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Feasibility of actinide separation from UREX-like raffinates using a combination of sulfur- and oxygen-donor extractants

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A synergistic combination of bis(o-trifluoromethylphenyl)dithiosphosphinic acid and trioctylphosphine oxide has been recently shown to selectively remove uranium, neptunium, plutonium and americium from aqueous environment containing up to 0.5 M nitric acid and 5.5 g/L fission products. Here the feasibility of performing this complete actinide recovery from aqueous mixtures is forecasted for a new organic formulation containing sulfur donor extractant of modified structure based on Am(III) and Eu(III) extraction data. A mixture of bis(bis-m,m-trifluoromethylphenyl)-dithiosphosphinic acid and TOPO in toluene enhances the extraction performance, accomplishing Am/Eu differentiation in aqueous mixtures up to 1 M nitric acid. The new organic recipe is also less susceptible to oxidative damage resulting from radiolysis.

I. INTRODUCTION

The interest in the recovery of actinides from the complicated mixtures of dissolved used nuclear fuel is mainly driven by the possibility to shorten the requirement for safe storage of such radiotoxic effluents. The removal of long-lived alpha emitters offers the advantage of reducing the requirement of environmental management of such materials to 1000 years.¹

Typically, the process of separation of actinides from dissolved used nuclear fuel occurs in sequence.² Bulk of uranium and plutonium are recovered initially for mixed oxide fuel fabrication, producing a highly radioactive raffinate mixture of fission products and minor actinides. A variety of methodologies have been proposed to manage the final destination of plutonium and neptunium.² The final (and most challenging) separation task calls for the differentiation of similarly-behaving trivalent americium and curium and lanthanides. Depending on the management route a complete actinide removal may involve a sequence of 4 or 5 solvent extraction steps guided by different chemistry.

An alternative approach to total actinide removal from dissolved used nuclear fuel mixtures has been recently developed by Aneheim and coworkers.³ The

authors proposed to simultaneously remove all actinides present in the effluent mixture produced by an initial removal of bulk uranium. This approach focuses mainly on the reduction of actinide content to limit waste management timeline in the geologic repository. The proposed concept capitalizes on the liquid-liquid distribution facilitated a combination of two extractants exhibiting different metal ion coordination properties. One – a hard donor ligand – relies of electrostatic (ionic) interaction with metal ions. The other – a soft donor ligand – introduces an opportunity for weak covalent interaction with 5f, 6d, or 7s orbitals of actinide ions, to complement dominant electrostatic bonding. Building on this concept, demonstrated for a mixture of tributyl phosphate (hard) and N-heterocyclic ligand (soft), Zalupski and coworkers have recently translated the feasibility of such complete actinide separation when using a sulfur-containing extractant as the source of soft bonding interaction.⁴

Here we present further evolution of this co-extraction concept, where the actual (practical) implementation of sulfur-containing reagents to accomplish such separation is evaluated. The efficiency of Am and Eu partitioning from nitric acid, and from acidic simulated Urex-like raffinate, was monitored for synergistic cocktails containing trioctylphosphine oxide (TOPO), and dithiophosphinic acid extractants. Two soft donor structures of dithiophosphinic acid were compared. Metal partitioning was also determined in liquid-liquid systems, where the organic mixtures have been exposed to varying doses of gamma radiation.

II. EXPERIMENTAL

The dithiophosphinic acid extractants were prepared following the procedure reported previously.⁵ Trioctylphosphine oxide (Aldrich, 99%) was further purified by a series of washes with sodium carbonate and de-ionized water to remove acidic impurities. Toluene (Aldrich, 99%) was used as received. 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. 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 either radiometric measurements using gamma spectroscopy (HPGe). Radionuclide stock solutions of ^{243}Am and ^{154}Eu were used to trace the behavior of metals in liquid-liquid systems. Americium-243 was obtained from laboratory stocks. Europium-154 ($2 \mu\text{Ci/mL}$ in 0.1 M HCl) which was obtained from Eckert & Ziegler. 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 dissolved used nuclear fuel.² The concentration of nitric acid in the simulant mixture was adjusted to 0.5 M for these tests. Gamma irradiations were performed using MDS Nordion GammaCell 220E self-contained Co-60 gamma irradiator. Approximate dose at the time of experiments was 7 kGy/hr.

