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Accomplishing Equilibrium in ALSEP: Demonstrations of Modified Process Chemistry on 3-D Printed Enhanced Annular Centrifugal Contactors

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Abstract

The major components of the modified ALSEP process have been demonstrated on a modified 2-cm annular centrifugal contactor with an enhanced mixing zone using stable fission products and radiotracers. The results show that by decreasing the pH of the minor actinide stripping solution, using HEDTA instead of DTPA, and increasing contact time, the process is very effective in separating americium from the lanthanides and the fission products.

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1. Introduction

In regards to the long-term management and disposal of spent nuclear fuel, the ALSEP (Actinide Lanthanide Separation Process) was developed to treat a PUREX raffinate stream by liquid-liquid extraction with the intent of separating trivalent minor actinides (Am/Cm; An) from trivalent fission-product lanthanides (Ln) and selected transition metals.^{1,2} The ALSEP solvent is comprised of a mixture of neutral diglycolamides such as N,N,N',N'-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) and acidic organo-phosphorous extractants such as 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester acid (HEH[EHP]) in a hydrocarbon diluent. When loaded with a

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number of PUREX raffinate metals from mild nitric acid, the solvent mixture can be contacted with a softer-donor complexant such as diethyaminetriaminepentaacetic acid (DTPA) or N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA) which can strip the minor actinides into solution significantly faster depending on the aqueous environment³. In addition to separating Ln/An, ALSEP contains a stage that is dedicated to removing fission-Mo as molybdenum was found to contaminate MA stream under certain conditions².

Batch equilibrium studies of ALSEP were encouraging since Am could be separated from Nd with separation factors over 30 and to an even greater extent for the rest of the early Ln series (La-Gd).^{1,2} To continue the technological development and scale-up of ALSEP we explored its separation capabilities on a 2-cm Argonne centrifugal contactor⁴ (CC) with a 3-D printed housing that featured a new/enhanced mixing zone. This allowed us some insight on extraction kinetics and phase disengagements that would be relevant to real-time processing.

2. Experimental

HEH[EHP] was purified using a third phase method;⁵ a sample was dissolved in methanol and titrated with alkali to achieve a new purity of > 99%. All other reagents were used without purification. T2EHDGA was purchased from Eichrom. HEDTA, ammonium citrate, n-dodecane, citric, malonic, acetohydroxamic acids were purchased from Sigma-Aldrich. The pH of aqueous solutions was adjusted using either concentrated nitric acid or ammonium hydroxide (J.T. Baker) and measured using a glass combination electrode that was calibrated with pH 4.01 and 7.00 standardized buffers. A simulated PUREX raffinate was prepared with stock chemicals as nitrate salts (Fe, Y, La, Ce, Pr, Nd, Sm, Eu, Gd), nitrosyl compounds of Ru and Pd, zirconium(IV) oxide, and sodium molybdate solutions in concentrated nitric acid and then diluted to 3M HNO₃. ²⁴¹Americium and ¹⁴⁷Pm were purchased from Eckert & Ziegler Isotope Products and were quantified using a liquid scintillation counter (PerkinElmer Tri-Carb 3100TR; α/β discrimination). Non-radioactive components were quantified using inductively coupled plasma mass spectrometry (PerkinElmer SCIEX ELAN DRC II) with an uncertainty of $\pm 10\%$. Distribution ratios were calculated as the ratio of metal (M) concentrations in the organic phase to the concentrations in the aqueous phase.

$$D_M = [M]_{\text{org}} / [M]_{\text{aq}} \quad (1)$$

The separation factors reported here are in terms of the distribution of Am.

