Numerical simulation for concentration profiles of americium and lanthanides in the CMPO TBP solvent extraction system

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A numerical simulation code is developed to predict the extraction behavior of americium and lanthanides in the TRUEX (**TR**ans**U**ranium **EX**traction) process. This code gives the concentration profiles of the components at steady state. The stage efficiency is included in this code as a parameter in order to simulate the extraction behavior of the components accurately. Concentration profiles of americium and typical lanthanides in some counter current experiments are calculated by means of the present code. The calculated concentration profiles are compared with the experimental results. The efficiency value for the mixer-settlers, which gives good agreement between the calculated and the experimental profiles, is evaluated.
Keywords: numerical simulation code, TRUEX process, americium, lanthanides, stage efficiency, mixer-settler

1. Introduction

Special attention has been paid to the separation and the recovery of TRU (**TR**ans**U**ranium) elements from HLLW (**H**igh **L**evel **L**iquid **W**aste) of the Purex (**P**lutonium **U**ranium **R**eduction **EX**traction) process. The HLLW is vitrified after recovery of uranium and plutonium by the Purex process. It is desirable to recover the TRU elements from the HLLW for transmutation to reduce the radiotoxicity of the vitrified wastes.

JNC (**J**apan **N**uclear **C**ycle Development Institute) started various studies on the TRUEX (**TR**ans**U**ranium **EX**traction) process[1,2], in order to separate the TRU elements from HLLW[3]. Various experiments on the TRUEX have been performed to verify the process applicability[3]. However, optimization of the process flow sheet was difficult because of the limited experimental conditions. Numerical simulation is useful for determining the optimum conditions for experiments and designing the extraction process reasonably by predicting extraction behavior at various process conditions. A numerical simulation code of the extraction behavior in the TRUEX process was developed in the previous paper[4]. This code was able to calculate the concentration profiles of americium and nitric acid. In the TRUEX process, the extraction of lanthanides(III) are considered because the extraction behavior of them is similar to that of americium.

The purpose of this study is to modify the numerical simulation code for the calculations of the concentration profiles of lanthanides. In this study, cerium and europium are selected as typical lanthanides. The calculated concentration profiles of Ce(III) and Eu(III) are compared with the experimental results and the applicability of the developed code is discussed. In order to minimize the difference between the calculated and the experimental concentration profiles of Ce(III) and Eu(III), the stage efficiency is numerically determined.

2. Numerical simulation

2.1. Outline of the numerical simulation code

Equations of material balance for a stage in the series of mixer-settlers and the distribution ratio are expressed as follows:

$$Q_{aq,in} C_{aq,in,j} + Q_{org,in} C_{org,in,j} + Q_{aq,f} C_{aq,f,j} + Q_{org,f} C_{org,f,j}$$
$$= Q_{aq,out} C_{aq,out,j} + Q_{org,out} C_{org,out,j} \qquad (1)$$

and

$$D_j = C_{org,out,j} / C_{aq,out,j}, \qquad (2)$$

where Q, C, D, f, and j denote flow rates [L/hr], concentrations [mol/L], distribution ratios [-], feed, and component, respectively. In the developed code, the followings are generally neglected because they are small in bench-scale counter current extractors: i) the variation in the volumetric flow rate by mass transfer; ii) the amount of the entrainment. The concentration in aqueous outlet stream, from Eqs. (1) and (2), can be calculated by

$$C_{aqQutj} = (Q_{aq,in}C_{aq,in,j} + Q_{org,in}C_{org,in,j} + Q_{aq,f}C_{aq,f,j} + Q_{org,f}C_{org,f,j})$$
$$/ (Q_{aq,out} + Q_{org,out}D_j) \qquad (3)$$

In this equation, the distribution ratio of nitric acid, D_{HNO_3} is calculated by

$$D_{HNO_3} = [\overline{HNO_3}]_t / [HNO_3], \qquad (4)$$

where $[\overline{HNO_3}]_t$ is the total concentration of nitric acid extracted by CMPO and by TBP. The distribution ratio of americium is calculated by

$$D_{Am} = \frac{[\overline{CMPO}]_{free}^3 \{NO_3^-\}^3}{\left(1 + \beta \frac{\{NO_3^-\}}{\{H_2O\}}\right)\{H_2O\}^9} \times \sum_{i=0}^{4} K_i \{H^+\}^i \{NO_3^-\}^i \qquad (5)$$