III. RESULTS

The non-aqueous formulations used in this study were based on a synergistic mixture of a hard-donating reagent – trioctylphosphine oxide – and soft-donating sulfur-containing liquid cation exchangers based on the dithiophosphinic acid structural backbone.

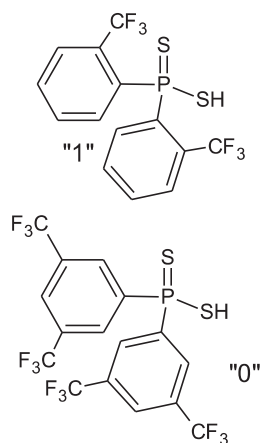


Fig. 1. Structures of “1”-bis(o-trifluoromethylphenyl)- and “0”-bis(bis-m,m-trifluoromethylphenyl)-substituted dithiophosphinic acids used in this study.

Initial investigations by Zalupski and coworkers illustrated the feasibility of a complete extraction of actinides (U, Pu, Np, Am) from aqueous environment containing up to 0.5 M nitric acid and 5.5 g/L fission products, when the organic formulation contained 0.1 M TOPO, 0.5 M compound “1” in toluene. Figure 2 compares Am(III) and Eu(III) extraction from varying aqueous nitric acid concentrations using either compound “1” or compound “0” in the organic recipes. A small enhancement in the extraction of Am(III), as well as the ability to differentiate Am(III) from Eu(III), is clearly noticeable for compound “0”.

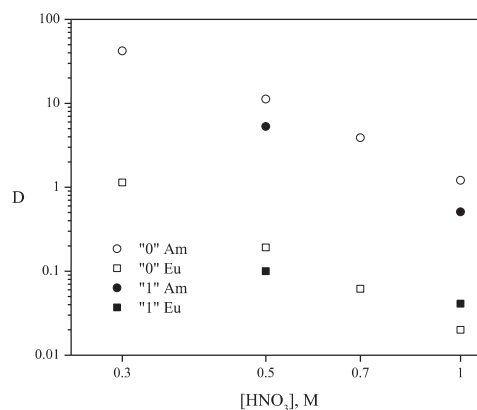


Fig. 2. Extraction of Am(III) (circles) and Eu(III) (squares) by 0.1 M TOPO / 0.5 M compound “1” or “0” / toluene from varying concentrations of nitric acid.

The comparison of ligand “1” and “0” formulations yields similar benefits in the Am/Eu separation when their extraction is studied from the simulated fission product mixture expected from a UREX-type raffinate adjusted to 0.5 M HNO₃. The composition of the raffinate and the liquid-liquid distribution of all metal ions present in the mixture (for the system containing ligand “1”) have been reported previously.⁴ Table I summarizes the distribution ratios for Am(III) and Eu(III), illustrating an enhanced performance of liquid-liquid system containing ligand “0” in the organic phase.

TABLE I. Comparison of the effectiveness of Am/Eu separation in liquid-liquid systems based on “1” and “0” soft donor structures. Org: 0.5 M soft donor / 0.1 M TOPO / toluene. Aq: UREX-type raffinate, 0.5 M HNO₃.

Soft donor	D (Am)	D (Eu)	SF Am/Eu
“1”	6.34 ± 0.02	0.08 ± 0.01	79
“0”	9.2 ± 0.4	0.06 ± 0.01	153

The combination of hard- and soft-donating extractant in this liquid-liquid system offers the opportunity to afford highly efficient Am/Eu differentiation in aqueous mixtures of moderate acidity.

The presence of a synergist (TOPO) must further assist in the complete dehydration of the metal ion, thus allowing to effectively counter-balance the enthalpic barrier of metal ion dehydration, which typically grows in solutions of increasing nitric acid concentrations. Such synergic combination of an ion-exchanging solvent extraction reagent with the solvating phase-transfer compound to enhance the efficiency of metal ion recovery from aqueous acidic media is one of several, now “textbook-type,” manipulations of solution chemistry in solvent extraction.⁶ Several classic reagent combinations, for instance β -diketones with organophosphorus⁷ or nitrogen heterocycle compounds,⁸ illustrate this synergistic effect on the extraction equilibrium constant very well.

