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TS-BTPhen as a promising hydrophilic complexing agent for selective Am(III) separation by solvent extraction

Peter Kaufholz,
Fabian Sadowski,
Andreas Wilden,
Giuseppe Modolo,
Frank W. Lewis,
Andrew W. Smith,
Laurence M. Harwood

Abstract. The novel hydrophilic back-extraction agent TS-BTPhen (3,3',3'',3'''-[3-(1,10-phenanthroline-2,9-diyl)-1,2,4-triazine-5,5,6,6-tetrayl]tetrabenzenesulfonic acid) was tested for its selectivity towards Am(III) over Cm(III) and Eu(III) with a TODGA (*N,N,N',N'*-tetraoctyldiglycolamide) based solvent. Batch experiments were carried out using TS-BTPhen dissolved in aqueous nitric acid solution with tracers of ¹⁵²Eu, ²⁴¹Am and ²⁴⁴Cm. A significant increase of the separation factor for Cm over Am from $SF_{Cm/Am} = 1.6$ up to $SF_{Cm/Am} = 3.3$ was observed compared to the use of a TODGA-nitric acid system alone. Furthermore, stripping was possible at high nitric acid concentrations (0.6–0.7 mol/L) resulting in a low sensitivity to acidity changes. The influence of the TS-BTPhen concentration was analyzed. A slope of –2 was expected taking into account literature stoichiometries of the lipophilic analogue CyMe₄BTPhen. However, a slope of –1 was found. Batch stripping kinetics showed fast kinetics for the trivalent actinides. As an alternative organic ligand the methylated TODGA derivate Me-TODGA (2-methyl-*N,N,N',N'*-tetraoctyldiglycolamide) was tested in combination with the hydrophilic TS-BTPhen. The Am(III) separation was achieved at even higher nitric acid concentrations compared to TODGA.

Key words: Am-Cm separation • TODGA • TS-BTPhen • liquid-liquid extraction

P. Kaufholz, F. Sadowski, A. Wilden, G. Modolo[✉]
Institut für Energie- und Klimaforschung,
Nukleare Entsorgung und Reaktorsicherheit (IEK-6),
Forschungszentrum Jülich GmbH (FZJ),
524 25 Jülich, Germany,
Tel.: +49 2461 61 4896, Fax: +49 2461 61 2450,
E-mail: g.modolo@fz-juelich.de

F. W. Lewis
Department of Applied Sciences,
Faculty of Health and Life Sciences,
Northumbria University,
Newcastle upon Tyne NE1 8ST, United Kingdom

A. W. Smith, L. M. Harwood
Department of Chemistry,
University of Reading,
Whiteknights, Reading RG6 6AD, United Kingdom

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Introduction

The transuranium (TRU) elements Pu, Np, Am and Cm dominate the long-term radiotoxicity and heat generation of nuclear waste. A limiting factor of the size of a final repository will be the long-term heat generation of the waste. Therefore, a reduction in TRU inventory could have a major impact on the repository footprint and subsequently favour a denser, hence smaller, repository [1]. Plutonium and neptunium can be removed from the spent fuel by the PUREX process and recycled to MOX fuel, reducing the problem to the minor actinides (MA) Am and Cm [2] which are currently vitrified for final disposal. The partitioning and transmutation (P&T) concept strives for the optimization of minor actinide handling by separation from PUREX-raffinate and transmutation of the MA to short-lived or stable nuclides [1, 3]. Due to the high neutron capture cross section of the lanthanides the separation of MA from lanthanides (Ln) is mandatory for the transmutation process. Due to the high neutron dose and heat generation any fabrication of Cm-containing transmutation targets would require special shielding. The low half-life (18 y) of the major isotope ²⁴⁴Cm enables disposal of Cm together with

the fission products. Therefore, the separation of americium from curium is desirable [3].

