

Addition of oxalic acid is effective to decrease *D* of tetravalent cations as zirconium. In the TRUEX studies on Mo [1] and Pd, [2] the *D* values have also been obtained with a mixture of ca. 0.1 M HNO_3 and 0.023 M $H_2C_2O_4$, which are shown in Figure 2 as open marks. From these values,

D_{Mo} and D_{Pd} with 0.023 M $H_2C_2O_4$ were estimated in 0.1~2.0 M HNO_3 range, which are shown in Figure 2 as dotted lines. In the estimation, following reactions were considered:

$$M^{2+} + 2NO_3^- + nCMPO \leftrightarrow M(NO_3)_2 \bullet nCMPO$$
$$M^{2+} + C_2O_4^{2-} \leftrightarrow MC_2O_4$$
$$H_2C_2O_4 \leftrightarrow H^+ + HC_2O_4^-$$
$$HC_2O_4^- \leftrightarrow H^+ + C_2O_4^{2-}$$

where M^{2+} means MO_2^{2+} or Pd^{2+}. The literature values [6] of the dissociation constants of oxalic acid were used for the calculation.

Figure 2. **Distribution ratios of Ce, Mo, Pd, and Sb**
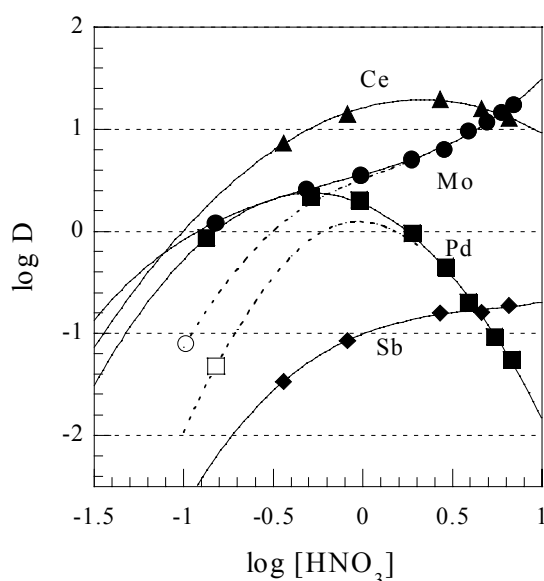
The distribution of HNO_3 in each stage of stage number 1 to 16 was evaluated by modified SEPHIS code. [7,8] From the obtained $[HNO_3]_{aq}$, the D values of Ce, Mo, Pd, and Sb in each stage were estimated by using curves shown in Figure 2. These D values were provided for the calculation by a multistage extraction simulation code, and the concentration profile in the extraction-scrubbing bank was obtained.

In the same manner, the concentration profile for U, Pu, and Am was also determined by using a reported figure of *log D vs.* $[HNO_3]$ (0.20 M OϕD[IB]CMPO and 1.2 M TBP in *n*-dodecane). [4] The typical concentration profile for 3.0 M HNO_3 feed solution system is shown in Figure 3. For other acidity conditions, the obtained concentration profiles were similar to the case of 3.0 M HNO_3 system. As shown in Figure 3, the recovery of U, Pu, and Am is well attained, but the decontamination performance of Ce, Mo, and Pd from Am is poor. Antimony can be separated from Am in any acidic conditions. The decontamination factor ($[Sb]/[Am])_{feed}/([Sb]/[Am])_{product}$ at 3 M HNO_3 was about 500.

To improve the decontamination factor of Mo and Pd, the addition of $H_2C_2O_4$ is considered to be effective. The concentration profiles for 0.5 and 1.0 M HNO_3 feed solutions are shown in Figure 4. In the case of the presence of oxalic acid, 0.023 M $H_2C_2O_3$ was added to the feed solution and the scrub solution. As shown in Figure 4, it can be seen that the effect of oxalic acid for Mo and Pd decontamination is not large.

