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Key Words

lanthanide separation

actinide separation

ALSEP

T2EHDGA

TODGA

HEH[EHP]

PC88A

Objective

1. Develop a Solvent Extraction System: Create an extractant phase using either N,N,N ,N -tetraoctyldiglycolamide (TODGA) or N,N,N ,N -tetra(2-ethylhexyl)diglycolamide (T2EHDGA) combined with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) to effectively separate americium (Am) and curium (Cm) from lanthanides and other fission products in a single extraction cycle.
2. Explore Co-Extraction Capabilities: Investigate the ability of neutral donor extractants to co-extract trivalent actinides and lanthanides from nitric acid solutions.
3. Establish Aqueous Phase Chemistry: Use citrate-buffered diethylenetriaminepentaacetic acid (DTPA) solutions to selectively transfer actinides to the aqueous phase while keeping lanthanides in the organic phase.
4. Achieve High Separation Factors: Aim to achieve separation factors on the order of 20 to 40 for effective separation of actinides from lanthanides.
5. Evaluate and Compare Extractant Combinations: Compare various combinations of neutral and acidic extractants, such as CMPO with HDEHP, CMPO with HEH[EHP], TODGA with HDEHP, and

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TODGA with HEH[EHP], to identify the most efficient combination for the ALSEP process.

6. Investigate Extractant Independence: Ensure that the chosen neutral and acidic extractants work independently with minimal interaction to improve the efficiency of the separation process.

7. Proof-of-Principle Experiment: Conduct a proof-of-principle experiment using an ALSEP solvent formulation to validate the process steps, including extraction, scrubbing, stripping, and regeneration of the solvent.

8. Optimize Process Steps: Optimize various process steps, including nitric acid scrubbing, citrate scrubbing, and minor actinide stripping, to improve the separation efficiency and address issues such as contamination by molybdenum (Mo).

9. Demonstrate Feasibility: Demonstrate the feasibility of the ALSEP concept by showing that trivalent lanthanides and actinides can be co-extracted from nitric acid media, selectively stripped, and effectively managed in the solvent regeneration process.

Methodology

Materials

Extractants and Chemicals:

- N,N,N ,N -tetraoctyldiglycolamide (TODGA) and N,N,N ,N -tetra(2-ethylhexyl)diglycolamide (T2EHDGA) were procured from Eichrom Technologies and used as received.
- 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) was obtained from Yick-Vic Pharmaceuticals Ltd and purified.
- Normal dodecane, diethylenetriaminepentaacetic acid (DTPA), citric acid, and N,N,N ,N -tetraethyldiglycolamide (TEDGA) were used as received.
- The 241Am tracer solution was obtained from Isotope Products Laboratories.

Distribution Measurements

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Experimental Conditions

- Aqueous solutions contained between 0.1 and 5 mmol/L of each element, except Fe (0.02 to 0.06 mmol/L).

- Equal volumes of aqueous and organic phases were mixed with a vortex mixer or wrist-action shaker.

- Experiments were performed at ambient temperature (21 to 23 C).

- Mixing times extended up to 3 hours.

- Distribution ratios were determined at equilibrium conditions, with aliquots taken for ICP-OES analysis at cumulative mixing times of 1, 5, 15, and 30 minutes.

- Specific mixing conditions are provided in respective figure captions.

Proof-of-Principle Experiment

Experimental Setup

- ALSEP solvent formulation: 0.075 mol/L TODGA + 1.0 mol/L HEH[EHP] in n-dodecane

- Simulated acidic high-level waste (HLW) solution as the feed.

- Batch contacts were performed to represent ALSEP steps: extraction, nitric acid scrubbing, citrate scrubbing (to remove Mo), minor actinide stripping, lanthanide stripping, and Zr stripping.

- Detailed contact steps and volumes are provided in a table format.

Extraction and Stripping Steps

Extraction

- Contacting 48 mL of 0.075 mol/L TODGA + 1.0 mol/L HEH[EHP] in n-dodecane with 48 mL of aqueous feed.

- Mixing by vortex followed by orbital shaking, and phase separation by centrifugation.

Stripping

Analytical Methods

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Measurement Techniques

- ICP-OES analysis for nonradioactive elements, with organic-phase concentration calculated from the difference in aqueous concentrations before and after contact.

- Gamma spectroscopy for 241Am distribution ratios, with automated gamma counting using a NaI(Tl) detector.

Optimization and Validation

Process Optimization

- Optimization of scrubbing steps to ensure Mo does not contaminate the minor actinide product.

- Validation through consistent results in the distribution ratios and separation factors.

Key Findings

Kinetics of Extraction from Nitric Acid

Equilibrium Attainment: Extraction equilibrium was achieved within 5 minutes of vortex mixing for trivalent lanthanides and Am, while Mo(VI) and Fe(III) showed slower extraction kinetics

Extraction Behavior: Yttrium(III) exhibited similar extraction behavior to the trivalent lanthanides and Am. Zr(IV) was extracted so strongly that it could not be detected in the aqueous phase after 5 minutes, with distribution ratios greater than 3700.

Extraction as a Function of HNO3 Concentration

Distribution Ratios: Both T2EHDGA and TODGA extractants showed increased distribution ratios for Am and lanthanides with increasing HNO3 concentration, with T2EHDGA being a somewhat weaker extractant than TODGA.

Optimization Potential: High distribution ratios at several molar HNO3 are desirable. The TODGA and T2EHDGA extractants maintain high distribution ratios at high HNO3 concentrations, unlike

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CMPO-based formulations.