$$SF_M = D_M / D_{Am} \quad (2)$$

Fabrication of contactor bodies was accomplished through the use of Additive Manufacturing (AM), also known as 3D Printing (3DP). Initial prototypes were made in polymethylmethacrylate (PMMA or acrylic) using the stereolithography (SLA) method with a desktop 3D printer from Full Spectrum Lasers (Las Vegas, NV, USA) with selected additional components made using Fused Deposition Modeling (plastic extrusion) in PETG (glycol-modified polyethylene terephthalate) from MadeSolid and printed on a Series 1 printer from Type A Machines (San Francisco, CA, USA). For the four tube design, a contactor body printed in 15-5PH stainless steel using Direct Metal Laser Sintering (DMLS) was also acquired (GPI Prototyping, Lake Bluff, IL). No measured chemical differences were observed for tests using either plastic or stainless contactor bodies and no degradation of the plastic housings were observed during tests with process solutions. Rotors were made of 316L stainless steel and had been machined using traditional methods. Rotors were designed so as to be 'partially pumping'—thus maintaining a non-zero liquid level in the annular space even at low to zero feed flow rates.⁶ The inlets and outlets of each CC were fitted with 3/8-inch stainless steel tubing which were connected with Swagelok fittings. The aqueous and organic solutions were fed via a Fluid Metering Incorporated Model QV Variable Speed Pump and the flow rates were controlled using a V300 Stroke Rate Controller. The flow rates were monitored gravimetrically with Ohaus Scout Pro portable balances that were connected to LabVIEW software (National Instruments). The densities of each phase were determined by gravimetry with a Cassini volumetric flask at the desired temperatures in a water bath. The total organic and aqueous feed rates varied from 6.7 mL/min to 15.1 mL/min depending on the trial. The temperature was monitored inside the mixing zone using a 1/16-inch thermocouple (J-KEM Scientific, Inc) that was inserted through the contactor drain tube.

3. Results & Discussion

3.1 Contactor Design

For stage-wise extraction equipment such as the annular centrifugal contactor, assuming a uniform concentration in the continuous phase the stage mass transfer efficiency of the dispersed phase η_D can be described by:

$$\eta_D = \frac{c_{i,in} - c_{i,out}}{c_{i,in} - c_{i,eq}} = 1 - \exp\left(\frac{-K_D a V}{Q_D}\right) \quad (3)$$

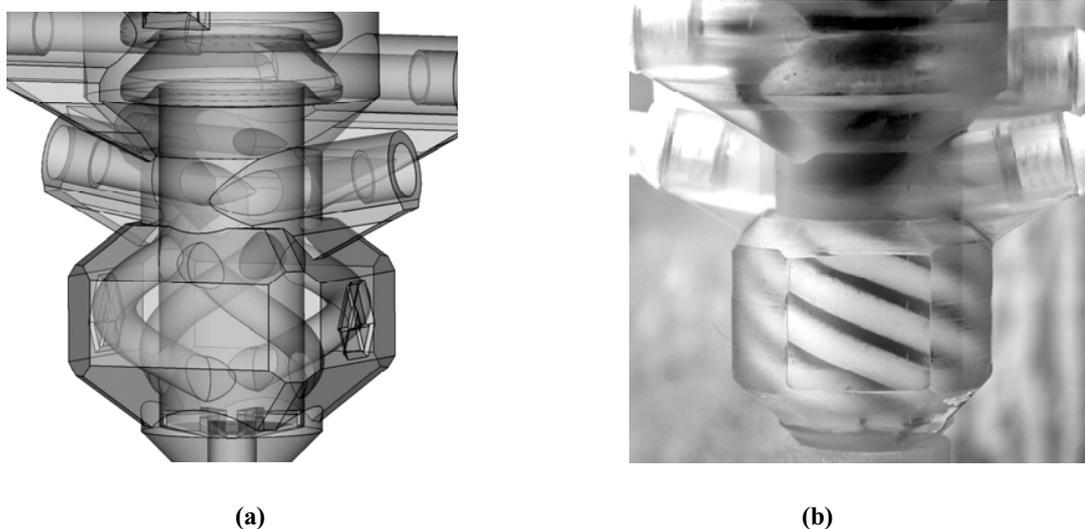
where $c_{i,in}$ is the concentration of the target component i entering the stage, $c_{i,out}$ is the concentration in the exit stream, and $c_{i,eq}$ is the concentration at thermodynamic equilibrium. When taken in terms of the mass transfer quantities relative to the dispersed phase (subscript D), the relation takes the form of the RHS of the equation above where the mass transfer coefficient K_D quantifies the rate of transfer per unit interfacial area, a is the specific interfacial area (area per unit volume), V the contacting fluid volume, and Q_D the volumetric flow rate of the dispersed phase.⁷ Consequently, enhancement of mass transfer efficiency for a given chemical system (a given K_D) can be achieved through the following means: (1) increasing the specific interfacial area through a reduction in dispersed phase droplet size via enhanced mixing intensity, (2) increasing the hold-up volume V , or (3) decreasing the volumetric flow rate of the fluids. In order to achieve the several-fold increase in effective contact time that is required in this case, the main aim of design modifications was to accomplish a significant increase in the holdup volume. At the same time, the need to decrease throughput can be minimized by ensuring that any design changes retain or even enhance mixing intensity leading to the production of smaller droplets and greater overall interfacial area for mass transfer (without any negative effect leading to incomplete physical separation of the phases in the rotor).

