Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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R. C. Harrington[a]; L. R. Martin[a]; K. L. Nash[a]
[a] Chemistry Department, Washington State University, Pullman, WA, USA

To cite this Article Harrington, R. C. , Martin, L. R. and Nash, K. L.(2006) 'Partitioning of U(VI) and Eu(III) between Acidic Aqueous Al$(NO_3)_3$ and Tributyl Phosphate in n-Dodecane', Separation Science and Technology, 41: 10, 2283 — 2298
To link to this Article: DOI: 10.1080/01496390600750909
URL: http://dx.doi.org/10.1080/01496390600750909

Separation Science and Technology, 41: 2283–2298, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600750909

Partitioning of U(VI) and Eu(III) between Acidic Aqueous $Al(NO_3)_3$ and Tributyl Phosphate in n-Dodecane

R. C. Harrington, L. R. Martin, and K. L. Nash
Chemistry Department, Washington State University, Pullman, WA, USA

Abstract: The preferred approach to removing Al from Hanford tank sludges, based on aqueous alkaline leaching, often does not achieve complete success. Previous laboratory investigations on the treatment of Hanford tank sludge simulant samples indicate that an acidic scrub can enhance the dissolution of Al from various sludge matrices. If acidic leaching was deployed to enhance removal of tank waste residues, the resulting acidic $Al(NO_3)_3$ leachate solution could contain measurable amounts of solubilized transuranic elements and so would demand treatment prior to disposal. In this study, a liquid-liquid extraction system for the decontamination of the $HNO_3/Al(NO_3)_3$ aqueous leachate by contact with 60% v/v tributyl phosphate (TBP)/*n*-dodecane organic solution has been examined. The partitioning of U and Eu between the TBP phase and solutions of varying $[HNO_3]$ and $[Al(NO_3)_3]$ containing small amounts of Cr or ascorbic acid have been investigated. The results indicate that >99% of both species could be removed from the aqueous phase using such a process.

Keywords: $Al(NO_3)_3$, solvent extraction, tributyl phosphate, tank waste cleanup

INTRODUCTION

The Department of Energy's Hanford Site, located in south central Washington state, was the first facility that produced weapons grade Pu for use in nuclear

Received 23 October 2005, Accepted 9 March 2006
Address correspondence to K. L. Nash, Chemistry Department, Washington State University, P.O. Box 644630, Pullman, WA 99164-4630, USA. Tel.: 509-335-2654; Fax: 509-335-8867; E-mail: knash@wsu.edu

weapons. The various separations processes employed at Hanford Site during 60 years of Pu production resulted in the creation of $\sim 2 \times 10^5\,m^3$ of highly radioactive waste, stored in 177 underground waste tanks. The Tri-Party Agreement, a reconciliation between the Washington state Department of Ecology, the U.S. Environmental Protection Agency, and the U.S. Department of Energy, requires the Department of Energy to remove and safely dispose of all the waste that resides in the underground tanks (1).

The raffinates from plutonium production processing, initially acidic, were made alkaline with excess NaOH prior to dispositioning to the underground tanks. Alkaline conditions favored precipitation of the metal species and reduced corrosion of the carbon steel liner of the tanks. Over time, the wastes in the tanks at Hanford Site stratified into three layers. The top layer is a solid crystalline phase containing predominantly sodium salts of CO_3^{2-}, SO_4^{2-}, NO_2^-, NO_3^-, PO_4^{3-}, and OH^-. The bottom layer (sludge) is composed of oxide, hydroxide, sulfate, phosphate, and silicate solids of metallic fission products, actinides, cladding materials, and tank corrosion products. The middle phase, referred to as the supernatant, is a saturated aqueous solution/slurry whose composition is defined by the salt cake above, the sludge phase below, and the amount of water present.

The Waste Treatment Plant (WTP), to which the tank waste will be sent to separate sludge components into Low Activity Waste (LAW) and High Level Waste (HLW), is currently under construction at Hanford to facilitate tank waste management and disposition. The LAW will be disposed of at the Hanford Site, while the HLW will be incorporated into a borosilicate glass matrix and stored at a government sponsored geologic repository (2). The phase that poses the most significant challenges in this process is the sludge. Two of the most problematic non-radioactive elements that plague the tank sludge remediation efforts are Al and Cr. Removing Al and Cr solids from the sludge for separate disposal as low-level waste would greatly reduce the volume, and consequently the overall cost for the HLW sludge disposal operations (3). The investigation of various Al and Cr removal processes has been the subject of research for the past decade.

Leaching of the sludge with caustic aqueous solutions to reduce their Al and Cr content has emerged as the preferred technique for sludge waste volume reduction. Contacting sludge samples with 2 M NaOH leaching solutions (alkaline leaching) has accomplished significant Al removal from some sludge samples and simulants. Excellent Cr removal has been demonstrated by treating the radioactive sludges with 2–3 M NaOH solutions that contain an oxidizing agent such as $KMnO_4$ (oxidative alkaline leaching) (4). However, variability in the chemical composition of each tank sludge inhibits the complete removal of Al by caustic leaching (5).

