

INL DPAH STAAR 2015 ANNUAL REPORT

Fuel Cycle Technology

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SUMMARY

Research conducted at the INL has demonstrated the synergistic extraction of americium using solvents comprised of bis(o,o-(trifluoromethyl)phenyl) dithiophosphinic acid (DPAH “1”) and trioctylphosphine oxide (TOPO), butyl bis(2,4,4-trimethylpentyl) phosphinate (BuCy272), or dibutyl butylphosphonate (DBBP). One potential drawback of this separations scheme is that soft metals such as silver, cadmium, or palladium and fission products such as zirconium are well extracted by these solvents. Several potential scrubbing reagents were examined. Of the scrubbing reagents studied, cysteine and methione exhibited some ability to scrub soft metals from the loaded solvent. More conventional scrub reagents such as ammonium fluoride or oxalic acid were not effective. Reagents like Bimet and CDTA were not soluble at the acidities used in these studies. Unfortunately, these results indicate that the identification of effective scrubbing reagents for use in a flowsheet based upon the INL DPAH is going to be very difficult.

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ACRONYMS

“1”	bis-(o,o-trifluoromethylphenyl)dithiophosphinic acid
Bimet	((2S,2'S)-4,4'-(ethane-1,2-diylbis(sulfanediyl))
BuCy272	Butyl ester of bis(2,4,4-trimethylpentyl)phosphinic acid
Cyanex 272	bis(2,4,4-trimethylpentyl)dithiophosphinic acid
DBBP	Dibutyl butylphosphonate
DPAH	Dithiophosphinic acid
CDTA	1,2-diaminocyclohexanetetraacetic acid
FCRD	USDOE Fuel Cycle Research and Development program
INL	Idaho National Laboratory
STAAR	Sigma Team for Advanced Actinide Recycle
TOPO	tri- <i>n</i> -octylphosphine oxide

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1. Introduction

The development of processes for MA separations is driven by the potential benefits: reduced long-term radiotoxicity of waste placed in a geologic repository, reduced timeframe of waste storage, reduced repository heat load, the possibility of increased repository capacity, and increased utilization of energy potential of used nuclear fuel.^[1-3] The research conducted within the Sigma Team for Advanced Actinide Recycle (STAAR) framework is focused upon the realization of significant simplifications to aqueous recycle processes proposed for MA separations. In particular, this report describes the development of a flowsheet concept for the separation of MA which is based upon the dithiophosphinic acid (DPAH) extractants previously developed at the Idaho National Laboratory (INL).

The interest in the use of solvent extraction reagents containing soft donor groups such as N or S for highly efficient MA separations is based upon the proposed differences in the extent of covalent bonding occurring within the $5f$ -orbitals for the actinides, relative to the $4f$ -orbitals of the lanthanides.^[4-8] The resulting slightly greater degree of covalent bonding for actinides permits effective, selective MA isolation by soft donor ligands. Studies have shown a much enhanced differentiation between trivalent actinides and trivalent lanthanides when substituted alkyl DPAH reagents are utilized as the active phase transfer reagents.^[5, 9] The focus of this research project during FY 2015 is to continue development of a solvent extraction process for minor actinide recovery from acidic solution based upon the use of INL's dithiophosphinic acid compounds and a synergist. A successful solvent extraction process would exhibit a combination of adequate extractant stability and actinide separation factors that permit the treatment of dissolved fuel raffinates at approximately 0.5 M total acidity in a single process step. This development work will focus upon the use of bis(*o*-trifluoromethylphenyl) dithiophosphinic acid (Lig "1") and a synergist dissolved in trifluoromethylphenyl sulfone (FS-13).

2. Significance

The current baseline flowsheet for the treatment of dissolved nuclear fuel requires several processing steps in order to realize the desired separations. At least two processes (i.e., TRUEX followed by TALSPEAK) are required for the selective separation of the minor actinides (Np, Am, and Cm) from a UREX-like or COEX-like raffinate containing lanthanides and other fission products. By utilizing a process based upon the combination of hard and soft donor compounds, a single process may serve to replace the combination of the TRUEX and TALSPEAK processes. In fact, simple batch extraction tests demonstrated that the combination of 0.5 M Lig "1" / 0.1 M TOPO / FS-13 can recover uranium, neptunium, plutonium, americium, and curium from a simulated UREX raffinate adjusted to 0.5 M HNO₃. The ability to operate a solvent extraction process at 0.5 M HNO₃ would represent a significant simplification in process control requirements.

3. Approach

The dithiophosphinic acid extractant was prepared following a literature procedure.^[10] Trioctylphosphine oxide (Aldrich, 99%) was further purified^[11] by a series of washes with sodium carbonate and de-ionized water to remove acidic impurities. Dibutyl butylphosphonate (Aldrich $\geq 99.0\%$) was used as received. The butyl ester of bis(2,2,4-trimethylpentyl)dithiophosphinic acid was synthesized using a modification of the synthetic procedure reported by Barnard.^[12] The scrub reagents DL-methionine (Aldrich (99%)), DL-cysteine (Aldrich 97%), oxalic acid (Aldrich $\geq 99\%$), ammonium fluoride (Aldrich 99%), mannitol (Aldrich $\geq 98\%$), and 1,2-diaminocyclohexanetetraacetic acid (CDTA) (Aldrich $\geq 98.5\%$) were used as received. The scrub reagent ((2S,2'S)-4,4'-(ethane-1,2-diylbis(sulfanediyl)) (Bimet), was synthesized by the procedure published by Aneheim and co-workers.^[13] Trifluoromethylphenyl sulfone, FS-13, (Marshallton Research Laboratories) was used as received.

