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Key Words

actinide

lanthanide

separation

extraction

N,O-hybrid extractant

Objective

1. Develop Efficient Separation Processes: Review and develop technological processes for the efficient separation of minor actinides from spent nuclear fuel (SNF) components.

2. Close the Nuclear Fuel Cycle: Investigate N,O-hybrid donor ligands for their potential in achieving a closed nuclear fuel cycle, which includes the reprocessing and reuse of separated fissile nuclides such as uranium, plutonium, and americium.

3. Evaluate Ligand Performance: Systematically review available literature and provide detailed explanations on the behavior and performance of the most promising N,O-hybrid donor ligands in liquid-liquid extraction processes.

4. Improve Nuclear Cycle Analytics: Discuss the application of N,O-hybrid donor ligands in nuclear cycle analytics through their incorporation in chemical sensors.

5. Optimize Separation Conditions: Determine optimal conditions for the separation of actinides from lanthanides and other components present in SNF, focusing on selective binding, radiation stability, hydrolytic stability, and extraction efficiency under various acid concentrations.

6. Explore New Extractants: Investigate new extractants, including diamides of dipicolinic acid (DPA), phenanthroline-2-carboxylic acid (PTA), and others, for their ability to selectively extract actinides from nitric acid solutions.

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7. Develop Flowsheets for HLW Processing: Propose and test technological flowsheets for the separation of actinides from high-level waste (HLW) based on the use of specific N,O-hybrid ligands and solvents.

8. Study Ligand Complexation and Stability: Obtain and characterize complexes of N,O-hybrid ligands with various actinides and lanthanides, studying their structural properties, binding energies, and extraction efficiency.

Methodology

Methodology

1. Literature Review: A comprehensive review of existing literature on N,O-hybrid donor ligands for the separation of actinides from spent nuclear fuel (SNF) is conducted. This involves examining previous studies and identifying the most promising ligands for further analysis.

2. Selection of N,O-Hybrid Donor Ligands: Various N,O-hybrid donor ligands, including amides of 2-pyridinecarboxylic acid, diamides of 2,6-pyridinedicarboxylic acid, amides of 1,10-phenanthroline-2-carboxylic acid, and others, are selected for detailed investigation based on their reported effectiveness in actinide separation.

3. Synthesis and Characterization of Ligands: The selected ligands are synthesized using established chemical procedures. Their structures are confirmed using spectroscopic methods such as NMR, UV-Vis spectroscopy, and mass spectrometry.

4. Liquid-Liquid Extraction Experiments:

- The extraction behavior of the synthesized ligands is studied using liquid-liquid extraction techniques. This involves preparing solutions of actinides and ligands in appropriate solvents and measuring the distribution ratios of actinides between the aqueous and organic phases.

- Various parameters such as ligand concentration, acidity of the aqueous phase, and type of solvent are systematically varied to optimize the extraction conditions.

5. Radiation and Hydrolytic Stability Tests: The stability of the ligands under radiation and acidic conditions is assessed. This involves exposing the ligands to simulated radioactive environments and high acid concentrations, followed by monitoring any degradation or loss of extraction efficiency.

6. Complexation Studies:

- The complexation of ligands with actinides is studied through various analytical techniques such as X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS), and computational methods.
- The structures of the formed complexes are analyzed to understand the binding interactions and selectivity of the ligands towards actinides over lanthanides.

7. Development of Separation Flowsheets:

- Based on the experimental results, flowsheets for the separation of actinides from SNF are developed. These flowsheets outline the step-by-step procedures for the extraction and purification processes.
- The proposed flowsheets are tested under dynamic conditions using simulated SNF solutions to evaluate their practical applicability.

Key Findings

1. Amides of 2-Pyridinecarboxylic (Picolinic) Acid (PA)

- Selectivity: Amides of picolinic acid show selective extraction towards actinides with the extraction capacity series U(VI) < Ln(III) < Th(IV).
- Limitations: These ligands are effective only at very low concentrations of nitric acid, limiting their practical applicability.

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2. Diamides of 2,6-Pyridinedicarboxylic (Dipicolinic) Acid (DPA)

- Extraction Ability: Tetraalkyldiamides of dipicolinic acid demonstrate high extraction ability for tetra- and hexavalent actinides.

- Selectivity: DPA ligands show high selectivity for americium over lanthanides, achieving a separation factor DAm/DEu of 6.

- Radiolytic Stability: DPA solutions exhibit high radiolytic stability, making them suitable for use in radioactive environments.

3. Amides of 1,10-Phenanthroline-2-carboxylic Acid (PTA)

- Selectivity: PTA ligands show increased selectivity for americium over europium, with separation factors (SFAm/Eu) reaching up to 20.

- Extraction Efficiency: These ligands are effective for extraction from low nitric acid concentrations but show decreased efficiency at higher acid concentrations.

4. Diamides of 2,2 -Dipyridyl-6,6 -dicarboxylic Acid (BPyDA)

- Actinide Extraction: BPyDA ligands selectively extract actinides from nitric acid solutions with high separation factors (SF) for Am/Eu exceeding 20.

- Complexation: BPyDA forms stable complexes with actinides, contributing to effective extraction processes.

5. Diamides of 6,6 (2,2 :6 ,2 -Tripyridine)-dicarboxylic Acid (TPyDA)

- Extraction Ability: TPyDA ligands exhibit high extraction ability for Pu(IV), Np(V, VI), and U(VI) but show weak extraction for lanthanides and americium.

- Limitations: The high basicity of TPyDA ligands results in decreased extraction efficiency at higher nitric acid concentrations.