The chemical similarity of 4*f*- and 5*f*-elements makes the inter-group separation of An(III) from Ln(III) difficult. Multi-step concepts, e.g. the DIAMEX-SANEX concept, have been developed to separate An(III) from Ln(III) and light fission products within consecutive processes [4–6]. The intra-group separation of Am(III) from Cm(III) is, due to their similar electronic properties and ionic radii, an even more difficult task. An Am(III) selective separation process has been implemented with the LUCA process as a SANEX-downstream option [7]. Recent developments within the ACSEPT project of the European Commission have focused on single cycle processes, recycling An(III) in a single process, e.g. the 1-cycle SANEX and innovative SANEX processes recently demonstrated at Forschungszentrum Jülich [8–10]. An even more complicated approach is the separation of americium alone in a single process. The first reported process for this purpose is the EXAm process developed by the CEA in France [11]. The chemistry in single cycle processes becomes more complex and results in a pH sensitive system with the need to change the aqueous conditions several times. The EXAm process starts with the co-extraction of Am(III) and some fission products (Mo, Pd, Ru, La, Ce, Pr, Nd, Fe) by DMDOHEMA (*N,N'*-dimethyl-*N,N'*-dioctylhexylethoxymalonamide) + HDEHP (di-2-ethylhexyl-phosphoric acid) in TPH while Cm(III) is preferentially complexed in the aqueous phase by the hydrophilic TEDGA (*N,N,N',N'*-tetraethyldiglycolamide). Afterwards, there is the necessity to adjust to pH 3 to back-extract co-extracted Mo, Ru and Pd using citric acid as hydrophilic complexing agent in a buffer solution. Americium is consecutively stripped using HEDTA in an aqueous citric acid solution at pH 3 [11, 12]. The final stripping of remaining Ln(III) + Fe from the organic phase was achieved by increasing the acidity to 1 mol/L nitric acid. The high acidity in the extraction and last stripping step and high pH needed for the interim stripping steps make the process sensitive to pH changes and the use of buffers is mandatory. The combination of the different conditions leads to a very complex chemistry of the EXAm process with the need for a precise pH control.

A common technique in solvent extraction processes for actinide recycling is the co-extraction of

several elements (i.e. An(III) + Ln(III)) followed by a back extraction (stripping) of the desired product from the loaded organic phase. In the innovative SANEX process the hydrophilic SO₃-Ph-BTP (2,6-bis(5,6-di-(hydroxysulfonylphen-3-yl)-1,2,4-triazin-3-yl)-pyridine) was used to strip An(III) selectively from a loaded organic phase containing co-extracted An(III) and Ln(III) [13]. The stripping was possible using 0.35 mol/L nitric acid containing 0.018 mol/L SO₃-Ph-BTP [9]. The prior co-extraction was carried out from solutions with high nitric acid concentrations. A TODGA based organic phase is known to co-extract reasonable amounts of nitric acid that would be released into a stripping step significantly changing the acidity [14]. Therefore, a stripping at high nitric acid concentrations is desirable, minimizing the effect of co-extracted nitric acid and making the process less sensitive to acidity changes. Adapting the actinide(III) selective stripping step in the innovative SANEX process to an americium(III) selective stripping step would lead to an Am(III) selective single cycle process. An Am(III) selective stripping at high nitric acid concentrations would additionally increase the robustness of the process and reduce the number of stages needed for acidity adjustment after extraction from the high acidic feed. As an alternative to TODGA, methylated derivatives of TODGA were developed in the ACSEPT project of the European Commission [15]. Me-TODGA (Fig. 1) has slightly lower distribution ratios compared to TODGA. The complexing agent TS-BTPhen (tetrasulfonated BTPhen, Fig. 1) was developed as a hydrophilic analogue of CyMe₄BTPhen (2,9-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)-1,10-phenanthroline) [16].

In this work, tracer-based extraction studies of Am(III), Cm(III) and Eu(III) and kinetics tests were carried out using a combination of TODGA and TS-BTPhen. The lipophilic extractant Me-TODGA was tested as an alternative ligand for the organic phase.

Experimental section

TODGA is commercially available and was purchased from Technochem Ltd. (UK). Me-TODGA was synthesized according to the literature by University of Twente [17]. TS-BTPhen was synthesized at the University of Reading (UK) as the sodium-salt according to the literature [18].

