REFERENCE: 20044

Key Words

solvent extraction

americium

curium

separation

high-level wastes

radioactive waste

Objective

1. Address the chemical similarity between americium (Am) and curium (Cm): Given their similar chemical properties, the article aims to review and identify extraction systems that can effectively separate these two elements.

2. Evaluate extraction systems for separating Am(III) and Cm(III): The focus is on systems developed in the last 20 years that use solvent extraction to achieve this separation from nitric acid solutions.

3. Discuss the chemistry behind improved separation: The article aims to provide a detailed discussion on the chemical principles that lead to the improved separation of americium from curium, including the role of various extractants and their thermodynamic and kinetic behaviors.

4. Review current technologies and methodologies: It aims to review the state-of-the-art solvent extraction systems used in nuclear waste reprocessing, particularly focusing on the mutual separation of americium and curium, which is a critical step for reducing the radiotoxicity of high-level waste.

Methodology

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1. Dynamic Mode Testing of Extraction Systems:

- Various extraction systems were tested dynamically to assess their efficiency in separating Am(III) and Cm(III).

- These tests involved multi-stage counter-current processes to achieve high purity of americium and curium products. The separation factors, distribution ratios, and stability of streams were evaluated.

2. Specific Processes:

- DMDOHEMA Process:

-- The DMDOHEMA extraction system, based on malonamide, was tested with americium and curium solutions.

-- The process consisted of 56 stages: 24 extraction, 24 scrubbing, and 8 back-extraction stages.

-- A separation factor (SFAm/Cm) of 1.5 was achieved, with the final americium product containing 0.7% curium and the curium product containing 0.6% americium.

- LUCA Process:

-- The LUCA process was tested using centrifugal extractors.

-- The initial solution contained trace amounts of americium-241, curium-244, europium-152, and californium-252.

-- The process achieved high separation efficiency with just 16 stages of extraction and scrubbing, achieving 99.53% purity of americium.

- ADAAM Process:

-- The ADAAM(EH) process used aliphatic diamide amine and was tested dynamically.

-- The system established equilibrium within 20 seconds for extraction and 90 seconds for back extraction.

-- The counter-current setup consisted of 32 mixer-settler stages: 8 extraction, 8 scrubbing, and 16 stripping stages.

- EXAm Process:

-- The EXAm (Extraction of Americium) process focused on extracting americium directly from PUREX raffinates.

-- The process used a mixture of N,N`-dimethyl-N,N -dioctyl-2(hexyloxy)ethyl malonamide and HDEHP with the addition of the water-soluble ligand TEDGA to increase the separation factor.

-- The process involved 32 stages of extraction/scrubbing.

3. Evaluation and Optimization:

- The methodology included the evaluation of the chemical stability, radiolysis resistance, and kinetic behavior of the extractants.

- Optimization was performed to address issues such as hydrodynamic problems during americium stripping and the tendency of extraction systems to extract light lanthanides.

Key Findings

1. DMDOHEMA Process:

- Achieved a separation factor (SFAm/Cm) of 1.5.

- Americium product contained 0.7% curium, and curium product contained 0.6% americium.

- Encountered hydrodynamic problems during Am stripping.

- Highlighted the challenges of separating americium and curium with a low separation factor

2. LUCA Process:

- Used centrifugal extractors for efficient separation.

- Initial solution contained trace amounts of various radionuclides.

- Achieved 99.53% purity of americium with a high separation factor in just 16 stages.

- Faced challenges related to organic phase stability and waste management due to sulfate and

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phosphate residues

3. ADAAM Process:

- Utilized aliphatic diamide amine ADAAM(EH) for separation.
- Achieved optimal separation factor at 1.5 M nitric acid concentration.
- Established equilibrium quickly, with 20 seconds for extraction and 90 seconds for back extraction.
- Dynamic tests showed high separation efficiency with a counter-current setup of 32 mixer-settler stages

4. EXAm Process:

- Focused on extracting americium directly from PUREX raffinates.
- Improved separation factor by adding the water-soluble ligand TEDGA.
- Achieved a separation factor of 2.5 in the presence of TEDGA.
- Faced issues with extracting light lanthanides, resulting in contamination of the americium product with neodymium and requiring 68 stages for effective separation

5. Comparison and Evaluation:

- ADAAM process was highlighted as promising due to high separation factors and adherence to the CHON principle
- Noted the lack of information on radiation stability of ADAAM ligands.
- Emphasized the complexity and difficulty in separating americium and curium due to their similar chemical properties.
- Identified the need for further research to improve extraction systems and achieve higher selectivity

6. General Observations:

- Reviewed various extraction systems, noting that only a few have been tested in counter-current mode.

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- Recognized the challenges posed by the chemical similarity of Am(III) and Cm(III), making selective extraction difficult.
- Suggested that structural changes in ligands might improve selectivity but require extensive studies to understand their effects

Conclusion

1. Difficulty of Separation:

- The separation of americium (Am) and curium (Cm) remains challenging due to their similar chemical properties.
- Few solvent extraction systems have been tested in counter-current mode, underscoring the difficulty in achieving effective separation.

