REFERENCE: 20036

Key Words

DAAP

fuel cycle

lanthanides

oxidized Am

sodium bismuthate

solvent extraction

Objective

1. Development of a partitioning scheme to separate

Am from lanthanides

2. Paritioning of bismuthate-oxidized Am-VI from the bulk of the lanthanides using 1M diamylamylphosphonate (DAAP)/dodecane extraction

Methodology

1. Acid extraction

2. Metals extraction

3. DAAP Analysis

4. Dispersion Number Measurements

Key Findings

1. Am Erxtraction in Dodecane and Isopar L

- dist. Rations for Am extraction in dodecane/Isopar L, highest in acidities of 6-7M HNO3,

typically greater than or equal to 4; sub. Isopar L for dodecane does not sig. affect the

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extraction efficiency of either metal

- obs. extraction values represent hexavalent Am, important to ntoe that the prescence of residual Am(III) could loweer the measured dist. ratios; efficienct of extraction is contingent on successfully creating and maintaining hexavalent oxidation state, optimal yield reported 80-94%
- at acidities less than 2M HNO3, the dist. ratio for Am decreases, suggestinign that Am is trivalent in this acidity range; as acid conc. inc., the dist. ratio initially dec. due to lack of sufficient oxidizing agent to maintain AM in hexavalent state but then staters to inc., indicate that enough oxidizing agent present to produce Am (VI)

2. Acid Extraction in Dodecane and Isopar L

- basic neutral organophosphorus ligands compete for active phosphoryl group during extraction, which can limit metal extraction efficiency at higher acid concentrations; acid is extracted in its undissociated form
- mass spec. has confirmed the formation of complexes with other neutral organophosphorus ligands, important to understand the extrant of nitric acid extraction when using DAAP in processes
- dist. ratio for HNO3 dec. as initial aq. nitric acid conc. inc., approaching a 1M HNO3 conc. that is equal to DAAP conc.; equilib. behavior does not prevent metal extraction

3. Behavior of Ln Fission Products and Cm Extracted from Nitric Acid Solution

- Sm extracted more efficiently than La w/ 1M DAAP in dodecane, highest dist. ratios seen at 2.0M nitric acid conc.; for Am extraction, the dist. ratioes signif. drop after 6.5M HNO3 conc.
- Cm extraction behavior is similar to lanthanidies w/ lower overall distrib. ratios; non-lanthanide fission products and other fuel dissolution constituents (Rh, Pd, Ag) have

varying distribution ratios, with only Pd showing any significant extraction
(a dist. ratio of 0.263 at 2M HNO_3)
- high yield fission products (Cs137 and Tc99) the extraction is minimal in the initial aq. phase w/ 1M DAAP/dodecane, and behavior is not signif. altered by bismuthate tratement, indicate extraction efficiences are generally low and not greatly affected by presence of bismuthate

4. Extraction of Ln Fission Products and Cm from Simulated First-Cycle Raffinate
- dist. ratios for extraction of lanthanides, Y and Cm from first simulated first-cycle raffinate using 1M DAAP in dodecane are similar to those from nitric acid soln, albeit slightly lower; lower extraction efficiency is attrib. to hgiher conc. of total metals in raffinate; dist. ratios dec. w/ inc. acidity, and only Ce was oxidized and extracted effectively
- dist. ratios for Cm show that behavior in simulated raffinate is similar to that from HNO_3 soln, and it was not oxidized by bismuthate tratement of raffinate
- Eu has one of highest lanthanide dist. ratios; separation factor for Am extraction from the remaining trivalent metals is hgiher than previously reported, with a reported value of approx. 133 for the Am/Eu sep, assuming a dist. ratio of 4

5. Other Fission Products and Fuel Dissolution Constituents
- extraction of non-lanthanide metals (Zr, Y, Cd, Pd) using 1M DAAP/dodecane from first-cycle raffinate adj. for nitric acid conc. was investigated; both bismuthate-treated and untreated Pd showed negligible extraction, while Zr showed measurable extraction, w/ dist. ratios approx. 2x hgiher in oxidized soln; suggests DAAP shares similar disadvg. w. thier fuel-cycle ligands in extracting Zr
- sodium bismuthate as an aq-phase oxidant introduces dissolved Bi(V) into solb, which is reduced to Bi(III); dist. ratios for Bi(III) were measured from bismuthate-treated nitric acid,

treated raffinate simulant, and from traced simulant that was oxidatively treated with sodium bismuthate

- extraction behavior of Bi(III) during DAAP is similar to that of trivalent lanthanides, w/ higher dist, ratios at low acid conc.; extraction of Bi(III) is low, which is considered an advantage for this ligand over what was previously reported for CMPO