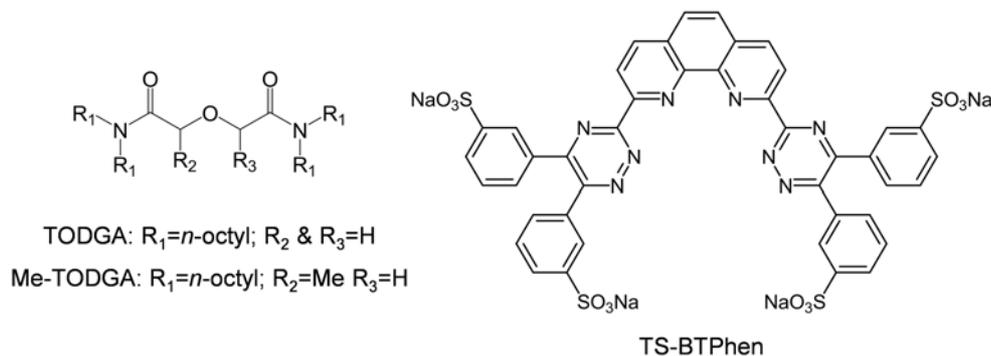


Fig. 1. Ligands used in this study.

Methods

Liquid-liquid extraction experiments were carried out using equal volumes of 500 μL per phase. A tracer in aqueous nitric acid solution containing 1.5 kBq/mL of ^{241}Am and ^{244}Cm each and 3 kBq/mL ^{152}Eu was used. The results are given as distribution ratios ($D = [M]_{\text{org}}/[M]_{\text{aq}}$) and separation factors ($\text{SF}_{M1/M2} = D_{M1}/D_{M2}$). The aqueous and organic phases were contacted for 30 min in a temperature controlled test tube shaker (IKA Vibrax VXR, 2200 rpm) at 22°C. Afterwards, 5 min of centrifugation at 4500 rpm was applied to achieve a complete separation of the phases. Experiments were carried out by either stripping from a loaded organic phase or as forward extraction with tracers added to the aqueous phase together with the hydrophilic complexant. Gamma measurements of ^{152}Eu (122 keV) and ^{241}Am (60 keV) were carried out simultaneously using an Eurisys EGC35-195-R coaxial N-type germanium detector. Alpha measurements were carried out after thin layer sample preparation for ^{241}Am (5486 keV) and ^{244}Cm (5805 keV) simultaneously using an Ortec Octète-pc eight chamber alpha measurement system equipped with PIPS detectors.

Results and discussion

The well-known TODGA and its methylated analogue Me-TODGA (Fig. 1) were used to provide an efficient extracting agent in the organic phase. Lanthanides(III) and actinides(III) were extracted into the organic phase, enabling a selective stripping of Am(III) with TS-BTPhen.

Nitric acid concentration dependence

TODGA extracts the 4f- and 5f-elements together with some non Ln fission products (e.g. Sr, Ru, Pd) [9]. The distribution ratios of An(III) and Ln(III) using TODGA in TPH + 1-octanol increased with the nitric acid concentration following the classical behavior of neutral solvating extractants (Fig. 2). This feature allows the direct extraction from highly acidic PUREX-raffinate [19]. However, the An(III) distribution ratios are similar to the distribution ratios of some Ln(III). Therefore, a separation between Ln(III) and An(III) using TODGA alone is not possible. The hydrophilic complexing agent TS-BTPhen was developed for selective complexation of trivalent actinides over lanthanides. Figure 2 shows the distribution ratios of Eu(III), Am(III) and Cm(III) with 0.2 mol/L TODGA in TPH + 5 vol.% 1-octanol as a function of the nitric acid concentration with (filled symbols) and without (open symbols) addition of TS-BTPhen. It is evident that the addition of TS-BTPhen significantly decreased the distribution ratios of all metal ions over the whole range of nitric acid concentrations studied. The distribution ratios of An(III) however are decreased greater (2 orders of magnitude at

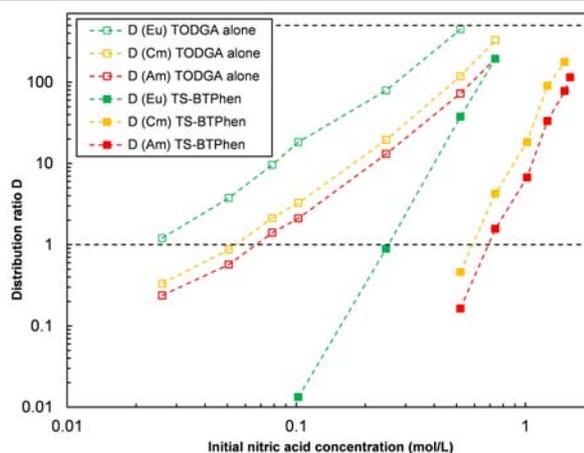


Fig. 2. Distribution ratios of Eu(III), Am(III) and Cm(III) using TODGA in the organic phase and nitric acid solutions with and without TS-BTPhen in the aqueous phase. Organic phase: 0.2 mol/L TODGA in TPH + 5 vol.% 1-octanol. Aqueous phase: open symbols – nitric acid; filled symbols – 10 mmol/L TS-BTPhen in nitric acid. Forward extraction experiment.