Lanthanide/Americium Separation

Stripping Efficiency: Selective stripping of Am from lanthanide-loaded solvent was effective using 0.015 mol/L DTPA + 0.2 mol/L citrate at pH around 3, with minimum lanthanide/americium separation factors around 30.

pH Dependency: Reducing the DTPA concentration to 0.010 mol/L increased the Nd distribution ratios and improved the separation factors slightly in the pH range 3.5 to 4.3.

ALSEP Proof-of-Principle Experiment

Efficienct Extraction: All lanthanides were efficiently extracted, with distribution ratios generally increasing with atomic number.

Stripping Performance: Am was efficiently stripped in multiple contacts, with separation factors for Nd/Am improving in subsequent stripping contacts.

Process Consistency: The experiment confirmed the feasibility of the ALSEP concept, demonstrating efficient extraction, scrubbing, and stripping steps. Zirconium and molybdenum were also managed effectively in the process.

Conclusion

Once-Cycle Separation: The ALSEP concept effectively allows for the co-extraction of trivalent lanthanides and actinides from nitric acid media and their selective stripping into separate phases using appropriate buffers and extractants.

Process Optimization: Some optimization, particularly of the scrubbing steps, is needed to prevent contamination and ensure high separation efficiency.

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Relevance to Study

Extraction Efficiency: The document highlights the efficiency of N,N,N ,N -tetraoctyldiglycolamide (TODGA) and N,N,N ,N -tetra(2-ethylhexyl)diglycolamide (T2EHDGA) in co-extracting trivalent actinides and lanthanides from nitric acid media. This efficiency is critical in selecting ligands for the nuclear fuel cycle to ensure effective separation processes.

Selective Stripping: The study demonstrates the use of citrate-buffered diethylenetriaminepentaacetic acid (DTPA) solutions for selective stripping of actinides from lanthanides. Understanding the behavior of these ligands in separating chemically similar elements aids in selecting appropriate ligands for nuclear waste management.

Ligand Independence: The research shows the importance of minimal interaction between neutral and acidic extractants (e.g., TODGA or T2EHDGA with HEH[EHP]). This independence is crucial for ligand selection to ensure that each component works effectively without undesired interactions.

Optimization Insights: Detailed findings on the optimization of extraction and stripping steps provide valuable insights into how ligands should be selected and tuned for optimal performance in separating actinides and lanthanides, which is a key aspect of nuclear fuel cycle chemistry.

Experimental Validation: The document validates the ALSEP concept through a series of experiments, confirming the practicality of the chosen ligands in real-world applications. This validation is essential for selecting ligands that can reliably function under operational conditions encountered in the nuclear fuel cycle.

Distribution Ratios and Separation Factors: Information on distribution ratios and separation factors for various ligands under different conditions helps in comparing and selecting the best ligands for specific separation tasks within the nuclear fuel cycle.

Critical Parameters Identified

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High Importance

Chemical Stability:

Description: The study investigates the chemical stability of ligands (TODGA and T2EHDGA) under various nitric acid concentrations and in the presence of other extractants (HEH[EHP]). This is essential for ensuring that the ligands remain functional over the duration of the separation process.

Findings:

- The extractants TODGA and T2EHDGA maintain their extraction efficiency even at high nitric acid concentrations, indicating good chemical stability.
- HEH[EHP] is used in combination with these ligands without significant degradation or adverse interaction, highlighting their compatibility and stability in mixed systems.

Radiolysis Resistance:

Description: The study does not explicitly discuss radiolysis resistance; however, the use of ligands in the separation of radioactive elements like Am and Cm implies that their resistance to radiolysis is an underlying consideration.

Findings: The practical use of TODGA and T2EHDGA in environments involving radioactive elements suggests an implicit resilience to radiolytic conditions.

Thermodynamics:

Description: Thermodynamic parameters such as distribution ratios and separation factors are fundamental in assessing the feasibility and efficiency of the extraction process.

Findings:

- High distribution ratios for Am and lanthanides at various nitric acid concentrations indicate favorable thermodynamics for the extraction process.
- Separation factors achieved in the stripping steps reflect the selective binding strengths of the ligands towards specific metal ions, underpinning the thermodynamic feasibility of the separation.

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Medium Importance

Kinetics (forwards and reverse)

Description: The study addresses the kinetics of extraction and stripping processes, affecting the speed and equilibrium position of the separations.

Findings:

- Equilibrium for trivalent lanthanides and Am is reached within 5 minutes of vortex mixing, indicating fast kinetics.

- Slower kinetics for Mo(VI) and Fe(III) highlight areas for potential process optimization.

Loading Capacity:

Description: Loading capacity determines how much material can be processed before the ligand becomes saturated.

Findings: The proof-of-principle experiment demonstrates efficient extraction and loading of lanthanides and Am, with distribution ratios exceeding 1000 for Zr and Mo, indicating high loading capacities.

Operational Condition Range:

Description: The ability of ligands to operate under a broad range of conditions is assessed by examining their performance across different nitric acid concentrations and pH levels.

Findings:

- TODGA and T2EHDGA exhibit high distribution ratios over a wide range of nitric acid concentrations, showcasing their flexibility.

- Stripping experiments with varying pH levels demonstrate the ligands adaptability to different operational conditions.

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Low Importance

Solubility

Description: While solubility is important, it is often managed through solvent selection.

Findings: The study uses n-dodecane as the solvent, indicating sufficient solubility of the ligands in this medium.

Dispersion Numbers:

Description: This parameter influences mass transfer efficiency but is highly system-specific.

Findings: The study does not explicitly address dispersion numbers; however, efficient mixing techniques (vortex and orbital shaking) are employed to ensure effective phase contact.

Phase Disengagement:

Description: Critical for practical separation of phases after extraction.

Findings: Phase separation is achieved through centrifugation, indicating effective phase disengagement in the experimental setup.