Nonetheless, to genuinely consider any aqueous partitioning process employing sulfur-containing phase transfer agents, the enhancement of liquid-liquid distribution of trivalent *f*-block elements facilitated by dithiophosphinic acids must be complemented by the demonstration of adequate hydrolytic and radiolytic stability of such compounds. Highly oxidizing environment produced after the dissolution of used nuclear fuel rods is very harsh, especially on those organic structures susceptible to reactivity with a variety of electrophiles. Electronic structure of sulfur-functionalized soft Lewis bases is easily polarizable, inviting such opportunity. Typically, the deposition of the energy of radioactive decay in matter produces free radicals, which are highly electrophilic. Free radical substitution reactions inevitably proceed, and, in an oxygen-rich environment, result in rapid replacement of soft sulfur atom with hard oxygen. These types of free radical induced reactions are detrimental to selective actinide extraction. Throughout the evolving application of dithiophosphinic acids in the area of minor actinide partitioning a persistent anxiety about their robustness remains.⁹

To investigate the effect of radiolytic damage, and its effects on the synergic chemistry presented in this study, the organic mixtures of TOPO with either ligand “1” or ligand “0” in toluene were exposed to gamma radiation field using a Co-60 source. The irradiated organic phases were then used to track liquid-liquid distribution of Am(III) and Eu(III). Figure 3 shows the results of the radiolysis study. Here, the organic mixtures consisted of 0.1 M soft donor, 18 mM TOPO in toluene. Liquid-liquid partitioning was monitored using 0.1 M HNO₃ / 0.9 M NaNO₃ as aqueous environment.

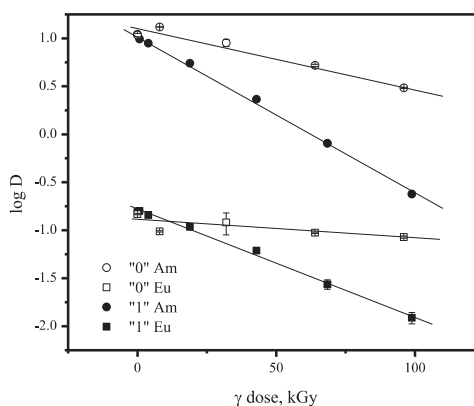


Fig. 3. Extraction of Am(III) (circles) and Eu(III) (squares) by gamma irradiated 0.1 M ligand “1” or “0” / 18 mM TOPO in toluene from 0.1 M HNO₃ / 0.9 M NaNO₃.

Significant deterioration of the overall extraction efficiency of both Am and Eu is clearly noticeable. The distribution ratios decrease as the organic formulation is exposed to increasingly higher doses of gamma radiation. The downward trend in the extraction of Am(III) is more pronounced highlighting the importance of the soft donor reagent in the actinide partitioning into the organic phase. The results of this degradation study demonstrate that, indeed, radiolytic damage to dithiophosphinic acids does occur in agreement with the previously reported studies.¹⁰ However, a clear enhancement in the robustness of ligand “0” relative to its “1” counterpart should be emphasized. The effect of gamma radiation on the liquid-liquid distribution equilibria is less pronounced for the formulation containing ligand “0.”

Modolo and coworkers reported a much smaller impact of gamma radiolysis on the distributions of Am and Eu in the synergic mixtures containing unsubstituted and chloro-substituted diorganyldithiophosphinic acids and TBP in toluene.¹¹ In their study no change in the metal ion distribution was observed after 100 kGy exposures. The comparison of Modolo’s experimental organic recipes (0.5 M dithiophosphinic acid, 0.25 M TBP) to those analyzed here suggests that the presence of larger quantities of the working soft donor extractant conceals the radiolytic damage effects illustrated in this study. The overall enhancement in the radiolytic stability illustrated for the organic recipe based on ligand “0” offers a promising formulation, which may show the flexibility to withstand radiation doses beyond 100 kGy, if present in the concentrations used to demonstrate the feasibility of total actinide extraction concept.⁴

