

Initiate test loop irradiations of ALSEP process solvent

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Fuel Cycle Technology

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SUMMARY

This report describes the initial results of the study of the impacts of gamma radiolysis upon the efficacy of the ALSEP process and is written in completion of milestone M3FT-14IN030202. Initial irradiations, up to 100 kGy absorbed dose, of the extraction section of the ALSEP process have been completed. The organic solvent used for these experiments contained 0.05 M TODGA and 0.75 M HEH[EHP] dissolved in *n*-dodecane. The ALSEP solvent was irradiated while in contact with 3 M nitric acid and the solutions were sparged with compressed air in order to maintain aerated conditions. The irradiated phases were used for the determination of americium and europium distribution ratios as a function of absorbed dose for the extraction and stripping conditions. Analysis of the irradiated phases in order to determine solvent composition as a function of absorbed dose is ongoing. Unfortunately, the failure of analytical equipment necessary for the analysis of the irradiated samples has made the consistent interpretation of the analytical results difficult.

Continuing work will include study of the impacts of gamma radiolysis upon the extraction of actinides and lanthanides by the ALSEP solvent and the stripping of the extracted metals from the loaded solvent. The irradiated aqueous and organic phases will be analyzed in order to determine the variation in concentration of solvent components with absorbed gamma dose. Where possible, radiolysis degradation product will be identified.

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ACRONYMS

ALSEP	Actinide Lanthanide Separation
ANL	Argonne National Laboratory
FCRD	Fuel Cycle Research and Development program
GC-FID	Gas Chromatography with Flame Ionization Detection
HEH[EHP]	2-ethyl(hexyl)phosphonic acid mono-2-ethylhexyl ester
HPGe	High Purity Germanium detector
INL	Idaho National Laboratory
O/A	Organic to Aqueous phase volume ratio
PNNL	Pacific Northwest National Laboratory
PUREX	Plutonium Uranium Reduction Extraction
TALSPEAK	Trivalent Actinide Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes
TODGA	<i>N,N,N',N'</i> -tetraoctyldiclycolamide
T2EHDGA	<i>N,N,N',N'</i> -tetra(2-ethylhexyl)digylcolamide

INITIATE TEST LOOP IRRADIATIONS OF ALSEP PROCESS SOLVENT

1. INTRODUCTION

Researchers at INL are studying the impacts of gamma radiolysis on the Actinide Lanthanide Separation (ALSEP) extraction process. The ALSEP process was developed through a joint collaboration between Argonne National Laboratory (ANL) and Pacific Northwest National Laboratory (PNNL).^[1, 2] This process uses an organic solvent consisting of a neutral diglycolamide extractant, *N,N,N',N'*-tetraoctyldiglycolamide (TODGA), and an acidic extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) dissolved in an aliphatic diluent. The actinides and lanthanides are co-extracted from relatively high nitric acid and the actinides are selectively stripped using a carboxylic acid buffered polyaminopolycarboxylic acid solution. The structures of the compounds used in the ALSEP process organic phase are depicted in Figure 1.

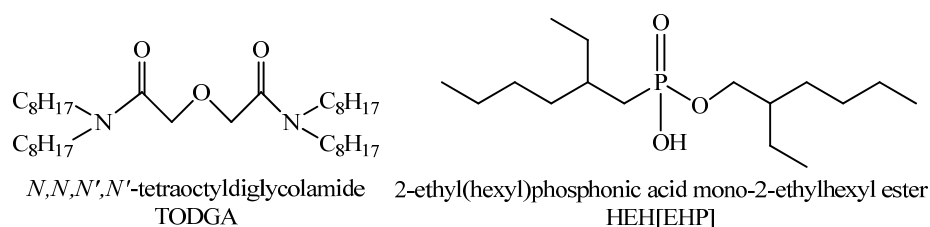


Figure 1. Structures of compounds used in the ALSEP process.