where $[\overline{CMPO}]_{free}$ refers to the concentration of free CMPO [mol/L] and the braces denote the activity [mol/L] for each component. The K_0 to K_4 (25 ,i=0 [(mol/L)$^{-6}$], 1 [(mol/L)$^{-4}$], 2 [(mol/L)$^{-2}$], 3 [-], 4 [(mol/L)^2]) in these equations are determined by the least-squares method using experimental results of the americium extraction in CMPO/TBP/n-dodecane system[4] and listed in Table 1. The activity for each component in Eq. (5) is calculated by the equation derived by
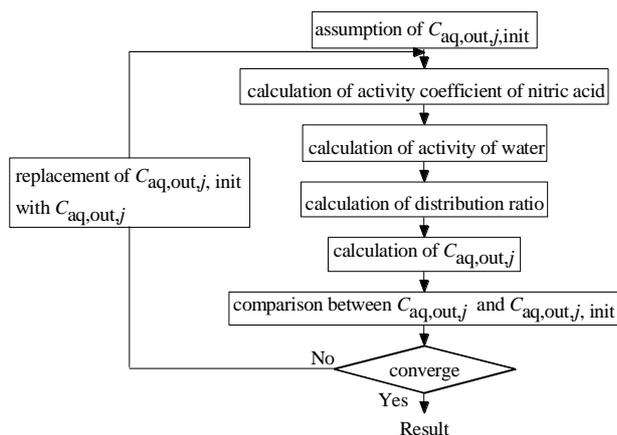
the experimental data[4].

The stage efficiency E [-] is defined as

$$E = \frac{C_{aq, in, j, t} - C^*_{aq, out, j}}{C_{aq, in, j, t} - C_{aq, out, j}}, \qquad (6)$$

where $C_{aq,out,j}$ is the concentration in the aqueous outlet stream at $E = 1$ and $C^*_{aq,out, j}$ is the actual concentration in the same stream. In this equation, $C_{aq,in,j,t}$ is expressed as
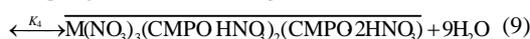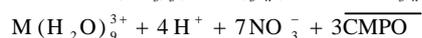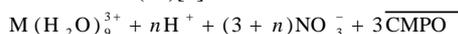
$$C_{aq,in, j, t} = \frac{Q_{aq,in} C_{aq,in, j} + Q_{aq,f} C_{aq,f, j}}{Q_{aq,in} + Q_{aq,f}}. \qquad (7)$$

The actual concentration is calculated by using Eqs. (3) through (7).

The procedures of this calculation are shown in Fig. 1[4]. In this calculation an initial concentration was given for each component in the aqueous outlet stream. Then, the distribution ratio for each component in each stage was calculated using the initial value in Eqs. (4) or (5). Next, by using the calculated distribution ratio, Eqs. (3), (6), and (7), a concentration value for each component in the stream was calculated. The calculated concentration was then compared with the initial concentration. An iterating calculation was carried out until the two values of concentrations became nearly equal by replacing the initial concentration by the calculation result. The concentration in each stage, at steady state, was obtained when the error between the calculated and the initial concentrations became 0.1% or less.

2.2. Modification of the numerical simulation code

In the previous paper[4], we showed the concentration profiles of americium and nitric acid could be calculated by our simulation code. The reactions for cerium and europium distribution ratio calculation were added to the simulation code in order to calculate concentration profiles of cerium and europium. In the modified code, stoichiometric relations for the extraction of lanthanides(III) in CMPO/TBP-HNO$_3$ system are assumed to be identical to those of americium(III)[5] as follows:

$$M(H_2O)_9^{3+} + nH^+ + (3 + n)NO_3^- + 3\overline{CMPO}$$

$$\xleftarrow{K_n} \overline{M(NO_3)_3(CMPO)_{3-n}(CMPO \cdot HNO_3)_n} + 9H_2O, \quad (8)$$

$$M(H_2O)_9^{3+} + 4H^+ + 7NO_3^- + 3\overline{CMPO}$$

$$\xleftarrow{K_4} \overline{M(NO_3)_3(CMPO \cdot HNO_3)_2(CMPO \cdot 2HNO_3)} + 9H_2O \quad (9)$$

where M and n represent the trivalent lanthanides such as europium and the numbers of hydrogen ions (0, 1, 2 and 3). K_i are the equilibrium constants of each extraction. Because the extraction equilibria of lanthanides(III) are the same as those of americium, the distribution ratios of lanthanides(III) are obtained by Eq. (5) that replaced the equilibrium constants of americium by those of lanthanides(III). The equilibrium constants for cerium and europium[6] involved in this code are listed in Table 1 together with those for americium[4].

