

Lawrence Berkeley National Laboratory

Chemical Sciences

Title

Bench-Scale Test for Separation of Sr² and Nd³ from HLLW Using TiBOGA

Permalink

<https://escholarship.org/uc/item/7kw8h12q>

Journal

Separation Science and Technology

Author

Tian, Guoxin

Publication Date

2012-08-02

DOI

10.1080/01496395.2012.697515

Bench-Scale Test for Separation of Sr^{2+} and Nd^{3+} from HLLW Using TiBOGA

Guoxin Tian*, Ping Zhang[†], Yifang Shen[†], Jianchen Wang[†], Linfeng Rao

[†]*Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 102201, China*

**Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.*

A bench-scale test for the separation of strontium and trivalent lanthanides/actinides, using Nd^{3+} as a surrogate, from a simulated acidic high level liquid waste (HLLW) has been performed with a set of 10-mm centrifugal contactors using N,N,N',N'-tetra-iso-butyl-3-oxa-glutaramide (TiBOGA) as extractant. The test shows that Sr^{2+} and Nd^{3+} can be co-extracted from the HLLW and then separated from each other by step stripping. The results indicate that 99.99% of Sr^{2+} and Nd^{3+} can be removed from the HLLW, and less than 0.01% of Nd^{3+} remains in Sr^{2+} product stream and 0.1% of Sr^{2+} in Nd^{3+} stream. In HNO_3 solutions – 0.2 M TiBOGA in 40% octanol/kerosene system the mass transfer stage efficiencies of HNO_3 and Sr^{2+} have also been studied on a single-stage 10-mm centrifugal contactor.

INTRODUCTION

A huge amount of high level nuclear waste (HLW) has been produced from weapon programs and civilian power plants in the world. How to safely dispose of the high level nuclear waste has been a great public concern and a challenge for nuclear industry. Partitioning and Transmutation (P&T) strategy is an option for the disposal of HLW. In P&T strategy, the small amount of radioactive nuclides could be separated from the bulky amount of non-radioactive materials, and then the small volume of radioactive nuclides could either be transmuted into non-radioactive and short-lived nuclides, or could be stored safely and economically because of the dramatically reduced volume.

A type of tetraalkyl-glutaramide extractants has been developed for the separation of actinides and some fission products from the high level liquid waste (HLLW) generated from the spent nuclear fuel reprocessing.(1-10) Our previous studies showed that N,N,N',N'-tetra-iso-butyl-3-oxa-glutaramide (TiBOGA) is able to extract not only actinide ions including An^{3+} , An^{4+} , AnO_2^+ , and AnO_2^{2+} , but also Sr^{2+} and Tc(VII) from acidic HLLW.(3, 9,10) These results suggest that it is possible to develop a process for separating fission products Tc(VII) and Sr^{2+} alone with all actinides from HLLW by just using one extractant. In the currently used PUREX process, with carefully adjusting the oxidation states of actinides, U, Np, Pu, and Tc(VII) may be extracted by 30% TBP in kerosene, while trivalent actinides, Am^{3+} and Cm^{3+} , along with fission products Ln^{3+} and Sr^{2+} remain in HLLW.

Insert Fig. 1 here

In this work, we present the results of a bench-scale test for the evaluation of the effectiveness of separating trivalent actinides and lanthanides, and Sr^{2+} from HLLW using TiBOGA as extractant and an eighteen-stage, 10 mm centrifugal contactor set. The results in our previous studies and the preliminary results from our tube tests indicated that the distribution ratio of Am^{3+} (D_{Am}) is about 2-5 times higher than that of Nd^{3+} (D_{Nd}), and is 50-300 times higher than that of Sr^{2+} (D_{Sr}) using 0.2 M TiBOGA in 40% octanol/kerosene as organic phase and 0.01-0.15 M HNO_3 solution or a simulated HLLW as aqueous phase. (3, 9, 10) Hence, the general idea for designing the flowsheet of the test is to co-extract Sr^{2+} and $\text{Ln}^{3+}/\text{An}^{3+}$ into the organic phase, then to strip Sr^{2+} first using an appropriate HNO_3 solution, and to strip $\text{Ln}^{3+}/\text{An}^{3+}$ using a more diluted HNO_3 solution. Because D_{Am} is always higher than D_{Nd} under the conditions in this work, in the co-extraction and Sr^{2+} stripping sections, if the expected separation