0.7 mol/L nitric acid) than those of Eu(III) (one order of magnitude at 0.5 mol/L nitric acid). The slope of $\log(D)$ as a function of the nitric acid concentration increased from 2 for TODGA alone to 6 for TODGA + TS-BTPhen which is assumed to be caused by protonation of TS-BTPhen. The complexation of An(III) in the aqueous phase is higher for Am(III) than for Cm(III) leading to an increase in the separation factor of Cm(III) over Am(III). The separation factor increases from $\text{SF}_{\text{Cm/Am}} = 1.6$ for the TODGA-nitric acid system without aqueous complexant to $\text{SF}_{\text{Cm/Am}} = 3$ with the addition of TS-BTPhen. This selectivity is higher than the selectivity observed for $\text{SO}_3\text{-Ph-BTP}$ used in the innovative SANEX process, although the $\text{SF}_{\text{Eu/Am}}$ is significantly lower ($\text{SF}_{\text{Eu/Am}} = 150\text{--}250$ in Fig. 2, compared to $\text{SF}_{\text{Eu/Am}} = 250\text{--}1000$ for $\text{SO}_3\text{-Ph-BTP}$) [13]. Furthermore, the distribution ratios of Am(III) become lower than 1 around 0.6 mol/L nitric acid; whereas the D_{Cm} is still greater than 1. These conditions are favourable for a mutual Am/Cm separation. It has to be mentioned that lighter lanthanides than Eu are less extracted in the TODGA based extraction system. The distribution ratios of Eu(III) and the Eu/Am separation factors are not representative for all Ln(III), and especially the light lanthanides could show small Ln/Am separation factors and interfere with an Am(III) separation. This will be further studied.

Influence of TODGA concentration

The ligand concentration in the organic phase and the complexant concentration in the aqueous phase play an important role for an effective stripping. Therefore, the influence of the TODGA concentration was tested, keeping the nitric acid and TS-BTPhen complexant concentrations constant. Figure 3 shows the $\log(D)$ values of Eu(III), Am(III) and Cm(III) as a function of $\log([\text{TODGA}])$ in the organic phase. From Fig. 3 it can be seen that the

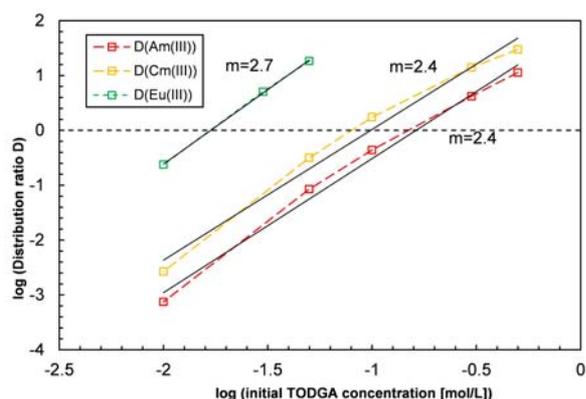


Fig. 3. Logarithm of the distribution ratios of Am(III) and Cm(III) as a function of the logarithm of the initial TODGA concentration. Organic phase: 0.01 to 0.5 mol/L TODGA in TPH + 5 vol.% 1-octanol. Aqueous phase: 10 mmol/L TS-BTPhen in 0.7 mol/L nitric acid. Forward extraction experiment.

data for the actinides follow a nonlinear curve with decreasing slope for increasing TODGA concentrations. This behavior has to be studied in more detail. However, to compare the data with the literature, linear regressions were applied. The slopes of the function added to the data are similar to the slope of TODGA without TS-BTPhen in the aqueous phase (slope of An(III) = 2.7) [20].

