REFERENCE: 20039

Key Words

amide

diamide

reprocessing

mizer-settlers

actinide-partitioning

Objective

1. Develop alternatice extractants for nuclear fuel reprocessing:

- Investigate amides and diamides as potential replacements for traditional extractants like tri-n-butyl phosphate (TBP) in the PUREX and THOREX processes.

- Explore the potential of N,N-dihexyl octanamide (DHOA) as a more efficient extractant for plutonium in uranium reprocessing compared to TBP.

2. Improve the separation efficiency of uranium and thorium:

- Evaluate the branched-chain amide N,N-di(2-ethylhexyl) isobutyramide (D2EHIBA) for the selective recovery of 233U from irradiated thorium.

- Compare the performance of D2EHIBA with TBP in terms of separation efficiency, especially in the presence of thorium and fission products.

3. Enhance the partitioning of minor actinides from high-level nuclear waste:

- Assess the performance of N,N ,N,N -dimethyl dibutyl tetradecyl malonamide (DMDBTDMA) for the partitioning of minor actinides from high-level waste containing a significant amount of uranium.

- Focus on the extraction behavior of various metal ions, including Pu, U, Am, and fission products, using DMDBTDMA in nitric acid medium.

4. Address challenges associated with TBP-based processes:

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- Identify and mitigate the drawbacks of using TBP, such as vulnerability to radiation, formation of degradation products, and issues with third-phase formation.

- Compare the degradation behavior, extraction efficiency, and operational conditions of amides and diamides with those of TBP.

5. Investigate the physicochemical properties and stability of amide extractants:

- Study the physical and chemical properties of amides and diamides, including their solubility, stability under irradiation, and extraction kinetics.

- Perform laboratory batch studies and mixer settler experiments to evaluate the practical applicability of these extractants in nuclear fuel reprocessing.

Methodology

N/A - review article

Key Findings

1. Efficiency of Amides and Diamides:

- N,N-dihexyl octanamide (DHOA) extracts Pu more efficiently than TBP under uranium loading conditions.

- N,N-di(2-ethylhexyl) isobutyramide (D2EHIBA) significantly improves the separation of 233U from Th and fission products compared to TBP.

2. Advantages Over TBP:

- Amides and diamides exhibit better chemical stability and can be incinerated, reducing secondary radioactive waste.

- They show higher resistance to radiation-induced degradation compared to TBP, producing benign degradation products like carboxylic acids and amines.

3. Selective Extraction:

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- DHOA and D2EHIBA selectively extract actinides (e.g., Pu and 233U) over other elements such as Zr, Ru, and Th.
- DMDBTDMA shows promise in extracting minor actinides (e.g., Am, Cm) from high-level waste with a high uranium content.

4. Thermodynamic and Kinetic Properties:

- DHOA has a higher extraction constant for U(VI) and Pu(IV) compared to TBP.
- The distribution coefficients (D values) for Pu(IV) with DHOA are significantly higher than those with TBP, both at trace and macro concentrations.

5. Operational Conditions

- The limiting organic concentration (LOC) for U(VI) with DHOA is higher than that for DHHA, making it more suitable for process applications.
- Mixer settler studies confirm that DHOA can achieve quantitative extraction of U and Pu with fewer stages compared to TBP.

6. Radiolytic Degradation

- The main degradation products of amides under gamma irradiation are carboxylic acids and amines, which are easily washable with dilute acid/water.
- Radiolytic degradation of DHOA results in higher decontamination factors (DF) for U and Pu compared to TBP.

7. Practical Applications:

- Mixer settler runs demonstrate the potential of D2EHIBA for the recovery of 233U from irradiated thorium, with lower uranium loss to the raffinate and higher decontamination factors compared to TBP.
- D2EHIBA exhibits better stripping behavior for U from the loaded organic phase compared to TBP.

8. Extraction of Minor Actinides:

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- DMDBTDMA efficiently extracts Am(III) and Cm(III) from nitric acid medium, showing higher distribution ratios for actinides compared to fission products like Sr and Cs.

- The extraction behavior of DMDBTDMA is influenced by the presence of nitric acid, with higher D values for actinides at 3-4 M HNO3.

