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Key Words

TODGA

modifier

third phase

diglucolamide

DGA

extraction

review

Objective

1. Review the Application of TODGA: To review the applications of N,N,N ,N -tetraoctyldiglycolamide (TODGA) in the extraction of trivalent lanthanide and actinide ions from PUREX high active raffinates or dissolved spent nuclear fuel.

2. Understand the Role of Phase Modifiers: To analyze how phase modifiers have been used to increase metal loading and enhance the operating process envelopes in TODGA-based extraction systems.

3. Evaluate Third Phase Formation and Organic Phase Speciation: To evaluate the effects of third phase formation and organic phase speciation in TODGA-based extraction systems.

4. Summarize Extraction Data and Process Development: To summarize extraction data and the development of new actinide separation processes using TODGA, including published flowsheet tests and the fundamental chemistry involved.

5. Assess Modifiers and Process Chemistry: To assess how modifiers affect TODGA extraction chemistry, specifically their impact on extractant speciation and metal loading capacity.

6. Propose Simplifications for Industrial Deployment: To explore the possibility of removing or

reducing the need for modifiers through improved extractant design, with the aim of simplifying the separation processes for industrial deployment.

Methodology

1. Literature Review and Process Deveopment:

- The article reviews existing literature on the application of N,N,N ,N -tetraoctyldiglycolamide (TODGA) in the extraction of trivalent lanthanide and actinide ions from PUREX high active raffinates or dissolved spent nuclear fuel.

- It summarizes the development and testing of new actinide separation processes using TODGA, including published flowsheet tests and the fundamental chemistry involved.

2. Assessment of Extraction Chemistry and Modifiers:

- Detailed analysis of how phase modifiers, such as DMDOHEMA, alcohols, and TBP, affect the TODGA extraction chemistry. This includes studying their impact on metal loading capacity and third phase formation.

- Investigation into the role of modifiers in altering third phase formation characteristics of the organic phase and their effects on solvent clean-up and regeneration.

3. Experimental Procedures and Flowsheet Tests:

- Various flowsheet tests were conducted to evaluate the performance of TODGA-based solvent extraction processes. These tests included the use of different modifiers to enhance the extraction efficiency and to prevent third phase formation.

- The processes covered include DIAMEX-type, SANEX-type, ALSEP, and GANEX-type methodologies, each tested under different conditions and with varied solvent compositions to assess their viability and efficiency for industrial deployment.

4. Dynamic Light Scattering (DLS) and Speciation Studies:

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- Studies on the aggregation behavior of TODGA and its correlation with the extraction behavior of metal ions using techniques like Dynamic Light Scattering (DLS).
- Speciation analysis of TODGA complexes using TRLFS (Time-Resolved Laser Fluorescence Spectroscopy) to determine the stability constants and aggregation tendencies of the organic phase post-extraction.

5. Kinetic and Thermodynamic Evaluations:

- Evaluation of the kinetics of mass transfer, including both extraction and stripping phases, to ensure the practicality of the TODGA-based processes.
- Assessment of thermodynamic parameters to understand the feasibility of the separation processes at a fundamental level, influencing selectivity and binding strength of ligands towards specific metal ions.

Key Findings

1. Modifiers in TODGA Systems: Phase modifiers like DMDOHEMA, alcohols, and TBP enhance the extraction efficiency and metal loading capacity of TODGA-based systems by preventing third phase formation and modifying the interfacial properties of the organic phase
2. Challenges with FIssion Products: Extraction of fission products (FPs) such as Zr, Pd, Sr, Ru, Mo, and Tc by TODGA is undesirable. Techniques to mitigate their extraction include aqueous feed conditioning with CDTA and scrubbing with lower HNO3 concentrations
3. Organic Phase Speciation: The post-extraction organic phase speciation of trivalent actinides and lanthanides typically results in 1:3 (M) complexes. Modifiers disrupt micellar formations, reducing the propensity for third phase formation
4. Effectiveness of Different Modifiers: DMDOHEMA allows TODGA solutions to handle high tetravalent actinide concentrations. TBP, while effective, does not adhere to the CHON principle and

its speciation effects are not fully understood. Alcohols like 1-octanol extract less acid and allow for high metal loading without forming a third phase

5. Process Flowsheets and Industrial Applications: Several TODGA-based processes, such as DIAMEX, SANEX, ALSEP, and GANEX, have been developed and tested for minor actinide (MA) and lanthanide (Ln) separations. These processes have been optimized with different modifiers and solvents to enhance performance and applicability

6. Hydrodynamic Properties and Radiolysis: Hydrodynamic properties like viscosity and density of the organic phase are generally acceptable, even post-irradiation. However, higher concentrations of TODGA can lead to increased viscosities in highly loaded systems

7. Kinetics and Thermodynamics: Studies on the kinetics and thermodynamics of TODGA-based extractions show that higher HNO3 concentrations increase the distribution ratios of actinides and lanthanides. The extraction efficiency is also influenced by the size and valence of the metal ions

8. Potential for Industrial Deployment: More studies are needed to fully understand the fundamental chemistry and to identify suitable modifiers empirically. Eliminating or reducing the need for modifiers could significantly enhance the implementation potential of TODGA-based flowsheets for industrial applications

Conclusions

1. Effectiveness of Modifiers:

- Modifiers like DMDOHEMA, TBP, and alcohols have been effectively used to enhance the extraction efficiency of TODGA-based systems by preventing third phase formation and increasing metal loading capacity.
- These modifiers disrupt micellar formations in the organic phase, which is crucial for maintaining the stability of the extraction system.