The design concept used to achieve these goals involves the addition of recirculation tubes into the outer cylinder of the stationary housing. These recycle channels are oriented so as to use the tangential momentum of the liquid being thrown off the bottom portion of the rotor in the annular space to carry the dispersion upwards and return it to the annular space just below the inlets. This feature increases the hold-up volume through the added space provided by the tube structures and at the same time provides the dispersion with an opportunity for multiple contact passes with the spinning rotor, enhancing mixing.⁸ Two of the design iterations were tested as shown in Figure 1. The first prototype had four helical tubes while the second had five longer tubes with additional modifications for enhanced mixing and stable low-flow operation—these designs are herein referred to as **CC1** and **CC2**, respectively.

3.2 Co-Extraction from PUREX Raffinate & Mo-Scrub

An organic phase solution consisting of 0.6M HEH[EHP] and 45mM T2EHDGA (n-dodecane) was contacted with the PUREX raffinate (spiked with ²⁴¹Am) at ambient temperature (24°C) in **CC1**. Two flow rates were tested: 1) 5.22 mL/min of the organic phase and 5.05 mL/min of the aqueous phase (total 10.27 mL/min) and 2) 6.96 mL/min of the organic phase and 8.07 mL/min of the aqueous phase (total 15.03 mL/min). The results reveal moderate extractions ($D > 4$) of Am at both flowrates, though the overall distribution ratios for the entire PUREX series was lower as the flow rate increased.

With the exception of La, the Ln series exhibited $D > 1$. Palladium and La were not well extracted in this step ($D < 1$ at 15 mL/min). The low distributions of these elements suggest that several stages of nitric acid scrubbing steps could potentially eliminate Pd and La from the later extraction flowsheets. These suggestions were also reported by Lumetta *et al.*² It should also be noted that Fe and Ru were present in solution but the distribution ratios were difficult to calculate by ICP-MS since they were hardly extracted. A separate quantification of Fe was performed using a colorimetric method⁹ which confirmed that the concentration of Fe in the PUREX raffinate was nearly the same before and after contact with the ALSEP solvent.



(a) CAD model rendering of 4-tube housing concept [CC1].
 (b) Snapshot from hydraulic testing of 5-tube enhanced residence time and mixing [CC2].

Molybdenum results were appreciably lower (yet still sufficiently high) than expected when compared with equilibrium values by Gelis and Lumetta.¹ In a separate set of experiments the equilibrium distribution of trace ⁹⁹Mo into either 45mM T2EHDGA or 0.6M HEH[EHP] from 3M HNO₃ was measured by gamma spectroscopy to give $D = 0.002$ and $D = 20.5$, respectively, concluding that Mo is coordinated almost entirely to the acidic extractant in the ALSEP co-extraction step. For the treatment and removal of Mo, two hundred mL of a fresh organic phase (0.6M HEH[EHP] + 45mM T2EHDGA in *n*-dodecane) was equilibrated with 200 mL of a PUREX raffinate (spiked with ²⁴¹Am) in a separatory funnel. The phases were separated and the loaded organic phase was then contacted with a solution of 0.75M AHA + 0.15M citrate, $\text{pH}_0 = 3.79$, $T = 24\text{ }^\circ\text{C}$ at two separate total flow rates. The organic phases were fed at 4.43 mL/min and 5.51 mL/min, the aqueous phases were fed at 4.90 mL/min and 6.18 mL/min, totaling 9.3 mL/min and 11.6 mL/min. Molybdenum was the only element that was significantly scrubbed during this step; palladium was scrubbed to a lesser extent. The results (determined by ICP-MS) showed $D_{\text{Mo}} = 0.34 \pm 0.04$ and 0.38 ± 0.05 for the lower and higher flow rate, respectively. In a separate experiment the same solutions that were used in the contactor were equilibrated with ⁹⁹Mo and quantified using gamma analysis. The result was $D_{\text{Mo}} = 0.13$ which is appreciably lower than the values obtained during the contactor runs. The discrepancy observed during the Mo-scrub could reflect kinetic parameters and warrants further investigations and optimizations. Yttrium, Zr, and the heavier lanthanides were hardly affected ($D > 100$) by the Mo scrub. The light lanthanides (except La) and Am exhibited a satisfactory $D > 17$ for this step.