efficiency for Nd^{3+} is achieved, a better separation efficiency for Am^{3+} should be obtained. Therefore, the test was performed with a non-radioactive feed solution, a simulated HLLW prepared based on the spent fuel reprocessing, containing stable Sr^{2+} isotopes and Nd^{3+} isotopes as a surrogate of $\text{An}^{3+}/\text{Ln}^{3+}$.

EXPERIMENTAL

Chemicals and Equipment

TiBOGA was synthesized at the Institute of Nuclear Energy Technology (INET), Tsinghua University, Beijing, China, and the purity analyzed by GC was >98%. Reagent grade octanol (Beijing Chemical Co.) was used as received. 240# hydrogenated kerosene (KO) (Jinzhou Petroleum Refinery, China) was redistilled and the fraction between 180 and 220°C was used. The mixture of 40% (volume) of octanol/KO was used as diluent. All other reagents used were of analytical grade.

The simulated HLLW (Table 1) was prepared by dissolving nitrates into nitric acid solution. The unit for HNO_3 concentration is M and the unit for the concentration of all cations is g/L through this work. The analysis of metal ions and nitric acid were described elsewhere. (11)

Insert Table 1 here

The 10-mm miniature centrifugal contactor was developed and manufactured at INET. The centrifugal contactor set consists of eighteen 10-mm centrifugal contactors all interconnected and mounted on a stainless steel base. Each centrifugal contactor was driven

and controlled by separate drivers and controllers. Solutions were delivered by six supply pumps. More detailed description of the contactors and equipment were reported elsewhere. (11)

The flowsheet was produced based on the mass transfer stage efficiencies of the centrifugal contactor and the extraction-distribution ratios of Nd^{3+} , Sr^{2+} , and HNO_3 . For the co-extraction section, because D_{Nd} is always much higher than D_{Sr} , only the separation efficiency of Sr^{2+} and the extraction of HNO_3 was considered, and the extraction-distribution models of Sr^{2+} and HNO_3 were developed by using the experimental homogeneous design method. (12, 13) For the stripping sections, the distribution ratios of Nd^{3+} , Sr^{2+} , and HNO_3 between 0.2 M TiBOGA in 40% octanol/KO and HNO_3 solutions were used. The mass transfer stage efficiencies were determined with one stage of the 10-mm centrifugal contactor. Eighteen extraction tests with various aqueous phase compositions and 0.2 M TiBOGA in 40% octanol/KO as organic phase were conducted to develop the extraction-distribution models of Sr^{2+} and HNO_3 as follows:

$$D_{\text{Sr}} = -14.8 + 0.897 \times C_{\text{HNO}_3}^{2.5} - 0.375 \times C_{\text{HNO}_3}^4 - 0.00398 \times C_{\text{Sr}}^{-1.5} - 33.26 \times C_{\text{Sr}} - 0.0589 \times C_{\text{Al}}^{1.2} - 0.00102 \times C_{\text{Na}}^3 - 0.134 \times C_{\text{Fe}}^{-0.7} - 0.890 \times C_{\text{Mo}}^{0.6} - 0.0669 \times C_{\text{Cs}}^{-0.7} - 26.7 \times I^{0.25}$$

$$D_{\text{HNO}_3} = 0.381 - 0.261 \times C_{\text{HNO}_3}^{0.1} - 0.132 \times C_{\text{Sr}}^{0.5} - 0.000104 \times C_{\text{Al}}^2 - 0.000172 \times C_{\text{Fe}}^{2.5} - 0.0160 \times C_{\text{Mo}}^{0.2} - 0.212 \times C_{\text{Cs}}^2$$

where D represents distribution ratio, C represents the value of concentration in g/L for cations and in M for HNO_3 , and I is the value of ionic strength from cations. The range of concentration was 0.5 – 2.2 M for HNO_3 , 0.5 – 10.2 g/L for Al^{3+} , 1.0 – 24 g/L for Na^+ , 0.5 – 8.5 g/L for Fe^{3+} , 0.01 – 0.45 g/L for Sr^{2+} , 0.1 – 0.65 g/L for Cs^+ , 0 – 0.64 g/L

for Mo(VI) in aqueous phase. The organic phase was 0.2 TiBOGA in 40% octanol/KO.