Initial irradiations, up to 100 kGy absorbed dose, of the extraction section of the ALSEP process have been completed. The organic solvent used for these experiments contained 0.05 M TODGA and 0.75 M HEH[EHP] dissolved in *n*-dodecane. The ALSEP solvent was irradiated while in contact with 3 M nitric acid and the solutions were sparged with compressed air in order to maintain aerated conditions. The irradiated phases were used for the determination of americium and europium distribution ratios as a function of absorbed dose for the extraction and stripping conditions. Analysis of the irradiated phases in order to determine solvent composition as a function of absorbed dose is ongoing. This report describes the initial results of the study of the impacts of gamma radiolysis upon the efficacy of the ALSEP process and is written in completion of milestone M3FT-14IN030202.

2. EXPERIMENTAL

All chemicals were reagent grade or higher and used without further purification except where noted. Aqueous solutions were prepared using de-ionized water (MilliQ, 18 M Ω). All analyses are performed in triplicate unless otherwise noted. The neutral diglycolamide extractants, *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) and *N,N,N',N'*-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) were purchased from Eichrom and used as received. The liquid cation exchanging extractant 2-ethyl(hexyl) phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) was obtained from a commercial source (Yick-Vic Chemicals, China) and purified by a literature procedure.^[3] The final purity of the HEH[EHP] was greater than 98 % based on ³¹P NMR and potentiometric analyses. Reagent grade *n*-dodecane (99%) was purchased from Aldrich and used as received. Concentrated nitric acid (70%, w/w, Aldrich, Trace Metal Grade) was used to prepare the nitric acid solutions used in this work. Acid solutions were standardized by titration against standard base (NaOH, Aldrich).

2.1 Irradiations

The irradiation source used for these experiments was a MDS Nordion GammaCell 220 Excel self-contained ^{60}Co gamma irradiator. The irradiated solutions were contained in air-sparged glass scintillation vials. Sparging was performed using a flow of compressed air (1 sccm) supplied by mass flow controllers (Sierra, Model C50L). Samples of the ALSEP solvent (0.050 M TODGA + 0.75 M HEH[EHP]) were prepared volumetrically and pre-equilibrated three times with 3.0 M nitric acid using an organic-to-aqueous phase volume ratio (O/A) of one. Aliquots of the pre-equilibrated organic phase and fresh 3.0 M nitric acid were irradiated at known positions in the GammaCell 220E sample chamber. The dose rate at known positions within the GammaCell 220E sample chamber was determined by Fricke dosimetry.^[4, 5]

2.2 Solvent Extraction Experiments

The effect of gamma radiolysis upon the extraction performance of irradiated aqueous and organic samples of ALSEP process solutions was evaluated by measuring americium and europium distribution ratios. The ^{243}Am radioisotope was obtained from Idaho National Laboratory (INL) stocks. The ^{154}Eu radiotracer was purchased from Eckert & Ziegler. The distribution ratio, D_M , was calculated as the ratio of the equilibrium concentration of the radiotracer in the organic phase to that in the aqueous phase. The metal distribution ratios were determined using irradiated aqueous and organic phases. After the addition of the radiotracers, the aqueous and organic phases were mixed for two minutes using a vortex mixer. Following vortex mixing, the samples were centrifuged to facilitate phase separation. Since the kinetics of stripping from the loaded ALSEP solvent were reported to be relatively slow,^[1] a four minute vortex mixing time was used for stripping studies. An aliquot of each phase was taken for radiometric analysis using gamma spectrometry. Radiometric analyses were performed using a Changer Lab 6000N sample changer equipped with an ORTEC GEM50P4 co-axial HPGe detector and DSPEC multichannel analyzer.

2.3 Gas Chromatographic Analysis

Due to the acidic functional group of the HEH[EHP] and the possibility of the generation of acidic degradation products, an aliquot of each solvent sample was diluted 100 fold with hexane and derivatized with 300 μL of an ~ 0.3 mol/L solution of diazomethane in hexane prior to analysis.^[6] This produced the methyl ester of the phosphoric acid functional groups in the target compounds. These samples were analyzed along with appropriate calibration and quality assurance samples for HEH[EHP] and radiolytic degradation products.

