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Publication Date
2014-04-21

DOI
10.1080/01496395.2012.697515
Bench-Scale Test for Separation of Sr$^{2+}$ and Nd$^{3+}$ from HLLW Using TiBOGA

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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 Ln$^{3+}$/An$^{3+}$ into the organic phase, then to strip Sr$^{2+}$ first using an appropriate HNO$_3$ solution, and to strip Ln$^{3+}$/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 An$^{3+}$/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:

$$D_{Sr} = -14.8 + 0.897 \times C_{HNO_3}^{2.5} - 0.375 \times C_{HNO_3}^{4} - 0.00398 \times C_{Sr}^{1.5} - 33.26 \times C_{Sr} - 0.0589 \times C_{Al}^{1.2} - 0.00102 \times C_{Na}^{3} - 0.134 \times C_{Fe}^{-0.7} - 0.890 \times C_{Mo}^{0.6} - 0.0669 \times C_{Cs}^{-0.7} - 26.7 \times I^{0.25}$$

$$D_{HNO_3} = 0.381 - 0.261 \times C_{HNO_3}^{0.1} - 0.132 \times C_{Sr}^{0.5} - 0.000104 \times C_{Al}^{2} - 0.000172 \times C_{Fe}^{2.5} - 0.0160 \times C_{Mo}^{0.2} - 0.212 \times C_{Cs}^{2}$$

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 $\text{Sr}^{2+}$ and $\text{Nd}^{3+}$, and cross contamination of $< 0.01\%$ for $\text{Nd}^{3+}$ in $\text{Sr}^{2+}$ product and of $< 0.1\%$ for $\text{Sr}^{2+}$ in $\text{Nd}^{3+}$ 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.

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):

\[ \eta_{aq} = \frac{(X_{in} - X_{out})}{(X_{in} - X_{eq})} \times 100\% \]  

(1)

\[ \eta_{org} = \frac{(Y_{out} - Y_{in})}{(Y_{eq} - Y_{in})} \times 100\% \]  

(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 (1\(^{st}\) to 6\(^{th}\) stage), \( Sr^{2+} \) in \( Sr^{2+} \) stripping section (7\(^{th}\) to 12\(^{th}\), 17\(^{th}\), and 18\(^{th}\) stage), and \( Nd^{3+} \) stripping section (13\(^{th}\) to 16\(^{th}\)), 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.

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 HNO₃, Sr²⁺, and Nd³⁺. 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 Sr²⁺ decreases both in organic and aqueous phases. After five extraction stages, the concentration of Sr²⁺ 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 Sr²⁺ stripping section, the concentration of Sr²⁺ decreases gradually both in organic and aqueous phases, and after six stripping stages over 99% of Sr²⁺ was stripped off. In Nd³⁺ stripping section, the concentration of Sr²⁺ is very low, less than 0.01% of Sr²⁺ in the Aq. Feed solution.

Because TiBOGA is a very strong extractant for Nd³⁺, the most of Nd³⁺ was extracted into the organic phase at the first extraction stage (5th stage) as expected, resulting in very low Nd³⁺ concentration in the aqueous phase in the extraction section. In Sr²⁺ stripping section, a small amount of Nd³⁺ was also stripped off, this small part of Nd³⁺
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 Nd\textsuperscript{3+}, after four stripping stages a very small amount of Nd\textsuperscript{3+} 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:

\[
RE = 1 - \frac{C_{\text{Raffinate}} \times \text{Flowrate}_{\text{Raffinate}}}{C_{\text{Feed}} \times \text{Flowrate}_{\text{Feed}}} \tag{3}
\]

\(C_{\text{Raffinate}}\) and \(C_{\text{Feed}}\) 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 HNO\textsubscript{3}.

The overall material mass balance for the metal ions and HNO\textsubscript{3} 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 Sr\textsuperscript{2+} and Nd\textsuperscript{3+} in the effluents show that these two ions are quantitatively separated from the simulated HLLW. However, while Sr\textsuperscript{2+} was completely stripped off into the product effluents, a very small portion of Nd\textsuperscript{3+} was retained in the used organic phase, suggesting the Nd\textsuperscript{3+} stripping section of the test should be modified. Reducing HNO\textsubscript{3} concentration of the Strip Feed 2 and adding one
more stages of contactor are two easy options.