IV. CONCLUSIONS

Synergic mixtures of bis(o-trifluoromethylphenyl)- and bis(bis-m,m-trifluoromethylphenyl)-substituted dithiophosphinic acids and trioctylphosphine oxide in toluene have been shown to effectively extract Am(III), leaving Eu(III) in aqueous mixtures of moderate acidity. Compound "0" (bis(bis-m,m-trifluoromethylphenyl)-dithiophosphinic acid) offers a slightly stronger extraction performance relative to compound "1" (bis(o-trifluoromethylphenyl)-dithiophosphinic acid), and achieves the Am/Eu separation even in 1 M HNO₃. The effects of radiolytic degradation on the extraction of Am(III) and Eu(III) are less pronounced on the liquid-liquid system based on the organic formulation containing compound "0," motivating further investigations.

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REFERENCES

1. P. A. BAISDEN and G. R. CHOPPIN, "Nuclear waste management and the nuclear fuel cycle." S. NAGY, Ed. In *Encyclopedia of life support systems (EOLSS)*, Developed under the Auspices of the UNESCO, Eolss Publishers, Oxford, UK, (2007), [http://www.eolss.net].
2. M. C. REGALBUTO, "Alternative separation and extraction: UREX+ processes for actinide and targeted fission product recovery," pp. 176-200, K. L. NASH and G. J. LUMETTA, Eds., In *Advanced separation techniques for nuclear fuel reprocessing and radioactive waste treatment*, Woodhead Publishing, Cambridge, UK (2011).
3. E. ANEHEIM, C. EKBERG, A. FERMEVIK, M. FOREMAN, T. RETEGAN and G. SKARNEMARK, "A TBP / BTBP - based GANEX Separation Process. Part 1 : Feasibility," *Solv. Extr. Ion Exch.* **28**, 437 (2010).
4. P. R. ZALUPSKI, D. D. ENSOR, C. L. RIDDLE and D. R. PETERMAN, "Complete recovery of actinides from UREX-like raffinates using a combination of hard and soft donor ligands," *Solv. Extr. Ion Exch.*, accepted.
5. J. R. KLAHN, D. R. PETERMAN, M. K. HARRUP, R. D. TILLOTSON, T. A. LUTHER and J. D. LAW and L. M. DANIELS, Synthesis of symmetric dithiophosphinic acids for "minor actinide" extraction. *Inorg. Chim. Acta* **2008**, 361, 2522-2532.
6. Y. MARCUS and A. S. KERTES, *Ion Exchange and Solvent Extraction of Metal Complexes*, pp. 815-858, John Wiley & Sons Ltd., London, UK (1969).
7. S. A. PAI, J. N. MATHUR, P. K. KHOPKAR and M. S. SUBRAMANIAN, "Thermodynamics of synergistic extraction of europium(III) with thenoyltrifluoroacetone and tributyl phosphate in various diluents," *J. Inorg. Nucl. Chem.*, **39**, 1209 (1977).
8. A. S. KERTES and E. F. KASSIERER, "Thermochemistry of lanthanide complexes in the thenoyltrifluoroacetone-bipyridyl system," *Inorg. Chem.*, **11**, 2108 (1972).
9. K. L. NASH, C. MADIC, J. N. MATHUR and J. LACQUEMENT, "Actinide separation science and technology," p. 2762, L. R. MORSS, N. M. EDELSTEIN, J. FUGER, Eds., In *The chemistry of the actinide and transactinide elements*, Springer, Dordrecht, The Netherlands (2008).
10. B. J. MINCHER, G. MODULO and S. P. MEZYK, "Review: The effects of radiation chemistry on solvent extraction 4: Separation of the trivalent actinides and considerations for radiation-resistant solvent systems," *Solvent Extr. Ion Exch.*, **28**, 415 (2010).
11. G. MODULO and R. ODOJ, "Synergistic selective extraction of actinides(III) over lanthanides from nitric acid using new aromatic diorganyldithiophosphinic acids and neutral organophosphorus compounds," *Solv. Extr. Ion Exch.* **17**, 33 (1999).