2. Extractants and Binding Centers:

- Extractants with soft binding centers, such as aromatic nitrogen or sulfur atoms, have shown reasonably high separation factors for americium from lanthanides (SFAm/Ln 50 100).
- However, only a small number of extractants or extraction systems achieve SFAm/Cm values higher than 1.5, highlighting the need for more selective extractants.

3. Challenges in Predicting Selectivity

- The reasons for the higher selectivity of certain extractants are not well understood and are not easily predicted by existing theories like Pearson s HSAB theory.

4. ADAAM Process:

- The ADAAM process shows promise due to its high separation factors and adherence to the CHON principle.
- However, there is a lack of information on the radiation stability of ADAAM ligands, which is crucial for practical applications.

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5. Need for Further Research:

- Extensive studies are needed to understand the structure-property relationships of ligands, model the structures of complexes, and analyze the chemical bonds between metal cations and organic molecules.
- This understanding is essential to improve the selectivity and efficiency of solvent extraction systems for americium and curium separation

Relevance to Study

Challenges of Americium and Curium Separation: The article underscores the inherent difficulty in separating Am(III) and Cm(III) due to their similar chemical properties, which is crucial for designing effective ligands in nuclear fuel reprocessing

Evaluation of Extractants: Various extractants are reviewed, highlighting their performance in separating americium and curium. The use of soft donor ligands (e.g., N-heterocyclic compounds) is shown to achieve higher selectivity, which is critical for ligand design

Selectivity and Stability: The article identifies the importance of both selectivity and stability under radiation and acidic conditions. Ligands that maintain stability while providing high selectivity for americium over curium are prioritized

Impact of Structural Modifications: Structural modifications of ligands, such as the introduction of specific functional groups (e.g., chlorine atoms in phenanthroline moiety), significantly affect their extraction properties and selectivity. This insight is vital for designing new ligands tailored for specific separation tasks

Practical Apllication and Testing: The study includes dynamic testing of various extraction processes (e.g., DMDOHEMA, LUCA, ADAAM), providing practical data on their efficiency and operational challenges, which are essential for real-world applications

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Radiation Stability: The review emphasizes the need for ligands that are resistant to radiolysis. The degradation of ligands under radiation exposure can lead to loss of efficiency and increased waste, making radiation stability a crucial factor in ligand selection

Future Research DIrections: The article suggests further research into the structure-property relationships of ligands, particularly focusing on enhancing selectivity and stability, which are key for advancing nuclear fuel cycle chemistry

Critical Parameters Identified

High Importance

1. Chemical Stability: Ligands with high chemical stability are essential for prolonged functionality in the harsh chemical conditions of nuclear fuel reprocessing.

- Finding: The stability of ligands such as ADAAM(EH) under various chemical conditions is highlighted as crucial for effective separation

2. Radiolysis Resistance: Resistance to degradation under radiation is vital to maintaining the efficiency of the separation process.

- Finding: The need for ligands that can resist radiolysis is emphasized. Extractants like those in the ADAAM process are promising, but their radiation stability needs further investigation

3. Thermodynamics: Understanding the thermodynamic properties of the separation process is critical for determining the selectivity and binding strength of ligands.

- Finding: Thermodynamic parameters such as the separation factor (SFAm/Cm) and distribution ratios (DAm, DCm) were evaluated to understand the efficiency of various extractants

Medium Importance

1. Kinetics: The kinetics of ligand interactions affect the speed and reversibility of the separation

process.

- Finding: The ADAAM process demonstrated quick equilibrium establishment, indicating favorable kinetics for separation

2. Loading Capacity: The ability of a ligand to handle large amounts of material before becoming saturated is important for process efficiency.

- Finding: The study evaluated various ligands' capacity to handle high concentrations of americium and curium without losing efficiency

3. Operational Condition Range: Ligands must perform well under a wide range of operational conditions to ensure process flexibility.

- Finding: Extractants like DMDOHEMA and LUCA were tested under varying nitric acid concentrations to assess their performance and operational range

Low Importance

1. Solubility: While important, solubility issues can often be managed by choosing appropriate solvents or conditions.

- Finding: Ligands such as H4TPAEN showed low solubility in nitric acid, which was a limitation but could potentially be managed with suitable solvent selection

2. Dispersion Numbers: The efficiency of mass transfer between phases is less critical and highly system-specific.

- Finding: The article did not focus heavily on dispersion numbers, as they are often conditional and dependent on specific system setups

3. Phae Disengagement: Critical for practical separation of phases but highly dependent on system design and operation.

- Finding: The study briefly mentioned phase disengagement issues, such as hydrodynamic problems encountered during the DMDOHEMA process, but this was not a primary focus