Given a phase ratio of 1/1 (v/v) for organic phase/aqueous phase in the extraction section, removal efficiencies of $> 99.99\%$ for both Sr^{2+} and Nd^{3+} , and cross contamination of $< 0.01\%$ for Nd^{3+} in Sr^{2+} product and of $< 0.1\%$ for Sr^{2+} in Nd^{3+} product, a flowsheet was developed as showed in Figure 1, and the effluents and the related pumps were set up as showed in Table 2.

Insert Fig. 2 here

Insert Table 2 here

The co-extraction section consists of 6 stages (1st to 6th). Sr^{2+} stripping section includes two parts, 6 stages for Sr^{2+} stripping (7th to 12th stage) and 2 stages for re-catching Nd^{3+} carried with the Sr^{2+} stream (17th and 18th stage). Stages 13th to 16th are for Nd^{3+} stripping.

In the experiments of single-stage and the bench-scale test, the rotor speed was maintained at 4000 ± 50 rpm for all centrifugal contactors. For the bench-scale test, the Scrub Feed, Strip Feed 1, and Strip Feed 2 were pumped into the system first, and after effluents were observed at the corresponding outlet the Org. Feeds were pumped in. When organic phases were observed at the outlet of the 6th stage, the Aq. Feed was fed in and the time was set as the starting point.

RESULTS AND DISCUSSION

Mass Transfer Efficiency of Single-Stage Centrifugal Contactor

The mass transfer stage efficiencies of the centrifugal contactors were determined on a

single-stage contactor using equations defined as below for aqueous phase (eqn. 1) and organic phase (eqn. 2):

$$\eta_{aq} = \frac{(X_{in} - X_{out})}{(X_{in} - X_{eq})} \times 100\% \quad (1)$$

$$\eta_{org} = \frac{(Y_{out} - Y_{in})}{(Y_{eq} - Y_{in})} \times 100\% \quad (2)$$

the subscripts *in*, *out*, and *eq* denote the inlet effluents, outlet effluents, and equilibrated solutions. The equilibration concentration was determined separately in a test tube. The results for Sr^{2+} and HNO_3 are listed in Table 3.

Insert Table 3 here

The high efficiencies (very close to 100%) in Table 3 indicates that under the selected experimental condition the performance of the 10-mm centrifugal contactor is almost ideal for the extraction, suggesting the feeding parameters and the contactor setup are well optimized.

Steady-State Confirmation of the Pilot Plant Test

Testing samples were taken at 15-minutes intervals for the raffinate, the Sr^{2+} product, and the Nd^{3+} product to monitor the approach to the steady state. As showed in Fig. 3, it takes about 45, 105, and 150 minutes to reach the steady state for HNO_3 in the extraction section (1st to 6th stage), Sr^{2+} in Sr^{2+} stripping section (7th to 12th, 17th, and 18th stage), and Nd^{3+} stripping section (13th to 16th), respectively. In general, after about 400 mL of the effluents (about 4 times of the hold-up volume of the set) run through

each contactor, the system can reach the steady state. The hold-up volume of each contactor is about 5-6 mL, so the total hold-up volume of the eighteen-stage set is about 100 mL for the organic and aqueous phases together.

Insert Fig. 3 here

Profile of the Reagents

After three hours, the system was shutdown, and samples were taken from each contactor and effluent outlet to obtain the profiles of HNO_3 , Sr^{2+} , and Nd^{3+} . The concentrations of other metal ions in the effluents were also analyzed to evaluate the flowsheet.