9. Comparative Analysis

- The DIAMEX process using DMDBTDMA offers advantages over the TRUEX process, including simpler synthesis, no need for phase modifiers, and complete incinerability.

- DIAMEX solvent shows comparable or better extraction capabilities for actinides and reduced secondary waste compared to TRUEX solvent.

10. Structural Influence

- The structure of amides and diamides, such as the nature of alkyl groups, significantly affects their extraction properties and stability.

- Branched-chain amides like D2EHIBA provide better separation efficiency due to steric hindrance effects on thorium extraction.

Relevance to Study

High Efficiency: Amides such as N,N-dihexyl octanamide (DHOA) and N,N-di(2-ethylhexyl) isobutyramide (D2EHIBA) demonstrated superior extraction efficiencies for uranium and plutonium compared to traditional extractants like TBP (Tri-n-butyl phosphate) .

Chemical Stability: Amides and diamides offer better chemical stability, reducing secondary waste volume due to their incinerability, compared to the non-incinerable nature of TBP, which results in significant secondary radioactive waste .

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Radiation Resistance: These ligands show higher resistance to radiolytic degradation. The degradation products are more benign (carboxylic acids and amines) compared to TBP's harmful degradation products (HDBP, H2MBP) .

Selective Extraction: D2EHIBA exhibits high selectivity in extracting uranium over thorium and various fission products, which is crucial for efficient separation processes in the nuclear fuel cycle .

Operational Efficiency: The amides tested allow for fewer mixer-settler stages and reduced uranium loss to the raffinate compared to TBP, indicating more efficient operational conditions .

Thermal Performance: The study shows that the distribution coefficients (D values) for uranium remain stable even at higher temperatures, which is beneficial for maintaining extraction efficiency under varying operational conditions .

Environmental Impact: The potential to incinerate used amide-based solvents helps in reducing the environmental impact of nuclear fuel reprocessing by minimizing the volume of secondary waste .

Critical Parameters Identified

High Importance

1. Chemical Stability

- Amides and diamides offer better chemical stability compared to TBP, reducing secondary waste volume due to their incinerability
- Degradation products of amides are benign (carboxylic acids and amines) and easily washable with dilute acid/water, unlike TBP which requires alkali wash, producing more secondary waste.

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2. Radiolysis Resistance

- Amides and diamides show higher resistance to radiolytic degradation.

- Radiolytic degradation of DHOA results in higher decontamination factors (DF) for U and Pu compared to TBP.

- Main degradation products are carboxylic acids and amines, which are less problematic than TBP's degradation products.

3. Thermodynamics

- DHOA has higher extraction constants (log Kex) for U(VI) and Pu(IV) compared to TBP.

- Distribution coefficients (D values) for Pu(IV) with DHOA are significantly higher than those with TBP, indicating stronger binding strength towards specific metal ions.

Medium Importance

1. Kinetics

- Mixer settler studies show that DHOA can achieve quantitative extraction of U and Pu with fewer stages compared to TBP, indicating efficient kinetics.

2. Loading Capacity:

- Limiting organic concentration (LOC) for U(VI) with DHOA is higher than that for DHHA, making it more suitable for process applications.

- DHOA exhibits better loading capacities for U and Pu under operational conditions.

3. Operational Condition Range

- Amides and diamides are stable under a broad range of nitric acid concentrations, with DHOA and D2EHIBA not forming third phases up to high acidities.

- D2EHIBA provides efficient separation of 233U from Th and Pa in the acidity range of 1 4 M HNO3.

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Low Importance

1. Solubility: Amides like DHOA readily dissolve in n-dodecane and do not form third phases with nitric acid (up to 7 M), demonstrating good solubility management.
2. Dispersion Numbers: Not specifically addressed in the study, but efficient mass transfer between phases was observed in mixer settler experiments with DHOA and D2EHIBA.
3. Phase DIsengagement: Mixer settler runs demonstrate efficient phase disengagement with DHOA and D2EHIBA, with lower uranium loss to the raffinate and higher decontamination factors compared to TBP.