In the code, the complexation of trivalent americium and lanthanides by a nitrate ion in the aqueous phase is also taken into account. This reaction proceeds as follows[8]:

$$M(H_2O)_9^{3+} + NO_3^- \xleftarrow{\beta_M} M(H_2O)_8(NO_3)^{2+} + H_2O \quad (10)$$

where β_M is the stability constant of $M(H_2O)_8(NO_3)^{2+}$. The β_{Am} value is 28.8 [-] that is determined by $< 0.5M$ HNO$_3$ and β_{Ln} (Ln : lanthanides) is 40.0 [-] determined by 0.1 and 0.2M HNO$_3$[6,7]. Although the complexation reactions with more than one nitrate ion also occur, they are not significant for the calculations of the distribution ratios[7]. Since the equations which give the distribution ratio of lanthanides are also derived from Eq. (8) through (10), they are identical to those of americium[6].

3. Results and discussion

A flow sheet of the counter current experiment in the extraction and scrub section of the TRUEX process was shown in Fig. 2. This experiment was carried out at room temperature with the series of mixer-settlers, totaling 19 stages. Feed composition is listed in Table 2[3]. The mixture of 0.2MCMPO/1.0MTBP/n-dodecane was used as a solvent[3].

Table 1 The equilibrium constants of the extraction[4]

Constants	Values		
	Am[4]	Ce[6]	Eu[6]
K_0 [(mol/L)$^{-6}$]	8.3×10^5	1.0×10^6	8×10^5
K_1 [(mol/L)$^{-4}$]	1.5×10^6	6.5×10^6	4×10^6
K_2 [(mol/L)$^{-2}$]	2.2×10^5	2.5×10^5	2×10^5
K_3 [-]	7.2×10^3	7.3×10^3	7×10^3
K_4 [(mol/L)^2])	62	32	80
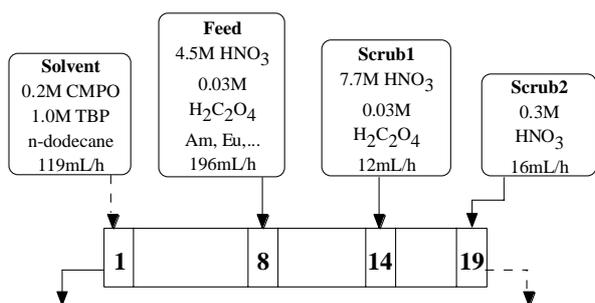
Fig. 2 Experimental flow sheet of Run A[3]

In this experiment, oxalic acid was added in the feed and scrub1 solution, in order to prevent extraction of FPs (**F**ission **P**roduct**s**) in the co-extracting process. The distribution ratios of americium and lanthanides decrease with increasing the concentration of oxalic acid. However, the effect of oxalic acid on the distribution ratios was neglected because the concentration of oxalic acid used in the experiment was 0.03 mol/L, such a low concentration of oxalic acid had little influence on the distribution ratios[2].

The comparisons of the experimental and the calculated concentration profiles of cerium-144 and europium-154 were shown in Fig. 3 and 4, respectively. In these figures, the *E* was varied at the range of 0.8 to 1. These figures indicate that the calculated profiles are in good agreement with the experimental results when *E* is equal to 0.9. This value is identical to that for americium[4] and for the mixer-settler

Table 2 The composition of the feed solution for the counter current experiment [3]

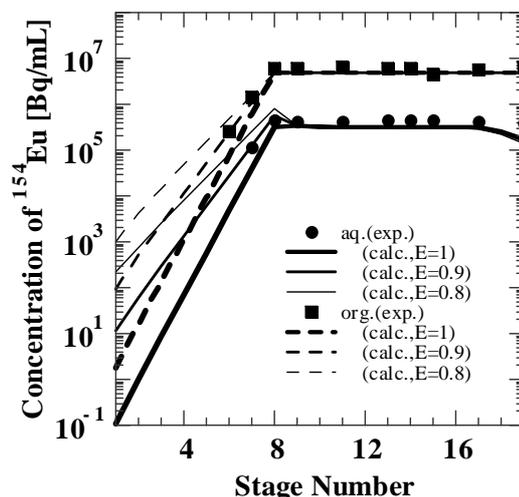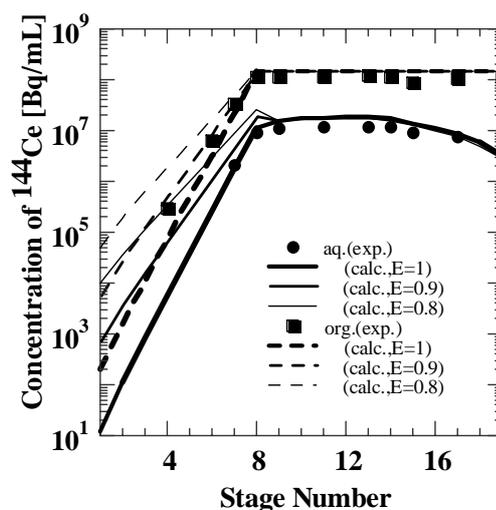| Element	Concentration [mol/L]
U	7.1×10^{-4}
Np	4.2×10^{-5}
Pu	6.7×10^{-5}
Am	5.0×10^{-4}
Cm	1.2×10^{-6}
Y	3.9×10^{-4}
La	6.1×10^{-4}
Ce	1.0×10^{-3}
Nd	1.7×10^{-3}
Sm	4.5×10^{-4}
Eu	6.0×10^{-5}
Cs	2.3×10^{-3}
Sr	5.1×10^{-4}
Zr	$< 3.3 \times 10^{-5}$
Mo	1.2×10^{-3}
Tc	2.1×10^{-4}
Ru	3.1×10^{-3}
Rh	2.5×10^{-4}
Pd	$< 1.9 \times 10^{-5}$