As showed in Fig. 4(a), in the extraction section, the concentration of Sr^{2+} decreases both in organic and aqueous phases. After five extraction stages, the concentration of Sr^{2+} in the aqueous phase decreases by about three orders of magnitude from the 5th to the 1st stage (about four orders of magnitude lower than in the Aq. Feed solution). In Sr^{2+} stripping section, the concentration of Sr^{2+} decreases gradually both in organic and aqueous phases, and after six stripping stages over 99% of Sr^{2+} was stripped off. In Nd^{3+} stripping section, the concentration of Sr^{2+} is very low, less than 0.01% of Sr^{2+} in the Aq. Feed solution.

Insert Fig. 4 here

Because TiBOGA is a very strong extractant for Nd^{3+} , the most of Nd^{3+} was extracted into the organic phase at the first extraction stage (5th stage) as expected, resulting in very low Nd^{3+} concentration in the aqueous phase in the extraction section. In Sr^{2+} stripping section, a small amount of Nd^{3+} was also stripped off, this small part of Nd^{3+}

was re-captured in the 17th and 18th stages. However, as showed in Fig. 4(b), also because of the strong affinity of TiBOGA to Nd³⁺, after four stripping stages a very small amount of Nd³⁺ was still retained in the organic phase.

Removal Efficiency and Material Mass Balance

After the system reached the steady state, samples were taken to analyze the concentration of the metal ions and nitric acid in all effluents. The removal efficiency is calculated from the analyzed concentrations using eqn. 3:

$$RE = 1 - \frac{C_{Raffinate} \times Flowrate_{Raffinate}}{C_{Feed} \times Flowrate_{Feed}} \quad (3)$$

$C_{Raffinate}$ and C_{Feed} represent the concentrations of ions. Table 4 shows the calculated results of the distribution, material balance, and the *RE* of the main metal ions and HNO₃.

Insert Table 4 here

The overall material mass balance for the metal ions and HNO₃ ranges from 97% to 102% which are within the expected margin of error of the analytical methods and the flowrate measurement uncertainty, indicating the performance of the test set is excellent during the test. The *RE* and distribution of Sr²⁺ and Nd³⁺ in the effluents show that these two ions are quantitatively separated from the simulated HLLW. However, while Sr²⁺ was completely stripped off into the product effluents, a very small portion of Nd³⁺ was retained in the used organic phase, suggesting the Nd³⁺ stripping section of the test should be modified. Reducing HNO₃ concentration of the Strip Feed 2 and adding one

more stage of contactor are two easy options.

As expected, other metal ions except Ba^{2+} were retained in the raffinate stream, giving very good separation for Sr^{2+} and Nd^{3+} over other metal ions in the simulated HLLW.

Evaluation of Extraction Model and Test

The distribution ratios of Sr^{2+} in the extraction section are showed in Fig.5 in comparison with the calculated values from the extraction model. The results indicate that the extraction models are well developed for the system and can well predict the experiment.

Insert Fig. 5 here

To evaluate the test, the distribution, RE , and recovery efficiency ($Reco.E$) of Sr^{2+} and Nd^{3+} are listed in Table 5 and compared with the calculated results.

Insert Table 5 here

As showed in Fig.5 and Table 5, the results of the bench-scale test are in good agreement with the predicted values from the flowsheet in the extraction and Sr^{2+} stripping sections. However, the Nd^{3+} stripping section in the flowsheet should be optimized further, especially if D_{Am} is used instead of D_{Nd} .

CONCLUSION

A bench-scale test for the separation of strontium and trivalent lanthanides/actinides,

using Nd^{3+} as a surrogate, from a simulated HLLW has been performed to evaluate the separation flowsheet based on N,N,N',N'-tetra-iso-butyl-3-oxa-glutaramide (TiBOGA) as extractant. The performance of the bench-scale test including steady state studies, removal efficiencies, recovery efficiencies, and material mass balance has been reported.

The overall performance was very good. The sample results for the extraction are in good agreement with the predicted values from the flowsheet calculation.