The materials resistant to mobilization by alkaline leaching could respond to alternative leaching protocols. The results of a series of investigations into the use of acidic solutions or complexants as alternative leachants have been reported (6, 7, 8). These studies employed a sequential sludge treatment technique following an initial NaOH leaching step with a series of increasingly aggressive acidic leachants, including dilute HNO_3 solutions. The acidic leaching treatments achieved a substantial increase in the efficiency of Al leaching in most of the sludge simulants. Enhanced Al dissolution was accompanied by slight increases in the amount of radioactive species Am, U, Np and Pu present in the resultant leachate.

In this report, we address the hypothetical problem of how to remove the radioactive components of the leachate solutions that could emerge if one were to attempt Al leaching with HNO_3 solutions. The decontamination method investigated examines the efficacy of a solvent extraction approach employing a 60% v/v TBP/*n*-dodecane organic extractant phase to selectively separate radioactive contaminants Eu(III) and UO_2^{2+} from aqueous solutions of HNO_3 and $Al(NO_3)_3$ in the presence of low concentrations of Cr.

EXPERIMENTAL

Materials and Instrumentation

All aqueous solutions were prepared from analytical grade reagents and deionized (18 MΩ) H_2O. Solutions of HNO_3 were prepared by mass using Fisher Scientific concentrated (15.8 M) HNO_3 solution. Solutions of K_2CrO_4, $Al(NO_3)_3$ and $NaNO_3$ were prepared by mass using analytical grade J.T. Baker solids. The L-ascorbic acid solutions were prepared by mass from Fisher Scientific ACS certified reagent. Experiments done using $UO_2(NO_3)_2$ and $^{152/154}Eu(NO_3)_3$ solutions were prepared by dilution of standardized stocks from the WSU inventory. Radioactive $^{152/154}Eu$ was created by neutron activation of 99.99% Eu_2O_3 (Arris International) at the Nuclear Radiation Center at WSU. The TBP organic solutions (TBP p.a., Acros Organics) were diluted volumetrically using *n*-dodecane (>99%, Sigma-Aldrich). All TBP/*n*-dodecane solutions were washed to remove acidic impurities using published procedures(9)

ICP-OES analysis was conducted using a Perkin Elmer Optima 3200 RL series instrument. UV/Vis spectroscopic analysis was done using an OLIS Cary-14 spectrophotometer. Radiotracer experiments using $^{152/154}$Eu(III) were analyzed on a Packard Cobra-II auto gamma counter. All pipetting was done using calibrated Finnpipette micropipettors.

PROCEDURE

All solvent extraction experiments were performed with equal volumes of organic and aqueous phases. Cr(III/VI) extraction studies were done using 2.50 mL volumes of each phase; $^{152/154}$Eu(III) extraction experiments with

1.0 mL volumes of each phase; UO_2^{2+} extraction experiments with 3.0 mL volumes of each phase. These adjustments were necessary to accommodate the accuracy of the analytical procedure employed (ICP or radiometric analysis).

Organic Phase

All extraction experiments, with one exception, were performed using an organic phase composition of 60% (v/v) TBP_{in} *n*-dodecane. The only exception is the investigation into the TBP dependence of the extracted Eu(III) species, which employed 15, 30, 45 and 60% v/v TBP/*n*-dodecane solutions. This extractant–diluent combination was selected because it is a system that has been widely investigated.

Aqueous Phase

The aqueous phase for the extraction experiments contained various amounts of HNO_3, $Al(NO_3)_3$, Cr(III/VI), Eu(III), UO_2^{2+}, and/or ascorbic acid. This study was designed to encompass a wide variety of aqueous phase conditions that could be encountered during HNO_3 leaching of Hanford tank sludges. Investigations of the extraction behavior of Eu(III) and UO_2^{2+} with changing $[HNO_3]$ in the presence of constant $[Al(NO_3)_3]$ and constant $[HNO_3]$ with variable $[Al(NO_3)_3]$ were completed. All aqueous solutions used in this study initially contained 1.0×10^{-3} M K_2CrO_4. The Eu(III) and UO_2^{2+} extraction experiments had a slight excess of ascorbic acid present ($<1.0 \times 10^{-3}$ M) in each solution.

Chromium Extraction

The extraction behavior of the CrO_4^{2-} ion was examined to determine the tendency of Cr (III or VI) to partition into the 60% TBP phase. After phase mixing (contact times ranged from 0.5–40 minutes), aqueous phase samples were diluted 10 fold and distribution ratios, D_{Cr}, were determined by mass deficit between $[Cr]_{init}$ and that remaining in the aqueous phase after equilibration. Spectrophotometric analysis of the TBP phase was done after contact with a 0.10 M HNO_3, 0.10 M $Al(NO_3)_3$, 5.0×10^{-3} M K_2CrO_4 aqueous solution.

