Key Words

ALSEP

minor actinides

lanthanides

solvent extraction

diglycolamide

T2EHDGA

TODGA

HEH[EHP]

nitric acid

paritioning

fission products

separation factors

DTPA

citrate buffer

radiolysis resistance

Objective

1. Develop a solvent extraction process to separate minor actinides (Am, Cm) from lanthanides at an industrial scale to enhance nuclear fuel cycle safety and cost-efficiency.

2. Minimize the number of separation steps, flowsheets, chemical consumption, and waste in used nuclear fuel (UNF) reprocessing.

3. Use a novel combination of neutral and acidic extractants (T2EHDGA, TODGA, HEH[EHP]) in an aliphatic diluent (n-dodecane) for effective actinide-lanthanide separation.

4. Conduct coextraction from moderate-to-strong nitric acid and selective stripping of minor actinides using a polyaminocarboxylic acid/citrate buffered solution at pH 3 to 4.5.

5. Achieve high separation factors (exceeding 30 for Nd/Am and up to 60 for Eu/Am) for effective actinide separation under varying HNO3 concentrations.

6. Ensure the process is robust, with extractants that withstand hydrolysis and radiolysis during contact with spent fuel constituents.

7. Conduct further studies on the radiation stability, hydrolysis resistance, and cation organic speciation in the ALSEP solvent.

Methodology

1. Materials and Reagents:

- All chemicals were purchased from Sigma-Aldrich, A.C.S. reagent grade.

- Aqueous solutions were prepared using Milli-Q deionized water.

- Lanthanide and fission product simulant stock solutions were prepared from corresponding nitrate salts.

- TODGA and T2EHDGA were purchased from Eichrom, anhydrous dodecane from Alfa-Aesar, and HEH[EHP] was obtained from Yick-Vick Chemicals.

2. Purity and Concentration Determination

- The purity of acidic extractants was determined by titration in a methanol-water mixture using a Metrohm automated titrator.

- Concentration of NaOH was determined by titrating with 0.1 M HCl and 0.1 M HNO3.

- Purity of extractants was found to be at least 99%.

3. Extraction Procedures

- Liquid scintillation counting (LSC) was performed with / discrimination using a PerkinElmer

Tri-Carb 3100TR.

- counting was performed with a Ge(Li) well detector.

- Inductively coupled plasma mass spectrometry (ICP-MS) was used for analyzing lanthanide and fission product concentrations.

- The pH of aqueous solutions was measured using an Orion 525A+ pH meter calibrated with NIST traceable standards.

4. Experimental Conditions

- Culture tubes containing organic and aqueous phases were shaken on a Genie-2 Vortex mixer.

- The volume ratio of phases was 1:1 unless stated otherwise.

- Contact time for equilibrium in Am extraction was established to be 50-60 seconds.

- Back-extraction kinetics experiments were conducted using organic phases contacted with nitric acid solutions spiked with 241Am and 152Eu.

5. Analysis and Results

- Distribution ratios (D values) for elements were calculated as the ratio of concentration in the organic phase to the aqueous phase.

- Separation factors (SF) were determined as the ratio of distribution ratios for different radionuclides.

- Am and lanthanide partitioning was tested over a range of nitric acid concentrations.

- Selective stripping of minor actinides was achieved using a DTPA/citrate buffered solution at specific pH levels.

6. Radiation Stability and Hydrolysis Resistance

- Studies on the radiation stability and hydrolysis resistance of ALSEP organic phases were planned.

- Investigations into the behavior of fission products and cation organic speciation in ALSEP were

described as ongoing.

Key Findings

Extraction from Nitric Acid Media

- Am Extraction Improvement: Using T2EHDGA or TODGA as neutral extractants significantly improved Am extraction from moderate nitric acid concentrations (1 5 M) compared to CMPO

- Partitioning Behavior: Am and Eu partitioning showed a minimum at around 0.5 M HNO3, and increasing concentrations of HEH[EHP] and T2EHDGA or substituting TODGA for T2EHDGA enhanced Am extraction

- Process Efficiency: Both TODGA and T2EHDGA based processes demonstrated effective An separation from fission products on a laboratory scale using centrifugal contactors

Lanthanide and Americium Separation

- Ln/Am Separation: The ALSEP solvent formulation achieved effective Ln/Am separation, with SF (Separation Factors) for Nd/Am being 36 and for Gd/Am being excessively high due to short contact time favoring heavy Ln/Am separation

- Europium Back-Extraction: The rate of Eu back-extraction decreased at higher pH levels, indicating the influence of citric acid concentration on the back-extraction process