A series of distribution ratios were collected to identify optimal conditions for the proposed separations. Metal extraction was quantified by the distribution ratio, D , calculated as the ratio of the equilibrium concentration of the metal ion in the organic phase to that in aqueous phase. A phase volume of 0.5 mL was used for all distribution ratio determinations. The organic solutions of the extractant were thrice pre-equilibrated with equal volumes of aqueous electrolyte solutions immediately prior to use. An aliquot of the pre-equilibrated organic phase was then contacted with an equal volume of the identical aqueous phase spiked with radiotracers. While kinetic experiments demonstrated equilibrium in the biphasic system was established in less than two minutes, for convenience, the two phases were vigorously shaken using a large capacity mixer (Glass-Col) for 1 hour at room temperature, 20 ± 2 °C. The samples were centrifuged to facilitate phase separation and an aliquot of each phase was taken for radiometric measurements using gamma spectroscopy (HPGe). The distribution of stable metal species was determined by inductively coupled mass spectrometry.

Radionuclide stock solutions of ^{243}Am (HPGe) and ^{154}Eu (HPGe) were used to trace the behavior of metals in liquid-liquid systems. Radiotracers were obtained from laboratory stocks, except for Eu-154 (20 $\mu\text{Ci/mL}$ in 0.1 M HCl) which was obtained from a commercial source (Eckert & Ziegler). Typically, 1 – 10 μL aliquots of each radiotracer stock solution were used.

The aqueous mixture of lanthanides, alkali and alkaline earth metals entitled “AFCI (Advanced Fuel Cycle Initiative) Simulant” was obtained from INL’s QC Laboratory. This solution has been prepared to mimic aqueous raffinate composition expected after an initial separation of uranium as envisioned in a UREX-type process for treatment of UNF. The concentration of nitric acid in the simulant mixture was adjusted to desired levels by the addition of appropriate volumes of concentrated nitric acid.

4. Summary of results

Continuous variation experiments were performed^[14] in the latter part of FY-2014 to confirm synergistic interactions between the DPAH and trioctylphosphine oxide (TOPO), butyl bis(2,4,4-trimethylpentyl) phosphinate (BuCy272), or dibutyl butylphosphonate (DBBP). The continuous variation experiments were performed using FS-13 as the diluent and an aqueous phase composition of 0.1 M HNO_3 . These experiments were repeated in order to determine an optimal

ligand and synergist composition for the INL DPAH solvent. The optimal solvent compositions are listed in Table 1.

Table 1. Optimal ligand and synergist concentrations for the INL DPAH solvent. Aqueous phase: 0.1 M HNO₃, Organic phase: FS-13.

Synergist	[Synergist], mol/L	["1"], mol/L
TOPO	0.23	0.37
DBBP	0.20	0.40
BuCy272	0.20	0.40

Previous results generated at the INL have demonstrated that the INL DPAH solvents extract several fission products.^[15] The extraction of soft metals such as silver, cadmium, or palladium and other metals such as zirconium represents a serious limitation to the implementation of the INL DPAH solvent extraction process for the recovery of minor actinides from acidic solutions. Several different scrubbing reagents were examined in order to identify a reliable means of selectively scrubbing extracted fission products out of the loaded solvent.

A combination of radiochemical and inductively coupled plasma mass spectroscopy experiments were used to determine the scrubbing efficiency of solutions of 0.01 M solutions of methionine, cysteine, oxalic acid, ammonium fluoride, mannitol dissolved in 0.5 M HNO₃. The CDTA and Bimet were not soluble at this concentration in 0.5 M HNO₃. The Bimet and CDTA reagents did not exhibit sufficient solubility at 0.5 M HNO₃ (solubility < 0.001 M) to justify further testing. The various organic solvents (see Table 1) were loaded with fission products by a single contact with aqueous UREX-like raffinate containing soft metals, and adjusted to 0.5 M HNO₃.^[15] For the remaining reagents, the values of D_{Am} remained well above one during scrubbing, but the fission products were not scrubbed from the loaded solvent. Unfortunately, these results indicate that the identification of effective scrubbing reagents for use in a flowsheet based upon the INL DPAH process was not successful.

5. References

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6. Publications and other Indicators of project quality and productivity

Oral Presentations:

Dean R. Peterman, Peter R. Zalupski, John R. Klaehn, Rocklan G. McDowell “Minor actinide separations using a mixture of DPAH extractants and hard donor molecules,” 2015 ACS Northwest Regional Meeting, Pocatello, Idaho, June 21-24, 2015.

Dean R. Peterman, Peter R. Zalupski, John R. Klaehn “Minor actinide separations using a combination of a dithiophosphinic acid and a synergist,” 249th American Chemical Society National Meeting, Denver, CO, March 22 – 26, 2015.

Publications:

Zalupski, P. R.; Klaehn, J. R.; Peterman, D.R., Complete recovery of actinides from UREX-like raffinates using a combination of hard and soft donor ligands. II. Soft donor structure variation. *Solv. Extr. Ion Exch.* **2015**, in press; DOI 10.1080/07366299.2015.1064296

7. Collaborators and participants

This project involves Drs. D. R. Peterman, P. R. Zalupski, and J. R. Klaehn at the Idaho National Laboratory. Drs. Peterman and Zalupski were responsible for experimental design and project management activities at INL. Dr. John R. Klaehn synthesized DPAH compounds or purified commercially available the DPAH compounds used in the work.