Europium Distribution

Eu(III) distribution, D_{Eu}, experiments were done by using $^{152/154}$Eu(III) radiotracer. Equal volumes of the organic and aqueous phases were mixed by vortexing for 10 minutes, and 200 μL samples of each phase were taken for radiometric assay. Counting times were adjusted to minimize counting error for each sample.

U/Eu Distribution

D_{Eu} values from solutions containing UO_2^{2+} were determined using 3.0 mL volumes of aqueous and organic phases. The investigation of UO_2^{2+} distribution, D_U, in the presence of Eu(III) was also done using 3.0 mL of each phase and 1.0×10^{-4} M UO_2^{2+}. After 10 minutes of phase contact, the samples were centrifuged and 2.50 mL aliquots of the aqueous phases were analyzed for U content by ICP-OES directly without dilution. The D_U values were determined by mass deficit between the initial [UO_2^{2+}] and the remaining [UO_2^{2+}] in the aqueous phase after mixing.

RESULTS

Chromium Extraction

Chromate extraction was studied as a function of both phase contact time and $[HNO_3]_{aq}$. The aqueous phase composition for each experiment was 0.10 M $Al(NO_3)_3$ and 1.0×10^{-3} M K_2CrO_4 with various HNO_3 concentrations between 0.10 M–0.80 M. The distribution ratios varied minimally with $[HNO_3]_{aq}$ with maximum observed values for D_{Cr} of ~0.30 at $[HNO_3] = 0.10$ M. D_{Cr} were seen to decrease for mixing times greater than one minute. Figure 1 presents a series of UV-visible spectra showing the results of a 22 hour analysis of the TBP organic phase after 1.0 min contact with an aqueous solution containing 0.10 M HNO_3, 0.10 M $Al(NO_3)_3$ and 5.0×10^{-3} M K_2CrO_4. During the 22 hour equilibration time, the peak corresponding to $\sim 2.0 \times 10^{-3}$ M extracted CrO_4^{2-} species at 354 nm is seen to decrease in intensity. Subsequent observations made at higher concentrations establish that a much less intense peak is present at 584 nm corresponding to a Cr(III) species. After 22 hours, the resulting organic phase had changed from a yellow to a light green color and blue aqueous droplets had appeared at the bottom of the cuvette.

Recognizing that CrO_4^{2-} could be present in acid-leached $Al(NO_3)_3$ and that Cr(VI) extraction would have a deleterious effect on the stability of the extractant, we elected in subsequent experiments to maintain the presence of Cr in our simulated leachates but to suppress the extraction of CrO_4^{2-}. To accomplish this adjustment, the $HNO_3/Al(NO_3)_3$ solutions containing CrO_4^{2-} were further adjusted with the addition of 2.0×10^{-3} M ascorbic acid which rapidly and quantitatively reduced Cr(VI) to Cr(III). Under these operating conditions, no Cr(III) was extracted into the 60% TBP phase, in agreement with published observations (10).

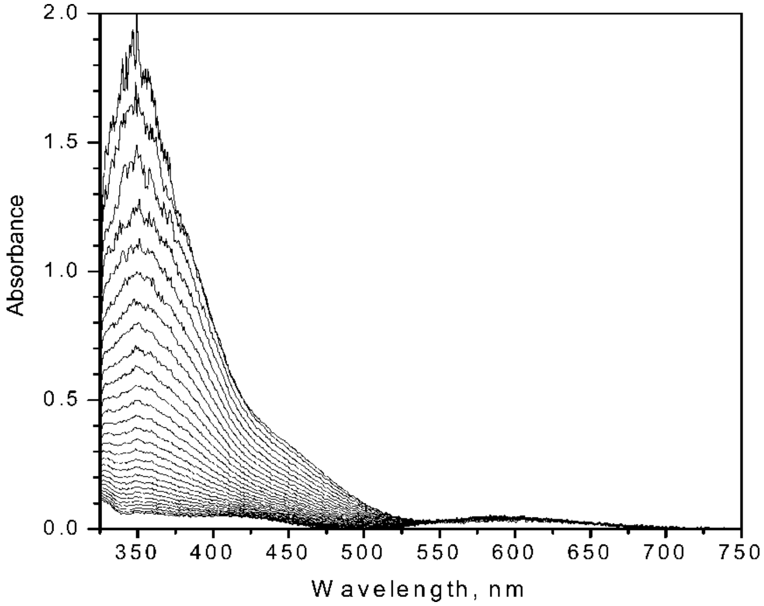

Figure 1. UV/Vis spectra of organic phase samples illustrating the reduction of Cr(VI) extracted into 60% TBP-dodecane. Twenty-seven spectra collected over 22 hours (at 50 minute intervals) with the highest peak at 354 nm representing t = 0 are shown.

HNO_3 Extraction

The partitioning of HNO_3 into the 60% TBP phase is presented in Fig. 2. There is negligible extraction of HNO_3 from aqueous solutions of $[HNO_3] \leq 0.18$ M. The extracted HNO_3 species for this and all systems presented in this paper is assumed to be the 1:1 ($TBP \cdot HNO_3$) adduct (11). These results were used to calculate the concentrations of free TBP and HNO_3 in all subsequent experiments.