3.3 Am Strip

Two-hundred mL of 0.75M HEH[EHP] + 50mM T2EHDGA in *n*-dodecane was pre-equilibrated with equal volumes of the same PUREX-raffinate and AHA solution described in the *co-extraction* and the *Mo-scrub*, included with a spike of ²⁴¹Am and ¹⁴⁷Pm. The aqueous phase contained 0.125M HEDTA, 0.2M citrate, $\text{pH} = 2.8$, $T = 21\text{ }^\circ\text{C}$. This pH value was chosen to improve the Am backward-extraction kinetics³. Three flowrates were tested using CC2. The organic phases were fed at 2.9, 3.7, and 4.9 mL/min. The aqueous phases were fed at 3.8, 4.9, and 6.2 mL/min., totalling 6.7, 8.6, and 11.2 mL/min., respectively.

The results of these trials are displayed in Figure 2. The curved trend ranging across La-Nd is not unusual for systems involving HEH[EHP] and HEDTA and reflects the aqueous complexation and extraction equilibria among

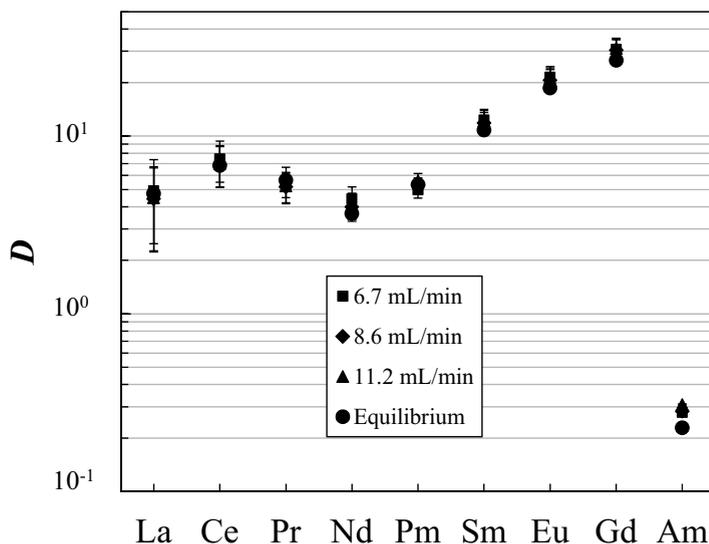


Figure 2: Distribution for Ln and Am and distribution ratios (D) of Am(III) at the Am-strip step using CC2. Organic phase: 50mM T2EHDGA / 0.75M HEH[EHP]; aqueous phase: 0.125M HEDTA / 0.2M citrate, pH 2.81; $T = 21 \pm 2^\circ\text{C}$.

Ln and Am.¹⁰ For nearly all trials the equilibrium batch studies exhibited the lowest D value, the exception to this was found for elements La, Pr, and Pm whose low concentrations in the initial solvent either disregard most practical concerns or assume relatively large error by mass-spectrometry quantification. The remaining elements' extraction efficiency decreased with increasing flow rates which reflect kinetic parameters and/or residence time in the contactor mixing zone. For all flow rates tested the SF of Ln/Am was over 10; the minimum being Nd ($SF = 13.1$) at the fastest flow rate as shown in Table 1. At the slowest flowrate, the SF (Nd/Am) approached the equilibrium value within the experimental error.

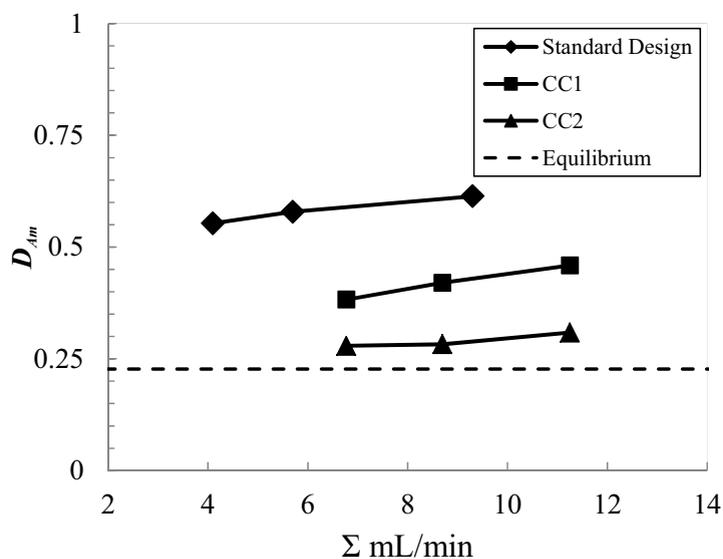


Figure 3: Distribution of Am as a function of centrifugal contactor. Organic phase: 50mM T2EHDGA / 0.75M HEH[EHP]; aqueous phase: 0.125M HEDTA / 0.2M citrate, pH 2.81; $T = 21 \pm 2^\circ\text{C}$.