Sr^{2+} and Nd^{3+} were completely extracted from the simulated HLLW by TiBOGA in the organic phase, and the two ions were well separated from each other with two diluted HNO_3 stripping solutions and one re-capturing organic solution. While the recovery of Sr^{2+} was almost complete, a small portion of Nd^{3+} (0.05%) was retained in the organic phase, suggesting that the Nd^{3+} stripping section should be further optimized.

ACKNOWLEDGEMENT

The experiment work was conducted at Institute of Nuclear and New Energy and Technology (INET), Tsinghua University, Beijing, and supported by the State High-Tech Development Plan (863 program, China), No. 2009AA050703. The preparation of this manuscript was supported by the Fuel Cycle Research and Development Program (Aqueous Separations: Thermodynamics and Kinetics) of Office of Nuclear Energy, under U.S. Department of Energy Contract No. DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory (LBNL).

REFERENCE

1. Suzuki, H.; Sasaki, Y.; Sugo, Y.; Apichaibukol, A.; Kimura, T. (2004) Extraction and separation of Am(III) and Sr(II) by N,N,N',N'-tetraoctyl-3-oxapentanediamide (TODGA). *Radiochim. Acta*, 92, 463-466.
2. Ansari, S. A.; Pathak, P. N.; Husain, M.; Prasad, A. K.; Parmar, V. S.; Manchanda, V. K. (2006) Extraction of actinides using N, N, N', N'-tetraoctyl

- diglycolamide (TODGA): a thermodynamic study. *Radiochim. Acta*. 94, 307-312.
3. Tian G.; Zhang P.; Wang J.; Rao L. (2005) Extraction of actinide(III, IV, V, VI) ions and TcO₄ by N,N,N',N'-tetraisobutyl-3-oxa-glutaramide. *Solv. Extr. Ion Exch.*, 23 (5), 631-643.
 4. Sasaki, Y.; Choppin, G. (1998) Extraction of Np(V) by N,N'-dimethyl-N,N'-dihexyl-3-oxapentanediamide. *Radiochim. Acta*, 80, 85-88.
 5. Nave, S.; Modolo, G.; Madic, C.; Testard, F. (2004) Aggregation properties of N,N,N',N'-tetraoctyl-3-oxapentanediamide (TODGA) in n-dodecane. *Solv. Extr. Ion Exch.* 22 (4), 527–551.
 6. Narita, H.; Yaita, T.; Tachimori, S. (2004) Extraction of lanthanides with N,N'-dimethyl-N,N'-diphenyl-malonamide and -3,6-dioxaoctanediamide. *Solv. Extr. Ion Exch.* 22 (2), 135–145.
 7. Shimada, A.; Yaita, T.; Narita, H.; Tachimori, S.; Okuno, K. (2004) Extraction studies of lanthanide(III) ions with N,N'-dimethyl-N,N'-diphenylpyridine-2,6-dicarboxyamide (DMDPhPDA) from nitric acid solutions. *Solv. Extr. Ion Exch.* 22(2), 147–161.
 8. Sasaki, Y.; Sugo Y.; Tachimori, S. (2001) The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in HNO₃-n-dodecane system. *Solv. Extr. Ion Exch.* 19(1), 91-103.
 9. Tian, G.; Wang, J.; Song, C. (2001) Study on extraction of transuranium elements and Tc by N,N,N',N'-tetra isobutyl-3-oxoglutaric amide. *J. Nucl. Radiochem.* (Chinese), 23(3), 135-140.
 10. Tian G.; Zhang P.; Shen, Y.; Wang J.; Rao L. (2005) Extraction of strontium from HLLW using N,N,N',N'-tetraisobutyl 3-oxa-glutaramide. *Solv. Extr. Ion Exch.*, 23 (4), 519-528.
 11. Wang J.; Tian G.; Chen J.; Song C. (2001) Application of miniature centrifugal contactors for treating high-level liquid waste. *Sep. Sci & Tech*, 36(13), 2983-2996.
 12. Wang J.; Song C.; Liu B. (1995) Studies on the extraction of americium with 30% TRPO from simulated HLLW medium. *J. Nucl. Radiochem.* 17 (3), 129-135 (in Chinese).
 13. Chen J.; Wang, J.; Song C. (1996) Computerized simulation of TRPO extraction process treating Chinese high level waste. *Nucl. Sci. Tech*, 17 (3), 129–133.