Europium Extraction

Correction for Aqueous Nitrate Complexes (D_o)

Throughout this report, experimentally obtained D_{Eu} values are presented in terms of their corrected D_o values, as follows. With the existence of the mono-nitrato Eu(III) species present in the aqueous $HNO_3/Al(NO_3)_3$ solution,

$$Eu^{3+} + NO_3^- \longrightarrow Eu(NO_3)^{2+} \quad \beta_1 \sim 2.0^{(12)} \tag{1}$$

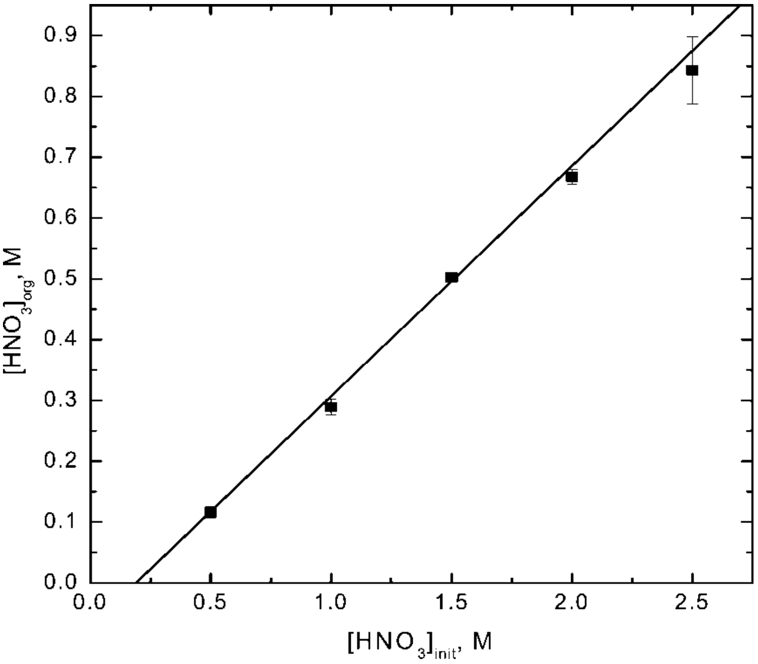

Figure 2. Partitioning of HNO_3 between aqueous and 60% TBP-dodecane solutions.

the experimentally determined D_{Eu} values are representative of the ratio for the organic Eu(III) species divided by both aqueous Eu(III) species.

$$D_{Eu} = \frac{[Eu]_{org}}{[Eu^{3+}]_{aq} + [Eu(NO_3)^{2+}]_{aq}} \tag{2}$$

The corrected term D_o represents the hypothetical Eu(III) distribution value between the TBP organic phase and an aqueous phase containing only the uncomplexed Eu(III) species ($D_o = [Eu]_{org}/[Eu^{3+}]_{aq}$). Equation (2) can be rewritten as:

$$D_{Eu} = \frac{D_o}{(1 + \beta_1[NO_3^-])} \tag{3}$$

Rearranging Equation (3) results in the corrected D_o term.

$$D_o = D_{Eu}(1 + \beta_1[NO_3^-]) \tag{4}$$

Extraction Stoichiometry

The phase transfer equilibrium has the general form:

$$\mathrm{Eu}^{3+}_{\mathrm{aq}} + \mathrm{mNO}^{-}_{3\mathrm{aq}} + \mathrm{nTBP}_{\mathrm{org}} \longrightarrow \mathrm{Eu(NO_3)_m} \cdot \mathrm{nTBP}_{\mathrm{org}} \tag{5}$$

Given the wide range of conditions considered in this study, expression of extraction equilibria in terms of activities might seem appropriate. However, since a significant number of the solutions investigated are in fact mixed electrolyte media for which such activity corrections are complex, we have elected to demonstrate the stoichiometry of extraction using the analytical concentrations of nitrate and TBP. The terms m and n in Equation (5) correspond to the stoichiometric dependence for NO_3^- and TBP respectively. The equilibrium constant expression for Equation (5) is written as:

$$K_{ex} = \frac{[\mathrm{Eu(NO_3)_m} \cdot \mathrm{n\ TBP}]_{\mathrm{org}}}{[\mathrm{Eu}]_{\mathrm{aq}}[\mathrm{NO_3^-}]^{\mathrm{m}}{}_{\mathrm{aq}}[\mathrm{TBP}]^{\mathrm{n}}_{\mathrm{org}}} \tag{6}$$

Substituting Equation (4) into Equation (6), the expression simplifies to:

$$K_{ex} = \frac{D_{Eu}(1 + \beta_1[\mathrm{NO_3}])}{[\mathrm{NO_3^-}]^{\mathrm{m}}{}_{\mathrm{aq}}[\mathrm{TBP}]^{\mathrm{n}}_{\mathrm{org}}} \tag{7}$$