For TODGA, the metal-to-ligand stoichiometry is known to be 1:3 predicting a slope of 3. Furthermore, with a constant concentration of the complexant TS-BTPhen in the aqueous phase, the slope of $\log(D_{\text{An(III)}})$ as a function of $\log([TODGA])$ is close to the slopes of $\log(D_{\text{An(III)}})$ as a function of the $\log[TODGA]$ of the TODGA-nitric acid system.

Plotting $\log(D)$ vs. $\log(\text{free ligand concentration})$ is commonly used in the literature to study complex stoichiometries by slope analysis [21]. The extraction equilibria can be expressed mathematically with the extraction constant, and the obtained slope gives the number of complexing ligands. As a complex mixture of lipophilic and hydrophilic complexes may form here and are yet unknown, extraction equilibria were not formulated here. First, the complexation shall be studied in more detail using spectroscopic techniques.

Influence of TS-BTPhen concentration

In order to find suitable conditions for a selective stripping of Am(III) a variation of the TS-BTPhen concentration was carried out at constant TODGA and nitric acid concentrations. The results are shown in Fig. 4 indicating a parallel linear trend for Am(III) and Cm(III) with a slope of -1 . Europium does not follow a linear trend and is therefore not fitted. The separation factor of Cm over Am stays constant over the studied range of TS-BTPhen concentrations. ($SF_{\text{Cm/Am}} = 2.6$; due to stripping from an organic phase loaded by a simulated HAW-raffinate).

In the literature a stoichiometry of 1:2 is reported for the lipophilic $\text{CyMe}_4\text{BTPhen}$ complex with Cm(III) and Eu(III) using TRLFS analysis in methanol [22]. In the experiment presented in

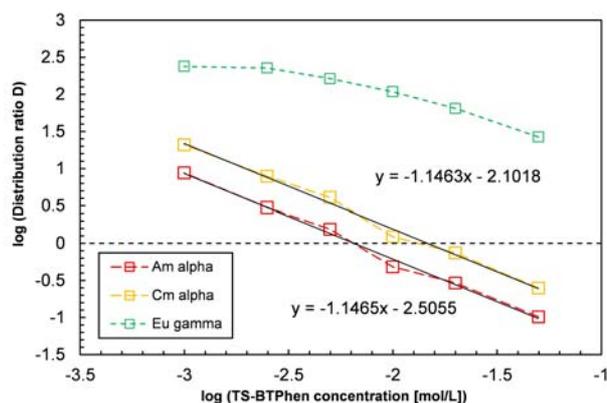


Fig. 4. Distribution ratios of Am(III), Cm(III) and Eu(III) as a function of the TS-BTPhen-concentration in the aqueous phase. Organic phase: 0.2 mol/L TODGA in TPH + 5 vol.% 1-octanol. Aqueous phase: 1 to 50 mmol/L TS-BTPhen in 0.7 mol/L nitric acid. Stripping experiment from a loaded organic phase prepared by co-extraction from a spiked simulated HAW-raffinate at 4.46 mol/L nitric acid.

Fig. 4 the aqueous complexant concentration was varied. Due to the reported formation of 1:2 complexes for An(III) – $\text{CyMe}_4\text{BTPhen}$ complexes, a slope of -2 was expected. The results in Fig. 4 show a slope of -1 , being in conflict with the results obtained for the lipophilic $\text{CyMe}_4\text{BTPhen}$ by TRLFS in methanol solution [22]. Further experiments will be carried out in an attempt to resolve the complex stoichiometry of the An(III)-TS-BTPhen complex by spectroscopic methods.

Batch kinetics

Batch test tube shaking experiments were carried out as back-extraction experiments from a loaded organic phase with varying mixing times. The loaded organic phase was prepared in advance by extraction of Am, Cm and Eu tracer from 0.6 mol/L nitric acid. It was found that the back extraction kinetics is fast. The equilibrium D values and separation factors of Am, Cm and Eu were achieved within only 1 min using a fast shaking device (described in the Methods chapter). The equilibrium distribution ratios in the batch kinetic experiment were $D_{\text{Am,eq}} = 0.26$, $D_{\text{Cm,eq}} = 0.87$, $SF_{\text{Cm/Am,eq}} = 3.3$.