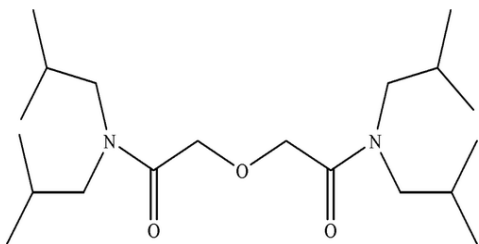


Fig.1 The structure of N,N,N',N'-tetra-iso-butyl-3-oxa-glutaramide.

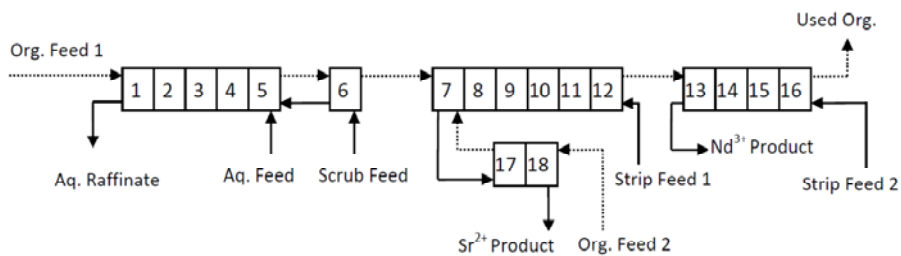


Fig. 2 Flowsheet of the bench-scale test

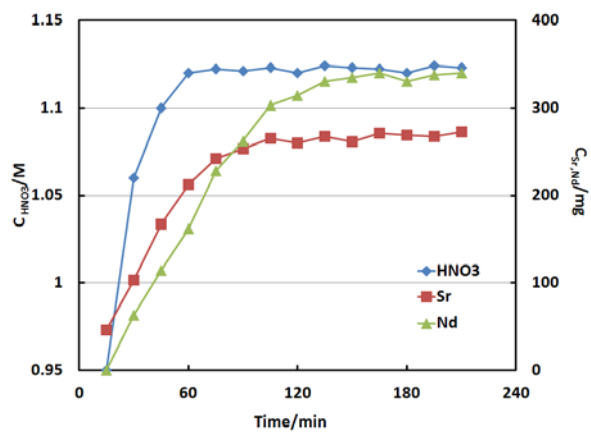


Fig. 3 Rate to achieve the steady state for the aqueous raffinate (HNO₃) and stripping products (Sr²⁺ and Nd³⁺).

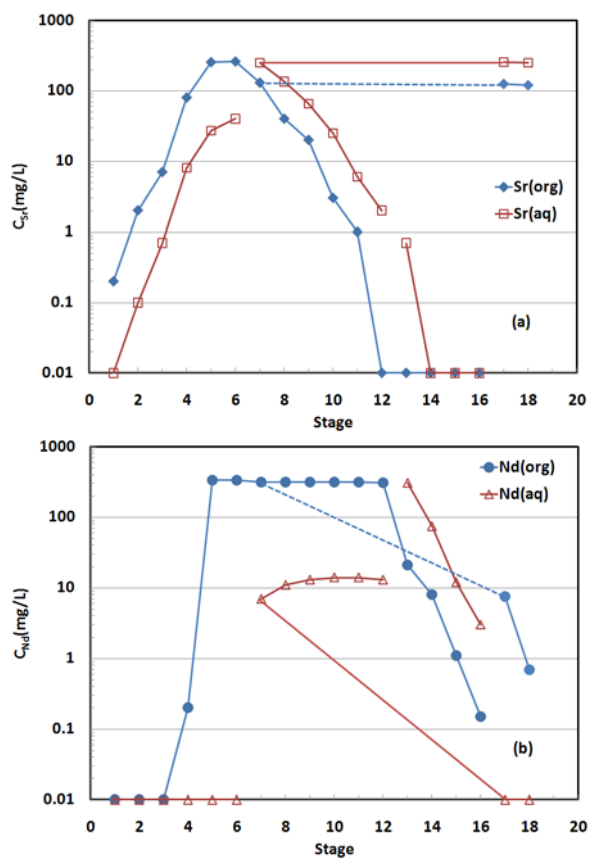


Fig. 4 Profile of Sr^{2+} and Nd^{3+} (the solid lines represent the effluent streams, and the dotted lines represent the linkage between the main and recapturing organic phase streams).