Taking the log of the rearranged Equation (7) term results in the linearized equation:

$$\log(D_{Eu}(1 + \beta_1[\mathrm{NO_3^-}]_{\mathrm{aq}}) = \mathrm{m}\log[\mathrm{NO_3^-}]_{\mathrm{aq}} + \mathrm{n}\log[\mathrm{TBP}]_{\mathrm{org}} + \log K_{ex} \tag{8}$$

Distribution Results

Figures 3 and 4 present Eu(III) distribution data as a function of aqueous $[NO_3^-]_{tot}$. Extraction behaviors were determined as a function of increasing $[Al(NO_3)_3]$ (0.010 M–2.50 M) at three constant $[HNO_3]$ (Fig. 3), and also for increasing $[HNO_3]$ (0.01 M–2.50 M) at two constant $[Al(NO_3)_3]$ (Fig. 4). The distribution of $Eu(NO_3)_3$ into organic solutions containing several different concentrations of TBP from several different nitrate solutions are shown in Fig. 5. In all aqueous solutions, 1.0×10^{-3} M Cr(III) and excess ascorbic acid were present, as described above.

The results shown in Fig. 3 indicate a near coincidence of values at 0.01 and 0.1 M HNO_3 and measurable depression of the D_o value at 1 M HNO_3. A possible limiting slope of 3 can be seen at the lower nitric acid concentrations but not at 1 M HNO_3. The non-linearity almost certainly reflects contributions from changing (mixed-electrolyte) activity coefficients rather than changes in the stoichiometry of the extracted complex, though the latter cannot be ruled out, particularly at higher concentrations of $Al(NO_3)_3$ and HNO_3.

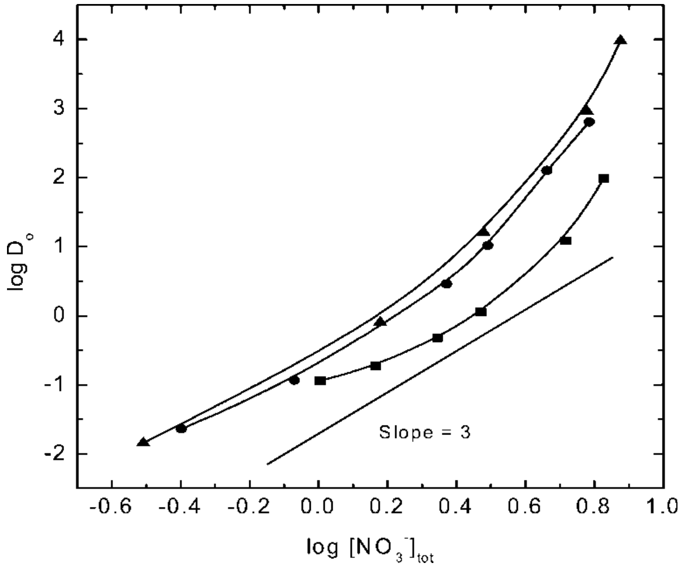

Figure 3. Extraction of $Eu(NO_3)_3$ into 60% TBP-dodecane from solutions containing constant $[HNO_3]$ and variable $[Al(NO_3)_3]$ ▲ 0.010 M HNO_3, ● 0.10 M HNO_3, ■ 1.0 M HNO_3.

To account for nitrate dependence in the experiments conducted as a function of $[HNO_3]$, it is necessary to rearrange Equation (8) to take into account the effect of changing $[HNO_3]$ on $[TBP]_{free}$:

$$\log(D_{Eu}(1 + \beta_1[NO_3^-]_{aq}) - m\log[TBP]_{org}$$

$$= n\log[NO_3^-]_{aq} + \log K_{ex} \qquad (9)$$

The correction to $[TBP]_{org}$ was done using the data plotted in Fig. 2. When Equation (4) is applied to the variable $[HNO_3]$ results (Fig. 4), slopes of ~3 are seen for both plots. The results shown in Fig. 5 demonstrate that in all cases, the TBP stoichiometry is ~2. The 1:2 stoichiometry of the extracted complex is consistent with previously reported results for the extraction of Eu(III) (and other trivalent lanthanides) by TBP from acidic NO_3^- aqueous solutions (13, 14).