6. Behavior of Irradiated DAAP

- Zr extraction from first-cycle raffinate simulant shows higher dist. ratios for bismuthate treated soln compared to the untreated one, indicating that oxidation improves the extraction efficienct of Zr using 1M DAAP/dodecane
- Bi(III) extraction from various nitric acid soln using 1M DAAO/dodecane exhibits higher ditribution ratios at low nitric acid conc., ratio dec. as the acid conc. inc.; extraction is more effective from the treated raffinate simulant than from the bismuthate-treated nitric acid or untreated simulant
- metals in the fuel dissolution process produce highly energetic alpha and beta radiation, which can ionize the diluents used in solv. extraction, potentially affecting their performance; important rxns of these diluents and their impact on the solv. extraction ligands, DAAP are summarized, w/ effects of alpha/beta radiation on 1M DAAP/dodecane soln being reported

7. Dispersion Numbers

- dispersion numbers for 1.0M DAAP/dodecane soln were consistent before and after irradiation
- samples were irradiated up to abs. dose of 130 kGy
- irradiation did not affect the phase-sep. characteristics of the solvent

8. Radiolytic Change in DAAP Concentration

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- DAAP conc in 1M DAAO/dodecane soln remained relatively stable under irradiation up to 500 kGy
- exp. included irradiation of DAAP in neat organic phase, in contact w/ 6.5M HNO_3, and with raffinate simulant
- rate of DAAP conc. decrease was similar across different irradiation conditions, indicating good radiolytic stability

CONCLUSIONS

- HDEHP selectively extracts tetra- and hexavalent metals with efficient Am extraction in oxidized soln
- only Cm was also extracted among lanthanides; other trivalent lanthanides showed lower extraction rates
- Cm behaves like the trivalent lanthanides, not affected by bismuthate oxidation
- method enables solvent extraction-based separation of Am from both lanthanides and Cm
- among non-lanthanide metals only Ru and Zr showed significant extraction

DAAP solns' radiolysis did not significantly affect their conc. or dispersion numbers even at high abs. rad. doses

Relevance to Study

*- Am/Lanthanides Speparation: The development of adv. Nuclear fuel cycles necessitates efficient sep. schemes, particularly for sep. Am from lanthanides due to their similar trivalent states and ionic radii. DAAP shows promise in achieving this sep. by oxidizing Am to higher oxidation states for selective extraction

- Oxidation Strategy: Utilizing sodium bismuthate as an oxidant, Am can be oxidized to its hexavalent state in acidic sols and effectively extracted into a DAAP/dodecane soln. this method addresses The challenge of Am/lanthanide spearation, with DAAP demonstrating selective extraction capabilities for oxidized Am over lanthanides.

- Extraction Efficiency: The research demonsrated that DAAP provides an effective medium for The extraction of hexavalent Am from Nuclear fuel raffinate siulant soln, offering high separation factors between Am and lanthanides like Eu, and allowing for The potential sep. of Am from Cm and other trivalent actinides and lanthanides.
- Radiation Stability: The DAAP solvent exhibited good Stability under gamma-radiolysis, with minimal conc. change even after expsure to high doses of radiation. this suggests that DAAP could be a viable ligand for Nuclear fuel-cycle applications where Radiation Stability is critical.
- Phase Separation: The dispersion numbers, which indicate Phase separation efficienct, remained uinchanged upon irradiation, suggesting that DAAP maintains excellent Phase separation characteristics even after exposure to Radiation, making it suitable for Nuclear fuel reprocessing.
- Extraction of Other Metals: While DAAP effectively extracts hexavalent Am, it also has The capability to extract other Metals like Ce when oxidized, but with minimal extraction of trivalents lanthanides and other fission products (Cs and Tc) under The conditions studied. this indicates its potential for selective extraction in Nuclear fuel cycle processes.
- Process Implications: The findings suggest that DAAP cold be integrated into Nuclear fuel cycle processes for The efficienct and selective separation of Am from lanthanides and other fisson products, contributing to The dfevelopment of adv. Nuclear fuel cycles and The management of radioactive waste.

Critical Parameters Identified

High Importance

- Radiolysis Resistance: The document reports that DAAP solutions do not show significant decreases in concentration even after exposure to high doses of radiation, demonstrating good radiolysis resistance, which is crucial for maintaining separation efficiency in the presence of radioactive materials.

Medium Importance

- Operational Condition Range: DAAP's effective extraction of hexavalent Americium (Am) from nuclear fuel raffinate simulant solutions over a range of acidic conditions demonstrates its flexibility and applicability under diverse operational conditions.
- Loading Capacity: While not directly addressed in detail, the study's focus on DAAP's extraction efficiency, especially for Am, suggests relevance to how much material (e.g., Am vs. lanthanides) can be processed before the ligand becomes saturated.

Low Importance

- Solubility: The document mentions the use of DAAP in dodecane and compares its extraction efficiency in dodecane versus Isopar L, indirectly touching on solubility aspects by demonstrating DAAP's utility in different solvent environments.
- Dispersion Numbers (for applied systems with conditional values): The document highlights that irradiation does not change the dispersion numbers for DAAP solutions, indicating efficient phase disengagement and mass transfer between phases in the system design tested.
- Phase Disengagement (for applied systems with conditional values): Related to dispersion numbers, the unchanged phase disengagement after irradiation suggests that DAAP maintains effective separation characteristics under the tested conditions.

Primary Categories

- Chemical Parameters
- Process Parameters
- Physical Parameters