Table 1: Separation factors of Ln and Am during the Am-Strip described in Figure 2. The uncertainties were derived from $\pm 10\%$ ICP-MS uncertainty through each stage of extraction; Pm was quantified radiometrically.

Σ mL/min	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
equilibrium	20.7 \pm 2.4	29.8 \pm 1.8	24.6 \pm 1.2	16.0 \pm 0.7	23.3 \pm 1%	47.3 \pm 1.9	81.6 \pm 3.2	116 \pm 4
6.7	17.6 \pm 2.4	26.6 \pm 1.9	19.9 \pm 1.0	15.8 \pm 0.7	17.8 \pm 1%	44.1 \pm 1.8	76.8 \pm 3	110 \pm 4
8.6	15.6 \pm 2.1	24.5 \pm 1.8	18.2 \pm 1.0	14.1 \pm 0.6	18.6 \pm 1%	41.8 \pm 1.7	72.9 \pm 3.0	107 \pm 4
11.2	14.5 \pm 2.2	22.6 \pm 1.8	16.9 \pm 1.0	13.1 \pm 0.6	18.1 \pm 1%	39.2 \pm 1.7	68.4 \pm 3.0	100 \pm 4

3.4 Relative contactor efficiencies

With regards to the technological nature of a centrifugal contactor, an advantageous characteristic of annular centrifugal contactors is the short residence time of the two fluids in the annular mixing space within the device—3 to 5 seconds for standard designs under typical operating conditions.¹¹ However, lanthanide/actinide separations processes such as ALSEP or TALSPEAK are known to have kinetic limitations that require liquid-liquid contact time of 30–60s or more to achieve equilibrium separation.^{3,12} Though equation (3) stresses that the separation efficiency can be improved via lower inlet flow rates, it should be noted that centrifugal contactors inherit a threshold minimum total flow rate (as well as a maximum depending on the size of the contactor). Total flow rates below the minimum may not cleanly separate the immiscible phases and phase-carryover can occur. Thus, liquid-liquid centrifugal contactor processes that are targeting higher efficiencies through lower flow rates are bound by this practical threshold that could be overcome by increasing the hold-up volume of a stage.

In order to probe the hold-volume parameter, relative to the standard design, a PUREX-loaded solution of 0.75M HEH[EHP] with 50mM T2EHDGA was tested for Am removal on all three designs using similar or equal total flow rates and an aqueous phase of 0.125M HEDTA with 0.2M citrate, pH 2.8 at 21°C. The results, shown in Figure 2, relay a clear distinction between the three designs. The least efficient was expectedly the standard design which employs the shortest residence time; the fastest exhibited by CC2 with the longest residence time. The batch equilibrium value of 0.22 is represented by the dashed line. Given that all practical considerations were equal to the best of our knowledge during these trials, reasonably sound evidence is provided that the enhanced mixing zones can substantially improve the overall efficiency of the contactor while maintaining the same inlet flow rate.

3.5 Additional Components of ALSEP

Before the spent solvent can be recycled to the *co-extraction* stage, it must be sufficiently voided of all extracted metals from the prior stages. These metals include Y, Zr, Pd, and the Ln series. It was found that the Ln metals (particularly the light Ln) can be adequately stripped into 0.4 – 0.6 M HNO₃ which corresponds to a minimum in extraction equilibria among the binary solvent mixture. This stage was tested using CC1 in a separate set of experiments but is still under development for optimization. It has also been reported that the ligand *N,N,N',N'*-tetraethyldiglycolamide (TEDGA) can effectively strip the Ln from an ALSEP solvent^{1,2} and so its capability should be tested with a CC. Batch experiments have shown that Zr can be stripped into an oxalate solution, though this stage will probably need to be completed outside of a centrifugal contactor at the risk of forming oxalate-precipitates with residual Ln components. Furthermore, the insolubility issues concerning Zr and Sn may be alleviated using the complexing agent CDTA¹³ which could prevent their loading during the initial *co-extraction* step. These applications are currently being tested and refined at Argonne and Pacific Northwest National Laboratory.

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4. Conclusion

In this work we have demonstrated the ALSEP process steps in a single stage 2-cm centrifugal contactor of various designs. The results indicate that Am can be effectively recovered and separated from the lanthanides and fission products. The co-extraction and scrub process steps show very fast interfacial mass-transfer kinetics. Nearly equilibrium separation factors for the Am stripping step have been accomplished when an HEDTA buffered solution at the optimized pH value was used in a modified contactor with an extended mixing zone.

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