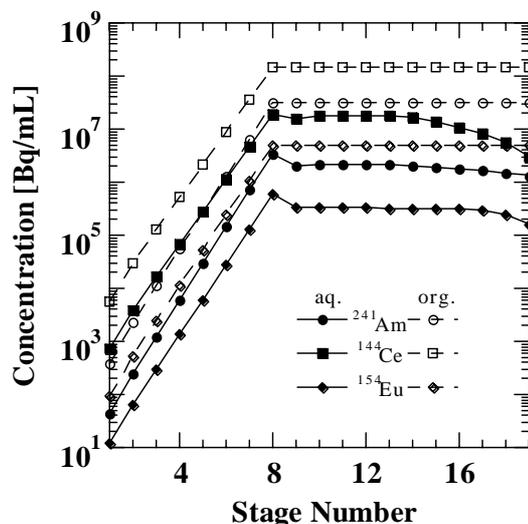**Fig.4 Concentration profiles of ^{154}Eu in Run A**

Fig.5 Comparison between concentration profiles of il ; **americium and lanthanides in Run A(E=0.9)[4]**

shown in the literature[8]. This result suggests that the extraction equilibria of lanthanides as well as americium are not completely achieved in the counter current experiments with the multicomponent system because of the short average residence time of the solution in mixer-settlers of the extraction section. However, about 100% of cerium and europium are extracted by the solvent and are transferred to the next section, namely the strip section. The trends of cerium and europium concentration profiles are the same as those of americium, which was shown in Fig. 5. The concentration profiles of not only americium but also lanthanides (cerium and europium) can be calculated by using the stage efficiency of 0.9.

4. Conclusion

The concentration profiles of americium and typical lanthanides, cerium and europium, were calculated for the extraction and scrub sections of the TRUEX process. The distribution ratios of those elements were considered in the simulation code in order to calculate their concentration profiles. Such modification had little influence on the calculated concentration profiles of americium. The stage efficiency value of 0.9 gives the best agreement between the calculated and the experimental concentration profiles of the lanthanides.

References

[1] Vandegrift, G. F., Leonard, R. A., Steindler, M. J., Horwitz, E. P.: Transuranic decontamination of nitric acid solutions by the TRUEX solvent extraction process - preliminary development studies, *ANL*-84/45 (1984).

[2] Horwits, E. P., Kalina, D. G., Diamond, H., Vandegrift, G. F., Shultz, W. W.: The TRUEX process – A process for the extraction of the transuranic elements from nitric acid wastes utilizing modified PUREX solvent. *Solvent Extr. Ion Exch.* **3**(1&2), 75-109 (1985).

[3] Ozawa, M., Nemoto, S., Togashi, A., Kawata, T., Onishi, K.: Partitioning of actinides and fission products in highly-active raffinate from PUREX process by mixer-settlers. *Solvent Extr. Ion Exch.* **10**(5), 829-846 (1992).

[4] Takanashi, M., Koma, Y., Koyama, T., Funasaka, H.: Numerical simulation of extraction behavior of americium and nitric acid in the TRUEX process. *J. Nucl. Sci. Technol.*, (in Press).

[5] Chaiko, D. J., Freadrickson, D. R., Reichley-Yinger, L., Vandegrift, G. F.: Thermodynamic modeling of chemical equilibria in metal extraction. *Sep. Sci. Technol.*, **23**(12&13),1435-1451 (1988).

[6] Steindler, M. J., Harmon, J. E.: Nuclear technology programs semiannual progress report April-September 1988, *ANL*-90/15, 86-89 (1990).

[7] Steindler, M. J., Harmon, J. E.: Nuclear technology programs semiannual progress report October 1987-March 1988, *ANL*-89/29, 60-64 (1990).

[8] Regalbuto, M. C., Aase, S., Vandegrift, G. F.: Validation of the generic TRUEX model using data from TRUEX demonstrations with actual high-level waste, *ANL*-95/21 (1995).