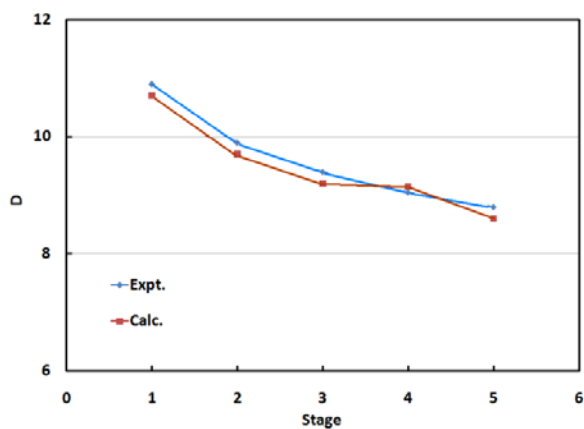


Fig.5 Distribution ratio of Sr^{2+} in the extraction section.

Table 1 Composition of the simulated HLLW for the test

Element	Na	Fe	Ba	Cr	Cs	Sr	Nd	HNO ₃
Concentration (g/L)	2.27	2.30	0.88	0.25	0.84	0.27	0.34	1.55 M

Table 2 Effluents in the bench-scale test

Effluent	Composition	Flowrate (mL/hr)
Aq. Feed	Simulated HLLW	70 ± 3
Scrub Feed	1.37 M HNO ₃	14 ± 1
Strip Feed 1	0.14 M HNO ₃	70 ± 3
Strip Feed 2	0.01 M HNO ₃	70 ± 3
Org. Feed 1	0.2 M TiBOGA	70 ± 3
Org. Feed 2	0.2 M TiBOGA	14 ± 1

Table 3 Mass transfer efficiencies for Sr²⁺ and HNO₃

Reagent	Aqueous phase			Organic phase		
	X_{eq}	X_{out}	η_{aq}	Y_{eq}	Y_{out}	η_{org}
HNO ₃ (M)	1.411	1.415	97%	0.141	0.143	100% *
Sr ²⁺ (g/L)	0.026	0.030	98%	0.241	0.239	99%

*: Calculated efficiency is greater than 100%, likely due to the experimental uncertainty.

Table 4 Distribution, mass balance and RE of the metal ions and nitric acid

Effluent	Sr (%)	Nd (%)	Cs (%)	Fe (%)	Na (%)	Ba (%)	Cr(%)	HNO ₃ (%)
Raffinate	-	-	98.0	100.2	97.1	87.1	98.0	86.3
Sr ²⁺ product	101.9	-	0.2	-	0.2	10.7	-	14.9
Nd ³⁺ product	0.1	102.0	-	-	-	-	-	0.9
Used Org.	-	0.05	-	-	-	-	-	-
Material	102.0	102.1	98.2	100.2	97.3	97.8	98.0	102.1
Balance								
RE	100*	100*	< 0.1	< 0.02	< 0.2	10.5	< 0.02	NA

*: Calculated value is 100%, due to the concentrations in the raffinate lower than the detection limits.

-: Either the value is less than 0.01% or the concentration is lower than the detection limit.

Table 5 Comparison between experimental and calculated results

	RE_{Sr}	$Reco.E_{Sr}$	Sr in Nd product	RE_{Nd}	$Reco.E_{Nd}$	Nd in Sr product
Experimental (%)	>99.99	99.9	0.10	>99.99	99.9	<0.01
Calculated (%)	99.999	99.95	0.097	>99.99	99.95	0.009

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.