U/Eu Extraction

The coextraction of UO_2^{2+} and Eu(III) was investigated by adding $UO_2(NO_3)_2$ (1.0×10^{-4} M) to a system containing $HNO_3/Al(NO_3)_3/$ Cr(III)/ascorbic acid/Eu(III). The aqueous phase compositions used for this study were 1×10^{-3} M Cr(III) with excess ascorbic acid, 0.10 M

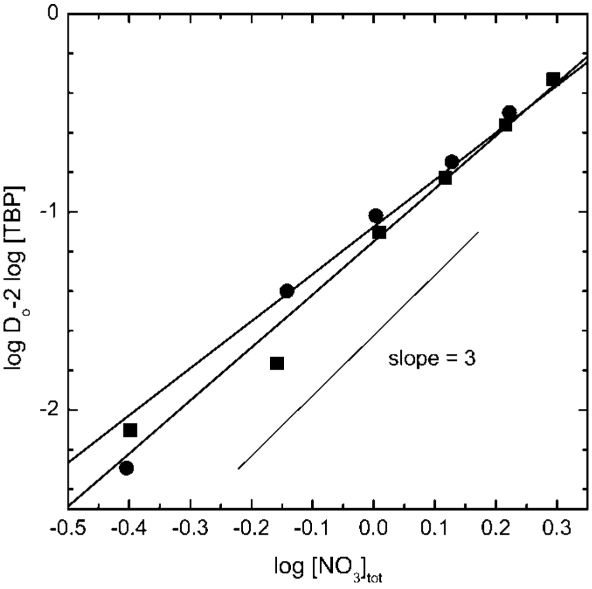

Figure 4. Extraction of $Eu(NO_3)_3$ into 60% TBP-dodecane from aqueous solutions containing constant $[Al(NO_3)_3]$ and variable $[HNO_3]$ ● 0.10 M HNO_3, ■ 0.010 M HNO_3.

$Al(NO_3)_3$ and variable $[HNO_3]$ (0.1–2.5 M). The distribution ratios of U and Eu as a function of $[NO_3^-]_{total}$ are shown in Figure 6. The observed D_U values range from 84% extracted UO_2^{2+} from 0.1 M HNO_3 up to 97% extracted UO_2^{2+} from the 2.5 M HNO_3. The two plots of D_{Eu} in Fig. 6 demonstrate that the presence of UO_2^{2+} does not effect Eu(III) extraction.

DISCUSSION

Chromium Extraction

There have been limited reports on the partitioning of Cr(VI) between aqueous HNO_3 and TBP phases. The most thorough study was published by Tuck and Walters in 1963 (15). Under the pH and [Cr(VI)] conditions used in their study, $Cr_2O_7^{2-}$ was the predominant aqueous phase species present. Their results indicated that between 0.1–3.0 M HNO_3 solutions, D_{Cr} values of <1 were attained. The same authors also proposed a mechanism and rate constant for the redox reaction between $Cr_2O_7^{2-}$ and TBP that was observed during the D_{Cr} investigation (16). The results from these two reports were of interest to this study because neither extraction nor reaction of Cr(VI)

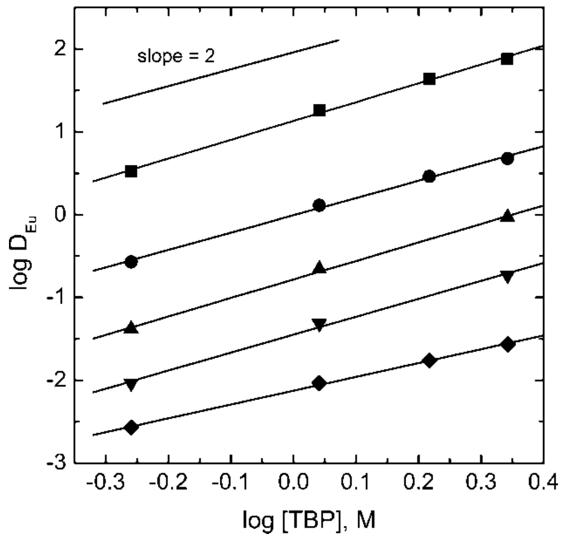

Figure 5. TBP dependence for the extracted Eu(III) species from $Al(NO_3)_3$, $NaNO_3$, and HNO_3 solutions. ■ 1.0 M $Al(NO_3)_3$ ● 0.50 M $Al(NO_3)_3$ ▲ 1.0 M $NaNO_3$ ▼ 1.0 M HNO_3 ◆ 0.10 M $Al(NO_3)_3$.

with TBP was desired. The aqueous $HNO_3/Al(NO_3)_3$ solutions used in this study were adjusted to pH$\leq$1 and contained 1.0×10^{-3} M Cr(VI). Under these conditions the dominant aqueous species are $HCrO_4^-$ and H_2CrO_4 (17, 18).

The results presented in Fig. 1 support the previous reports which stated that Cr(VI) will both be partially extracted and subsequently reduced in the TBP-containing organic phase. Further investigation into this system found that stripping of the CrO_4^{2-} from the 60% TBP phase was incomplete (19). The percent CrO_4^{2-} recovery decreased as a function of the time between extraction and back extraction experiments. This result suggests that the retained species may be a complex between a TBP degradation product, like dibutyl phosphoric acid, and the reduced Cr(III) organic species. Neither the current study nor the prior investigation(15) have identified the organic phase Cr(III) species. To eliminate these complications in the solvent extraction study, CrO_4^{2-} was introduced and intentionally reduced by adding ascorbic acid to the acidic solutions prior to phase mixing. We elected to adopt this procedure rather than eliminate Cr from the system to maintain as much relevance to possible sludge-leaching protocols as possible. The addition of 2.0×10^{-3} M ascorbic acid was found to be adequate for complete reduction of the CrO_4^{2-} to Cr(III), which remained in the aqueous phase due to the presence of the substitution inert Cr_{aq}^{3+} cation.