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

**Evaluation of Extraction Model and Test**

The distribution ratios of $\text{Sr}^{2+}$ 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 ($\text{Reco}.E$) of $\text{Sr}^{2+}$ and $\text{Nd}^{3+}$ 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 $\text{Sr}^{2+}$ stripping sections. However, the $\text{Nd}^{3+}$ stripping section in the flowsheet should be optimized further, especially if $D_{\text{Am}}$ is used instead of $D_{\text{Nd}}$.

**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


Fig. 1 The structure of N,N,N’,N’-tetra-isobutyl-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

<table>
<thead>
<tr>
<th>Element</th>
<th>Na</th>
<th>Fe</th>
<th>Ba</th>
<th>Cr</th>
<th>Cs</th>
<th>Sr</th>
<th>Nd</th>
<th>HNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (g/L)</td>
<td>2.27</td>
<td>2.30</td>
<td>0.88</td>
<td>0.25</td>
<td>0.84</td>
<td>0.27</td>
<td>0.34</td>
<td>1.55 M</td>
</tr>
</tbody>
</table>

Table 2 Effluents in the bench-scale test

<table>
<thead>
<tr>
<th>Effluent</th>
<th>Composition</th>
<th>Flowrate (mL/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aq. Feed</td>
<td>Simulated HLLW</td>
<td>70 ± 3</td>
</tr>
<tr>
<td>Scrub Feed</td>
<td>1.37 M HNO₃</td>
<td>14 ± 1</td>
</tr>
<tr>
<td>Strip Feed 1</td>
<td>0.14 M HNO₃</td>
<td>70 ± 3</td>
</tr>
<tr>
<td>Strip Feed 2</td>
<td>0.01 M HNO₃</td>
<td>70 ± 3</td>
</tr>
<tr>
<td>Org. Feed 1</td>
<td>0.2 M TiBOGA</td>
<td>70 ± 3</td>
</tr>
<tr>
<td>Org. Feed 2</td>
<td>0.2 M TiBOGA</td>
<td>14 ± 1</td>
</tr>
</tbody>
</table>

Table 3 Mass transfer efficiencies for Sr²⁺ and HNO₃

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Aqueous phase</th>
<th>Organic phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃ (M)</td>
<td>Xeq</td>
<td>Xout</td>
</tr>
<tr>
<td>1.411</td>
<td>1.411</td>
<td>97%</td>
</tr>
<tr>
<td>Sr²⁺ (g/L)</td>
<td>0.026</td>
<td>0.030</td>
</tr>
</tbody>
</table>

*: 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

<table>
<thead>
<tr>
<th>Effluent</th>
<th>Sr (%)</th>
<th>Nd (%)</th>
<th>Cs (%)</th>
<th>Fe (%)</th>
<th>Na (%)</th>
<th>Ba (%)</th>
<th>Cr (%)</th>
<th>HNO₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raffinate</td>
<td>-</td>
<td>-</td>
<td>98.0</td>
<td>100.2</td>
<td>97.1</td>
<td>87.1</td>
<td>98.0</td>
<td>86.3</td>
</tr>
<tr>
<td>Sr²⁺ product</td>
<td>101.9</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>0.2</td>
<td>10.7</td>
<td>-</td>
<td>14.9</td>
</tr>
<tr>
<td>Nd³⁺ product</td>
<td>0.1</td>
<td>102.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.9</td>
</tr>
<tr>
<td>Used Org.</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Material Balance</td>
<td>102.0</td>
<td>102.1</td>
<td>98.2</td>
<td>100.2</td>
<td>97.3</td>
<td>97.8</td>
<td>98.0</td>
<td>102.1</td>
</tr>
<tr>
<td>RE</td>
<td>100*</td>
<td>100*</td>
<td>&lt; 0.1</td>
<td>&lt; 0.02</td>
<td>&lt; 0.2</td>
<td>10.5</td>
<td>&lt; 0.02</td>
<td>NA</td>
</tr>
</tbody>
</table>

*: 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

<table>
<thead>
<tr>
<th>Effluent</th>
<th>REₜₛ</th>
<th>Reco.ESₜₛ</th>
<th>Sr in Nd product</th>
<th>REₙᵈ</th>
<th>Reco.ESₙᵈ</th>
<th>Nd in Sr product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental (%)</td>
<td>&gt;99.99</td>
<td>99.9</td>
<td>0.10</td>
<td>&gt;99.99</td>
<td>99.9</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Calculated (%)</td>
<td>99.999</td>
<td>99.95</td>
<td>0.097</td>
<td>&gt;99.99</td>
<td>99.95</td>
<td>0.009</td>
</tr>
</tbody>
</table>
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