Alternative extraction agent Me-TODGA

Using TODGA as an extractant for Ln(III) and An(III) works very well over a wide range of nitric acid concentrations. However, due to its high affinity for trivalent *f*-elements TODGA leads to high distribution ratios of An(III) and Ln(III) making stripping of these elements difficult. In order to find an extractant which extracts well at high nitric acid concentrations but does not reach high distribution ratios at low HNO_3 concentrations, derivatives of TODGA were synthesized [17]. The methylated TODGA derivative Me-TODGA was found to provide extraction by reaching slightly lower distribution ratios compared to TODGA. Me-TODGA was

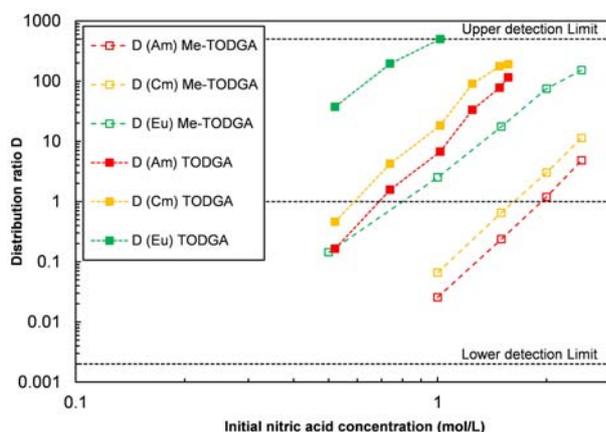


Fig. 5. Comparison of TODGA and Me-TODGA as organic extractants for the selective stripping of Am(III). Organic phase: 0.2 mol/L TODGA (filled symbols) or Me-TODGA (open symbols) in TPH + 5 vol.% 1-octanol. Aqueous phase: 10 mmol/L TS-BTPhen in different nitric acid concentrations; 30 min of extraction at 22°C; 5 min of centrifugation.

tested as an alternative extractant to strip Am(III) selectively using TS-BTPhen. Figure 5 shows preliminary results of a comparison of the distribution ratios of Am(III), Cm(III) and Eu(III) using TODGA and the alternative ligand Me-TODGA both with TS-BTPhen in the aqueous phase. The lower distribution ratios of Me-TODGA combined with TS-BTPhen resulted in an Am(III) selective strip using nitric acid concentrations greater than 1 mol/L. The application of Me-TODGA in combination with TS-BTPhen can thus reduce the difference in nitric acid concentration over the whole process leading to a very stable system with respect to sensitivity towards changes in the nitric acid concentration. In addition, stripping at high nitric acid concentrations opens the possibility of reducing the number of steps needed for the nitric acid scrubbing from the organic phase.

Conclusion and outlook

The novel hydrophilic complexing agent TS-BTPhen shows selectivity for Am(III) over Cm(III) in tracer experiments and is furthermore able to increase the separation between Eu(III) and Am(III) compared to the TODGA-nitric acid system without an aqueous complexant. The separation factor of Cm(III) over Am(III) is increased from 1.6 (TODGA-nitric acid) to 3 using 10 mmol/L of TS-BTPhen in the aqueous phase with an organic phase of 0.2 mol/L TODGA in TPH 5 vol.% 1-octanol, which is significantly higher compared to $\text{SO}_3\text{-Ph-BTP}$ that was used in the innovative SANEX process. However, the behavior of the lighter lanthanides still has to be studied, as especially the light lanthanides may show small La/Am separation factors and interfere with a selective Am(III) separation. The distribution ratios as a function of the TS-BTPhen concentration show no change in $\text{SF}_{\text{Cm/Am}}$ in the analyzed range. The plot of $\log(D)$ as a function of $\log([\text{TS-BTPhen}])$ shows a slope of -1 which is divergent to the 1:2

An(III)/BTPhen complex formed by the lipophilic $\text{CyMe}_4\text{BTPhen}$ with Cm(III) described in the literature. Further experiments will be carried out to analyze the complex stoichiometry by spectroscopic methods. A selective stripping is possible at relatively high nitric acid concentrations for TODGA and even higher nitric acid concentrations for Me-TODGA (>1 mol/L HNO_3), making the system less sensitive to acidity variations. Process development will be continued with respect to fission product and Ln(III) behavior in the system.

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