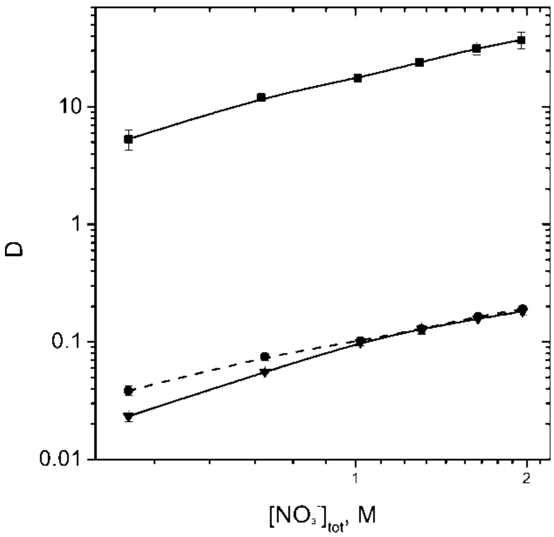

Figure 6. Extraction of $UO_2(NO_3)_2$ and $Eu(NO_3)_3$ into 60% TBP-dodecane from aqueous solutions of composition 1.0×10^{-4} M UO_2^{2+}, 1×10^{-3} M Cr(III), 1.0×10^{-6} M Eu(III), 0.1 M $Al(NO_3)_3$, excess ascorbic acid, with variable $[HNO_3]$. ■ D_U, ● D_{Eu}, ▲ D_{Eu} (no UO_2^{2+} present).

Europium Extraction

The partitioning of Eu(III) into the 60% TBP phase from solutions of constant $[HNO_3]$ increased significantly with increasing $[Al(NO_3)_3]$ (Fig. 3) over the $[Al(NO_3)_3]$ range of 0.10–2.50 M. The highest value observed for D_{Eu} was ~1000. The partitioning of Eu(III) between the 60% TBP phase from solutions of constant $[Al(NO_3)_3]$ with increasing $[HNO_3]$ (Fig. 4) increased slightly over the $[HNO_3]$ range of 0.10–2.50 M with a maximum D_{Eu} of ~0.2. Not unexpectedly, $Al(NO_3)_3$ and HNO_3 affect the partitioning of Eu and the performance of the proposed decontamination system differently.

$Al(NO_3)_3$ Effects

D_o values shown in Fig. 3 decrease as $[HNO_3]_{aq}$ increases in large part because of the increased association of TBP with HNO_3 in the organic phase. The loss of free extractant molecules to a 1 : 1 HNO_3:TBP complex in the organic phase accounts for the decrease, and illustrates the substantial weakness of the thermodynamic driving force for TBP extraction of $Eu(NO_3)_3$ relative to that for HNO_3. The steep increase in D_o seen at $[Al(NO_3)_3] > 1.0$ M is probably not attributable to a change in the NO_3^- dependency of the extracted species, but rather the result of the change in nitrate ion activity at high $[Al(NO_3)_3]$.

HNO_3 Effects

The persistent change in activities that plagues the linearity of the Al(NO_3)$_3$ analysis was not an issue for the HNO_3 system. Figure 4 reveals the linear nature of the log-log plot for the variable [HNO_3] data over an ionic strength range of 0.10–2.50 M. The straight lines with slopes equal to ~3 indicate nearly constant activity coefficients for HNO_3 over this concentration range.

Salting Out

D_{Eu} values as a function of aqueous $[NO_3^-]_{total}$ for three different electrolyte systems, HNO_3, $NaNO_3$, and Al(NO_3)$_3$, are shown in Fig. 7. From 0.1 to approximately 0.5 M, the similarity of the plots for the three systems indicates that the NO_3^- activity coefficients remain nearly constant as the cation identity changes. At higher concentrations, the D_{Eu} values for the three electrolyte systems diverge, with a slight increase seen for substitution of $NaNO_3$ for HNO_3 and a significant enhancement for substitution of the 1:3 electrolyte Al(NO_3)$_3$, particularly notable at nitrate concentrations