Solvent Stability and Efficiency

- Fe and Mo Handling: While Fe was difficult to scrub from the organic phase, three scrub stages of citric acid at pH 3 effectively removed Mo

- Radiation Stability: The radiation stability of ALSEP organic phases and their hydrolysis effects were to be determined in separate studies

Selective Stripping

- Buffered DTPA Solutions: Selective Am stripping was effective with buffered DTPA solutions,

achieving high separation factors (Nd/Am SF > 30, Eu/Am SF > 60 under some conditions)

- Effect of TODGA Concentration: The Eu/Am separation factor decreased with increasing TODGA concentration, but remained high at concentrations below 0.1 M

Relevance to Study

Extractant Efficiency: Demonstrates the effectiveness of neutral extractants (TODGA, T2EHDGA) in combination with acidic extractants (HEH[EHP], HDEHP) for minor actinide extraction from nitric acid media. This highlights the importance of selecting extractants that can efficiently separate actinides from lanthanides and fission products

Separation Factors: Provides data on separation factors for various lanthanides and actinides, essential for evaluating the selectivity of ligands in nuclear fuel reprocessing. High separation factors (e.g., Nd/Am > 30, Eu/Am > 60) indicate efficient ligand systems

Radiation Stability: Emphasizes the necessity of ligands that can withstand radiolysis and hydrolysis. This is crucial for the long-term stability of solvent extraction systems used in the nuclear fuel cycle

Complexing Agents: Discusses the use of complexing agents like CDTA and oxalic acid to manage the extraction of problematic elements such as zirconium. This insight is valuable for selecting ligands that can selectively bind to desired elements while minimizing interference from others

Process Optimization: Describes optimization strategies for solvent formulations, including adjusting concentrations and phase modifiers. This information is relevant for refining ligand selection to achieve optimal performance in specific nuclear fuel reprocessing scenarios

Industrial Applications: Demonstrates the practical application of ligand systems in industrial-scale processes using centrifugal contactors, underlining the importance of scalable and efficient ligand systems for real-world applications

Buffered Stripping Solutions: Highlights the use of buffered DTPA solutions for selective stripping of

americium, showcasing the importance of ligand systems that can facilitate selective separation processes

Phase Modifer Role: Explains the role of phase modifiers in preventing third phase formation, which is crucial for maintaining the efficiency and stability of the extraction process. This aspect is vital for ligand selection to ensure compatibility and stability in the extraction system

Critical Parameters Identified

High Importance

Chemical Stability

Extractant Purity and Stability

- The article discusses the purification of extractants (HEH[EHP], HDEHP) and the importance of their stability under extraction conditions
- Stability of extractants in the presence of nitric acid and during the separation process is crucial for consistent performance

Radiolysis Resistance

Radiation Stability

- The document emphasizes the necessity for ligands that can withstand radiolysis, highlighting the stability of TODGA and T2EHDGA under radiation
- Further studies on the radiation stability of ALSEP organic phases are planned to ensure long-term performance

Thermodynamics

Separation Factors

- High separation factors (e.g., Nd/Am > 30, Eu/Am > 60) indicate strong thermodynamic selectivity of the ligands towards specific metal ions, crucial for effective separation

- The thermodynamic feasibility of using diglycolamide extractants in combination with acidic extractants for efficient actinide-lanthanide separation

Medium Importance

Kinetics (forwards and reverse)

Extraction and Stripping Kinetics

- The kinetics of Am and Eu extraction and back-extraction were studied, showing the importance of optimal contact times for achieving equilibrium

- The influence of extractant concentration on the kinetics of separation processes, with specific attention to TODGA and HEH[EHP] mixtures

Loading Capacity

Capacity of Ligands: The document mentions the concentration ranges of extractants used and their loading capacities, which are important for determining the efficiency and scalability of the separation process

Operational Condition Range

Flexibility of Extraction Conditions

- The ability to conduct effective extraction over a wide range of nitric acid concentrations (1 5 M) showcases the operational flexibility of the ligands used

- Adjustments in ligand concentrations and combinations to optimize separation under varying conditions

Low Importance

Solubility

Solubility of Extractant: While the solubility of extractants like TODGA and T2EHDGA in aliphatic

diluents (e.g., n-dodecane) is noted, it is considered less critical than other factors as it can be managed through solvent selection

Dispersion Numbers:

Mass Transfer Efficiency: The influence of phase modifiers to prevent third phase formation and improve mass transfer efficiency is discussed, but this is more specific to system setup and considered lower priority

Phase Disengagement: The document touches on the importance of phase disengagement, particularly the role of phase modifiers in preventing third phase formation, which is essential for practical separation but highly dependent on system design