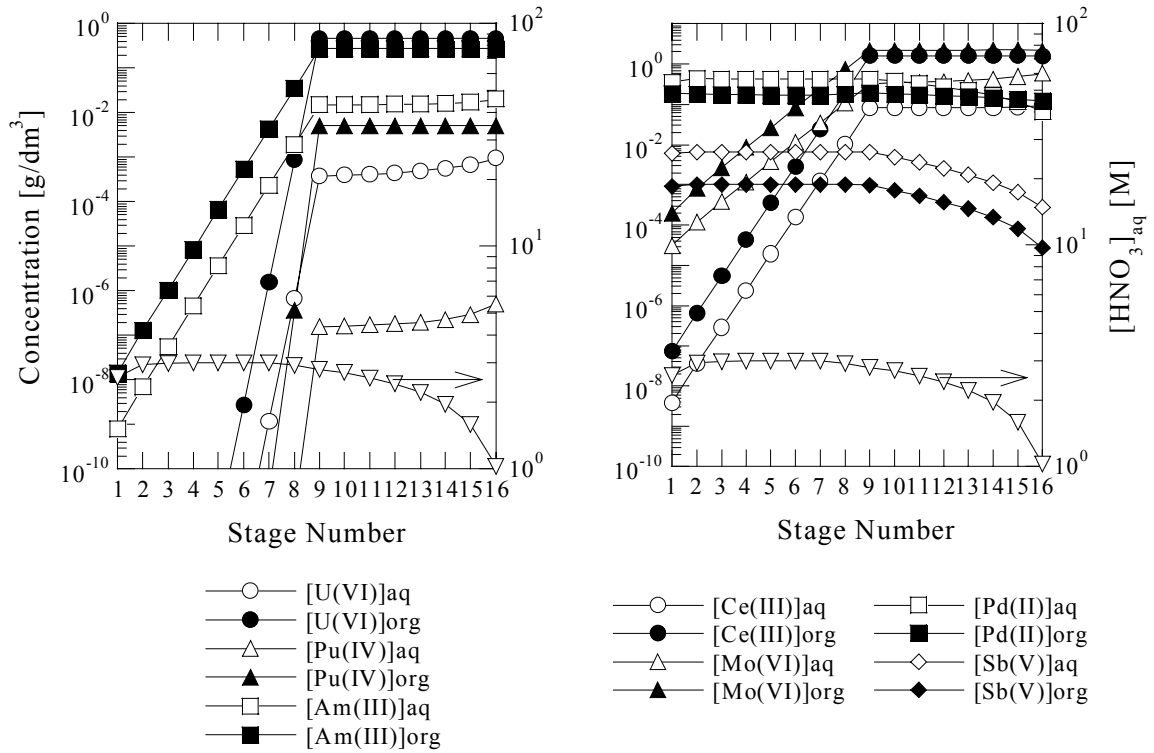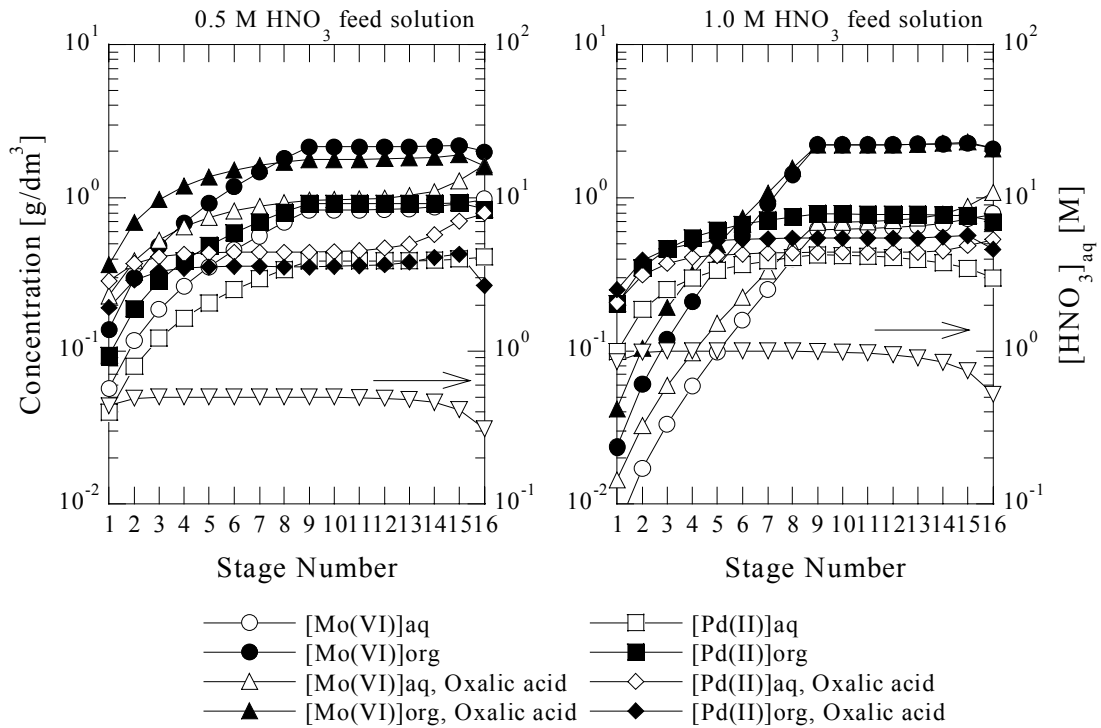Figure 3. **Concentration profile for actinides and FPs (3 M HNO$_3$ feed)**