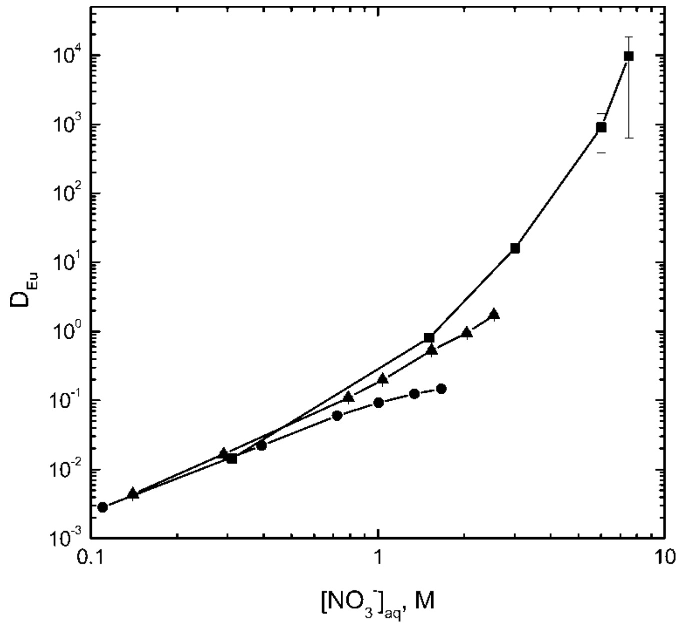

Figure 7. Extraction of Eu(NO_3)$_3$ into 60% TBP-dodecane from ■ Al(NO_3)$_3$ (0.01 M $NaNO_3$, 0.01 M HNO_3), ▲ $NaNO_3$ (0.01 M Al(NO_3)$_3$, 0.01 M HNO_3), ● HNO_3 (0.01 M Al(NO_3)$_3$, 0.01 M $NaNO_3$). Each solutions also contained 1.0×10^{-3} M Cr(III), and excess ascorbic acid.

above 2 M (0.65 M $Al(NO_3)_3$). The latter observation indicates a coincident decline in the activity of water, which allows more effective release of the $Eu(NO_3)_3$ complex to the organic phase. From the perspective of the intended cleanup application, these results imply that 60% TBP in dodecane will only be an effective extractant for Eu(III) (and/or any trivalent lanthanide or actinide) for effluents containing high concentrations of $Al(NO_3)_3$.

U/Eu Extraction

Figure 6 showed that one contact of a $HNO_3/Al(NO_3)_3/UO_2^{2+}$ solution with the 60% TBP phase achieves >80% removal of the initial UO_2^{2+}. This result was expected, as there is ample evidence of the effectiveness of TBP for solvent extraction applications of U(VI) from nitrate media (20). The D_{Eu} results also plotted in Fig. 6 demonstrates that Eu(III) partitioning is not effected either favorably or unfavorably by the presence of UO_2^{2+} at low total U concentrations.

Process Applications

The objective of this investigation was to demonstrate a solvent extraction technique that could be used to decontaminate Hanford tank leachate solutions by selectively removing radioactive species (UO_2^{2+} and Eu(III), representative in general of oxidized and reduced actinide species) using TBP in dodecane. The results from all the extraction experiments indicate that the TBP-dodecane system is only suitable for complete decontamination of the leachate solutions when high concentrations of Al are present. Uranyl and other hexavalent actinides would be effectively removed under a wide array of conditions.

Pu, which could be found as Pu(IV) and/or Pu(VI) in the HNO_3 leaching solutions, can easily be reduced to Pu(III) by the addition of excess ascorbic acid (21). If Pu(III) is the dominant species in the dilute HNO_3 leachate solutions, its chemistry in this system will follow the extraction behavior of Eu(III). If the medium remains oxidizing, Pu and possibly Np in the leachate could be stabilized in the hexavalent oxidation state, in which case these species should be expected to mimic uranium in any solvent extraction processing.

CONCLUSIONS

This investigation has addressed the concept of applying conventional solvent extraction separations method to the task of decontaminating radioactive sludge leachate solutions that could result if acidic leaching procedures were adopted for the cleanup of recalcitrant, aluminum-containing tank waste sludge residues at the Hanford Site. The results presented indicate that 60% TBP in dodecane can remove >90% of both Eu(III) and UO_2^{2+} from HNO_3 solutions containing $Al(NO_3)_3$, though in the case of Eu(III), not uniformly. This observation is in general accord with previous reports on TBP extraction, though the particular combinations of conditions studied herein have not been reported previously. The results for Eu(III) and UO_2^{2+} can be taken as generally representative of the behavior of trivalent and hexavalent actinide (and lanthanide) cations in a system of this type. A possible adjustment of this protocol that would certainly increase the efficiency of trivalent ion extraction would be to introduce a stronger extractant system, many of which are available. However, such adjustments would potentially lead to the increased removal of non-radioactive matrix ions, hence would have to be carefully considered. Fe(III), Mn(III), and Mn(IV) are important components that might have a significant impact in the deployment of a system modeled after this research. Further studies will likely focus on the adaptation of this approach to the development of decontamination strategies applicable to alkaline solutions that are relevant to more conventional sludge leaching procedures.

ACKNOWLEDGMENTS

The authors would like to thank the Department of Energy Environmental Management Science Program for funding this work. Much appreciation is felt towards all the members of the Dr. Kenneth L. Nash and Sue B. Clark radiochemistry laboratories at Washington State University. A final acknowledgement is due to the Nuclear Radiation Center (NRC) at WSU for the production of the Eu radioisotopes used in this study.

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