The gas chromatography analyses were performed on a Thermo Scientific Trace ULTRA gas chromatograph. The chromatograms were processed using Thermo Scientific Xcalibur software. The chromatographic separations were carried out utilizing a Thermo Scientific TG-35MS capillary column (30m x 0.32mm ID x 0.5 μm film). Analytical conditions were set at 2.0 mL/min constant flow with helium as the carrier gas and an 80 mL/min split flow. Oven operating conditions started with a 2 min hold at 70°C, followed by a ramp at 20°C/min to 240°C then 40°C/min to 280°C, finished with an 8.25 min hold at 280°C. A Thermo AS3000 auto sampler was used for all injections, employing a 1 μL hot injection with the inlet set at 250 °C and 5 second pre-injection dwell time. The FID was held constant at 250°C. The fuel gas for the FID is a mixture of 350 mL/min air and 35 mL/min hydrogen with 30 mL/min nitrogen as a makeup gas.

3. RESULTS AND DISCUSSION

Zarzana *et al.*^[7] used mass spectroscopic techniques to compare the γ -radiolysis of TODGA and T2EHdGA. In their work, solutions of diglycolamide extractants in n-dodecane were subjected to γ -irradiation in the presence or absence of an acidic aqueous phase and subsequently analyzed using

electrospray ionization mass spectrometry. These authors reported an exponential decrease in the concentration of TODGA or T2EHDGA which was independent of the acidic aqueous phase. A number of radiolysis products were identified corresponding to the cleavage of bonds within the diglycolamide functionality; C–O_{ether}, N–C_{carbonyl}, N–C_{side-chain} bonds, and to a lesser extent the C–C_{carbonyl} bond. Sugo *et al.*,^[8] Sharma *et al.*,^[9] and Deepika *et al.*^[10] all reported similar radiolytic degradation products of either TODGA or T2EHDGA.

In order to evaluate the potential impacts of gamma radiolysis upon the efficacy of the ALSEP process, simple batch contact experiments were performed using aqueous and organic phases irradiated up to 100 kGy absorbed dose. The actinides and lanthanides were co-extracted from relatively high nitric acid and the actinides were selectively stripped using a carboxylic acid buffered polyaminopolycarboxylic acid solution. The organic phase used in these experiments contained 0.05 M TODGA + 0.75 M HEH[EHP] dissolved in n-dodecane and aqueous phase was 3 M nitric acid. The organic composition was chosen based upon available literature.^[11] The nitric acid concentration was set at 3 M HNO₃ since this acid concentration led to the highest extraction of lanthanum, which is the least extracted lanthanide ion by the ALSEP process.^[11] The americium and europium distribution ratios measured using the irradiated phases are presented in Table 1.

Table 1. Distribution ratios, D_{Am} and D_{Eu}, determined using static irradiated ALSEP solvent and nitric acid. Organic: 0.05 M TODGA / 0.75 M HEH[EHP] / n-dodecane. Aqueous: 3 M nitric acid.

Absorbed Dose, kGy	D _{Am}	D _{Eu}
0	290 ± 16	2200 ± 480
25	270 ± 6	2000 ± 350
50	290 ± 12	320 ± 250
100	140 ± 4	120 ± 6

The decrease in the measured distribution ratios appears to be consistent with the decrease in TODGA or T2EHDGA concentration reported by Zarzana *et al.*^[7] (~20% decrease at 100 kGy absorbed dose). The americium distribution ratios obtained for the 0 – 50 kGy absorbed dose samples agree reasonably well with D_{Am} values reported by Gelis and Lumetta.^[11] Unfortunately, these authors do not report values for D_{Eu}, however, the values of D_{La} and D_{Ce} from 3 M HNO₃ are approximately D_{La} ~10 and D_{Ce} ~ 20. Based upon the reported values of D_{La} and D_{Ce}, the D_{Eu} values reported in Table 1 seem unreasonably high.