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2. Extraction of Fission Products (FPs):

- The extraction of undesirable fission products such as Zr, Pd, Sr, Ru, Mo, and Tc remains a challenge. Techniques like aqueous feed conditioning with CDTA and scrubbing with lower HNO3 concentrations have shown some success in mitigating these issues.

- Further research is needed to understand and control the behavior of these elements, especially post-irradiation.

3. Organic Phase Speciation:

- Post-extraction organic phase speciation of trivalent actinides and lanthanides typically results in 1:3 (M) complexes.

- The presence of modifiers helps to reduce the tendency for third phase formation by disrupting micellar organization in the organic phase.

4. Industrial Deployment Potential:

- There is a growing understanding of the fundamental chemistry involved in TODGA-based extraction systems, but more studies are needed to make these processes industrially deployable.

- Improved extractant design and a better understanding of modifier effects could potentially eliminate the need for modifiers, simplifying the separation processes for industrial applications.

5. Radiolysis and Hydrolysis Resistance:

- TODGA-based systems have shown good resistance to radiolysis and hydrolysis, making them suitable for the harsh conditions of nuclear fuel reprocessing.

6. Loading Capacity and Kinetics:

- Studies on the loading capacity and kinetics of TODGA-based extractions indicate that higher HNO3 concentrations improve the distribution ratios of actinides and lanthanides.

- The extraction process is influenced by the size and valence of the metal ions, highlighting the importance of understanding the thermodynamics and kinetics involved.

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Relevance to Study

1. Evaluation of TODGA for Actinide Separtion: The study reviews the use of N,N,N ,N -tetraoctyldiglycolamide (TODGA) in extracting trivalent lanthanides and actinides from high active raffinates or dissolved spent nuclear fuel
2. Role of Modifiers: Analysis of how phase modifiers such as DMDOHEMA, TBP, and alcohols like 1-octanol enhance the extraction efficiency and metal loading capacity of TODGA-based systems by preventing third phase formation and modifying interfacial properties
3. Impact on Chemical Stability and Radiolysis Resistance: The study discusses the importance of modifiers in improving the chemical stability and radiolysis resistance of TODGA-based systems, which is crucial for maintaining the functionality of ligands under the harsh conditions of nuclear fuel reprocessing
4. Organic Phase Speciation: Evaluation of the speciation of TODGA complexes in the organic phase, particularly the formation of 1:3 (M) complexes, and how modifiers help in reducing micellar formations, thereby minimizing third phase formation
5. Loading Capacity and Third Phase Formation: Findings indicate that TODGA has a high metal loading capacity, but the presence of modifiers is often necessary to prevent third phase formation and ensure efficient extraction processes
6. Application in Varous Processes: TODGA-based processes such as DIAMEX, SANEX, ALSEP, and GANEX are reviewed, highlighting their development and optimization for minor actinide and lanthanide separations
7. Industrial Deployment Potential: Emphasis on the need for further studies to fully understand the fundamental chemistry and to identify suitable modifiers empirically. Simplification of the separation processes through improved extractant design could enhance the industrial deployment potential of TODGA-based flowsheets

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Critical Parameters Identified

High Importance

1. Chemical Stability: The study discusses the chemical stability of TODGA ligands, highlighting their resistance to hydrolysis and radiolysis, which is crucial for maintaining their functionality during the separation process

2. Radiolysis Resistance: The resistance of TODGA-based systems to radiolysis is emphasized as essential for ensuring the ligands' durability under the radioactive conditions of nuclear fuel reprocessing. Modifiers like DMDOHEMA and TBP enhance radiolysis resistance

3 Thermodynamics: The thermodynamic parameters of TODGA-based extractions are discussed, showing how higher HNO_3 concentrations improve the distribution ratios of actinides and lanthanides. This influences the selectivity and binding strength of the ligands

Medium Importance

1. Kinetics: The study evaluates the kinetics of TODGA-based extractions, highlighting that efficient mass transfer is achieved within practical time frames. The kinetics of both extraction and stripping phases are analyzed to ensure the practicality of the processes

2. Loading Capacity: TODGA's high metal loading capacity is discussed, with modifiers playing a crucial role in preventing third phase formation and enhancing loading efficiency. This is important for processing larger amounts of material before ligand saturation

3. Operational Condition Range: The ability of TODGA-based ligands to operate under a broad range of conditions is evaluated, emphasizing their flexibility and applicability in different nuclear fuel reprocessing scenarios. This includes varying HNO_3 concentrations and the presence of different metal ions

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Low Importance

1. Solubility: Solubility issues are addressed by selecting appropriate solvents and modifiers. While solubility is important, it can often be managed through the selection of suitable solvent systems, making it less critical compared to other parameters

2. Dispersion Numbers: Dispersion numbers are mentioned in the context of specific system setups, but their influence on the efficiency of mass transfer between phases is less emphasized compared to other factors. This parameter is highly dependent on the specific design of the extraction system

3. Phase Disengagement: The practical separation of phases after extraction, or phase disengagement, is discussed as a critical factor for some systems but is considered highly dependent on system design and operation parameters. The use of modifiers helps improve phase disengagement