Figure 4. **Effect of oxalic acid for Mo and Pd decontamination**

Decontamination factors are shown in Figure 5. In the previous study [9] on the batch experiments, we have suggested that the system at 1~3 M HNO_3 region with oxalic acid is preferable for establishing the TRUEX process. The poor decontamination performance for Mo has also been pointed out. [9] From this study on the multistage extraction simulation, the effective decontamination of Sb, the increase of the Pd decontamination performance with acidity, and the low decontamination factor of Mo were confirmed. The use of oxalic acid at low acidic region is not effective for the Mo and Pd decontamination.

Figure 5. **Decontamination factors**
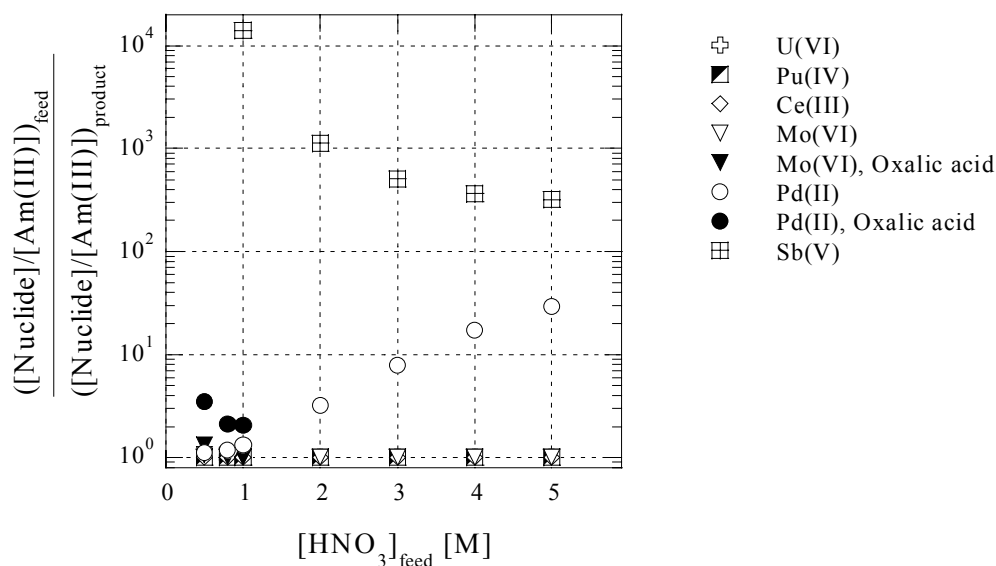
In this study, the effect of oxalic acid at 0.1~2.0 M HNO_3 was estimated by extrapolating the experimentally obtained D value at *ca*. 0.1 M HNO_3 on above described ideal complexation and dissociation reactions. In this extrapolation, the variations of activity coefficients of related species were not taken into account. Hence, the effects may have been underestimated at 1~2 M HNO_3 region as shown in Figure 2. Experimentally, D_{Mo} under coexistence of $H_2C_2O_4$ at 3 M HNO_3 showed lower value than that estimated in this study. [1,9] However, because the reproducibility of D_{Mo} was low, [1,3,9] we had to adapt a conservative estimation. The effect of oxalic acid in the TRUEX extraction at 1~3 M HNO_3 region for Mo, Pd, and other noticeable FPs should be studied. By using experimental determined dependence of D's on $[HNO_3]$ under coexistence of $H_2C_2O_4$, the decontamination performance of these FPs would be improved. The improvement of the decontamination performance of Mo and Pd in the TRUEX process is strongly suggested.

Conclusions

Decontamination performance of some noticeable fission products from TRU elements by the TRUEX process was calculated with a multistage extraction simulation code. Antimony was well separated from americium. However, molybdenum and palladium could not be sufficiently separated from americium. Since the D_{Mo} and D_{Pd} values with oxalic acid at 0.1~2.0 M HNO_3 were extrapolated from the low acidic region, the effect of oxalic acid at high acid region may have been estimated to be small. By using experimental D's with oxalic acid, the decontamination performance of Mo and Pd would be possibly improved. The improvement of the TRUEX flowsheet to obtain higher performance for Mo and Pd decontamination is needed.

Acknowledgement

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