Due to the apparent inconsistent data, the acid dependence of the distribution ratios for the ALSEP solvent was measured. Due to the failure of the HPGe (High Purity Germanium) detector used for gamma analysis, these extraction experiments were not analyzed. The large error associated with the values of D_{Eu} reported in Table may be attributable to the failure of the HPGe detector system. Therefore, the eventual failure of the HPGe detector calls into question the distribution ratio data reported in Table 1.

In addition to radiochemical measurements, the concentration of the components of the ALSEP process will be determined by various analytical methods. The analytical methodology for the determination of HEH[EHP] has been developed at INL.^[11] This method utilizes sample derivatization and gas chromatography with flame ionization detection (GC-FID) to determine HEH[EHP] and its degradation products present in organic solvents.

A similar method, which does not require sample derivatization determination, was developed for TODGA analysis. A typical calibration curve TODGA determination by GC-FID is shown in Figure 2.

The error associated with the individual data points in the plot is smaller than the data marker used. The calibration curve is linear.

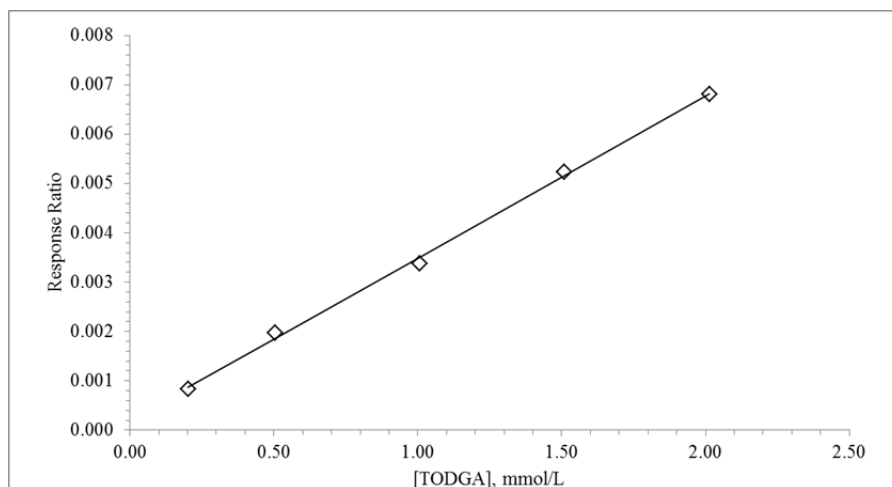


Figure 2. Calibration curve for the GC-FID analysis of TODGA. Equation of linear best-fit: $y = 3.281 \times 10^{-3}x + 2.087 \times 10^{-4}$, $R^2 = 0.9985$.

The analysis of the irradiated ALSEP organic phases is ongoing. When the analyses are complete, the results should provide the data necessary to determine whether or the observed decrease in measured values of D_{Am} and D_{Eu} with increasing dose are due to the radiolytic degradation of the ALSEP solvent or due to an experimental artifact.

4. CONCLUSIONS AND CONTINUING WORK

Initial irradiations, up to 100 kGy absorbed dose, of the extraction section of the ALSEP process have been completed. The organic solvent used for these experiments contained 0.05 M TODGA and 0.75 M HEH[EHP] dissolved in *n*-dodecane. The ALSEP solvent was irradiated while in contact with 3 M nitric acid and the solutions were sparged with compressed air in order to maintain aerated conditions. The irradiated phases were used for the determination of americium and europium distribution ratios as a function of absorbed dose for the extraction and stripping conditions. Analysis of the irradiated phases in order to determine solvent composition as a function of absorbed dose is ongoing. Unfortunately, the failure of analytical equipment necessary for the analysis of the irradiated samples has made the consistent interpretation of the analytical results difficult.

Continuing work will include of study of the impacts of gamma radiolysis upon the extraction of actinides and lanthanides by the ALSEP solvent and the stripping of the extracted metals from the loaded solvent. The irradiated aqueous and organic phases will be analyzed in order to determine the variation in concentration of solvent components with absorbed gamma dose. Where possible, radiolysis degradation product will be identified.

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