6. Diamides of 1,10-Phenanthroline-2,9-dicarboxylic Acid (PhenDA)

- Extraction Efficiency: PhenDA ligands have high extraction efficiency for actinides, with the extraction order Th(IV) > U(VI) > Pu(IV) > Np(V) > Am(III) > Cm(III).

- Separation Factors: These ligands achieve high separation factors for Th(IV), U(VI), and Am(III) over Eu(III), making them effective for selective extraction.

- Structural Analysis: X-ray diffraction and other analytical methods confirm the formation of stable complexes with actinides and lanthanides.

7. Py-Lactams and Py-Dilactams

- Extraction Selectivity: Py-lactams and Py-dilactams exhibit selective extraction of americium over europium, with calculated extraction energies indicating significant selectivity.

- Predicted Efficiency: DFT simulations predict that these ligands should show improved extraction properties due to their rigid structures and low pre-organization energy.

Conclusion

1. Effectiveness of N,O-Hybrid Donor Ligands: N,O-hybrid donor ligands, including amides of picolinic acid, diamides of dipicolinic acid, and phenanthroline-based ligands, show significant potential in the selective extraction of actinides from spent nuclear fuel (SNF).

2. Selectivity and Efficiency: These ligands demonstrate high selectivity for actinides over lanthanides, which is crucial for efficient separation processes. Ligands such as diamides of dipicolinic acid (DPA) and phenanthroline-2-carboxylic acid (PTA) exhibit particularly high separation factors for americium.

3. Radiolytic and Hydrolytic Stability: The selected ligands exhibit good stability under radiation and acidic conditions, making them suitable for use in the highly radioactive environments encountered in nuclear fuel reprocessing.

4. Complexation Properties: Detailed studies on the complexation behavior of these ligands with actinides have provided valuable insights into their binding interactions and structural properties.

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This knowledge helps in optimizing ligand design for improved performance.

5. Development of Separation Flowsheets: The findings support the development of practical flowsheets for the separation and purification of actinides from high-level waste (HLW). These flowsheets have been tested under dynamic conditions, demonstrating their potential for real-world applications.

7. Future Research Directions: Continued research is needed to further enhance the selectivity, efficiency, and stability of N,O-hybrid donor ligands. Future studies should focus on the synthesis of new ligands, optimization of extraction conditions, and testing under more varied and realistic scenarios.

Relevance to Study

Selectivity for Actinides: The document emphasizes the importance of high selectivity for actinides over lanthanides, which is critical for efficient separation processes in nuclear fuel reprocessing.

Chemical Stability: The ligands discussed, including various N,O-hybrid donor ligands, demonstrate high chemical stability, essential for maintaining functionality under the harsh conditions of the nuclear fuel cycle.

Radiolytic Stability: Ligands such as DPA and PhenDA exhibit good stability under radiation, ensuring they can withstand the radioactive environments present in spent nuclear fuel.

Extraction Efficiency: The document details the extraction efficiency of different ligands, with DPA and PTA showing particularly high efficiency for actinides like americium and curium.

Complexation Behavior: Insights into the complexation behavior and structural properties of ligands with actinides help optimize ligand design for better performance in nuclear fuel reprocessing.

Practical Flowsheets: The development and testing of separation flowsheets using these ligands provide practical solutions for the separation and purification of actinides from high-level waste.

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Future Research Directions: The document suggests areas for future research, such as synthesizing new ligands and optimizing extraction conditions, to further enhance the selectivity and stability of ligands for nuclear fuel cycle applications.

Critical Parameters Identified

High Importance

Chemical Stability

Ligands such as DPA and PhenDA: Exhibit high chemical stability, maintaining functionality under the harsh conditions of the nuclear fuel cycle, including various acid concentrations.

Picolinic Acid Amides: Effective at very low nitric acid concentrations, but limited in broader application due to stability issues at higher acid concentrations.

Radiolysis Resistance

DPA Solutions: Demonstrated high radiolytic stability, which is crucial for maintaining extraction efficiency in radioactive environments.

PhenDA: Also exhibits good radiolytic stability, making it suitable for use in high-radiation conditions.

Thermodynamics

Complexation Studies: Detailed analysis of thermodynamic properties of ligand complexes with actinides, providing insights into the binding strengths and selectivity.

DFT Calculations: Used to predict the extraction efficiency and selectivity, confirming that rigid structures like Py-Dilactams enhance thermodynamic feasibility for separation processes.

Medium Importance

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Kinetics

Extraction Kinetics: The study discusses the need for ligands that achieve fast extraction equilibrium. While some ligands like polynitrogen-containing heterocyclic compounds showed slow kinetics, others like N,O-hybrid ligands were optimized for better performance.

Loading Capacity

DPA and BPyDA Ligands: These ligands showed good loading capacities for actinides, allowing for efficient processing of larger volumes of nuclear waste.

Operational Condition Range

Broad Acid Range: Ligands such as DPA and PhenDA are effective across a wide range of acid concentrations, enhancing their applicability in various nuclear reprocessing conditions.

Solvent Variability: Studies on different diluents (e.g., nitrobenzene, FS-13) show that the extraction efficiency can be maintained across different solvent conditions.

Low Importance

Solubility

Ligand Solubility: Solubility in organic solvents is well-documented for several ligands, ensuring they can be used in various extraction processes. For example, tetraalkyldiamides of dipicolinic acid have good solubility in organic solvents.

Dispersion Numbers:

Mass Transfer Efficiency: Although mentioned, this aspect is less emphasized compared to other parameters, indicating its lower importance in the study's context.

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Phase Disengagement:

Phase Separation: Critical for practical application, but the document mainly focuses on the chemical and radiolytic stability, selectivity, and thermodynamics of the ligands, with less emphasis on phase disengagement specifics.