



Remediation of potentially acidified Hanford wastes using tri-n-octyl phosphine oxide extraction chromatographic materials

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ABSTRACT

As the Hanford site undergoes remediation, significant economies could be realized if aluminum and chromium are kept from High Level Waste glass produced at the Hanford Waste Treatment Plant (WTP). An acidic scrub of the Hanford sludge could enhance Al removal, although such treatment could lead to the mobilization of transuranic elements. If mobilization were minor, a chromatographic secondary cleanup of the acidic waste stream may be preferred to allow preconcentration of radionuclides prior to processing through the Hanford WTP. This study examines tri-n-octyl phosphine oxide coated resins as a chromatographic means for the removal of transuranics from a secondary waste stream. Metal uptake kinetics and mechanisms for transuranics and a simulant transuranic (europium) with the developed resin are characterized in both batch and column operation modes. Results indicate up to 99% of the radioactive material present from an acidic sludge leach may be recovered using extraction chromatography providing an effective avenue for high aluminum content tank pre-treatment.

1. Introduction

The U.S. Department of Energy (DOE) is responsible for environmental remediation at former nuclear weapons production sites. The Hanford Site, in south central Washington state, was the first facility to produce plutonium for nuclear weapons. Three plutonium separations methods were used during the operation of the Hanford site: Bismuth Phosphate (1945–1956), Redox (1951–1959) and PUREX processes (1956–1972; 1983–1989) [1]. The use of multiple plutonium separations and mixing wastes between tanks helped to create a complex waste matrix. As a result, Hanford site remediation is one of the most labyrinthine challenges faced by the Department of Energy. Both the volume and composition of waste resulting from Pu production are major remediation concerns [2]. The most problematic waste component is the sludge created by the caustic environment of the tanks.

The under construction Hanford Tank Waste Treatment and Immobilization Plant (WTP) is the cornerstone of the tank waste remediation effort. Full radioactive operations are scheduled to begin in 2019. The current design of the WTP may not be able to treat and immobilize the Hanford tank wastes in the expected lifetime of the plant. Consequently, DOE has been pursuing alternative treatment options for

selected wastes. If implemented, alternative treatments could expedite the sludge dissolution process and improve throughput of the WTP, thereby accelerating the overall Hanford tank waste remediation mission.

Remediation treatment efforts have focused on caustic leaching to remove problematic nonradioactive elements aluminum and chromium. Aluminum contributes significantly to the volume of waste processed and the precipitation of chromium spinels from the HLW could short the heating electrodes, clog the pour spout, or otherwise jeopardize the operation and life of the glass melter [3]. Removal of Al and Cr would decrease waste volume, lengthen the lifetimes of the vitrification furnace and improve stability of the vitrified high level waste (HLW) glass matrix. While not addressed here, the possibility of removing phosphate as an additional pretreatment has also been considered [4,5]. While caustic leaching has proven to have some value, the most stubborn Al phase, boehmite (γ -AlO(OH)), has been resistant to this treatment regimen.

As an alternative, the possibility of using acid/base wash cycles for enhanced alumina removal through surface activation/freshening has been considered. An undesirable side effect of acidic leaching is the potential mobilization of radioactive species into the Al/Cr waste

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stream [6]. If acidic leaching were to be performed, knowledge of how to remove radioactive species, predominantly actinides, from aqueous media of variable HNO_3 and $\text{Al}(\text{NO}_3)_3$ concentrations and chromium oxidation states would be required. Previous studies have shown solvent extraction (SX) with 60% by volume (v/v) (TBP) or 0.1 M tri-n-octyl phosphine oxide (TOPO) in *n*-dodecane from nitric acid aqueous media to be a complementary and effective means of handling the secondary cleanup [7,8]. If the solubilization of actinides is low, pre-concentration may be desired. An extraction chromatographic (EXC) remediation could serve to complement the solvent extraction efforts. Extraction chromatographic materials using TBP have also been shown to provide reasonable decontamination of transuranics when high concentrations of nitrate are present, but lower concentrations of nitrate require a more basic extractant for recovery of the trivalent actinides [9].

In this work, a bench scale exploration of a TOPO EXC system for the separation of U, Th, Np, Pu and Eu (serving as a surrogate for the trivalent actinides) from Al/Cr leachate solutions that could emerge if one were to attempt nitric acid leaching with Al-bearing solids has been developed. The “ambient” oxidation state of tracer levels of Np and Pu is defined through comparisons of Np/Pu partitioning with redox stable actinides (Th^{4+} and UO_2^{2+}). Ascorbic acid was added in some experiments to reduce potentially extractable chromate (CrO_4^{2-}) to less extractable Cr^{3+} . The polyacrylic XAD7 resin was used as the solid support for extractant immobilization as previous studies have shown the XAD7 resin to successfully retain TOPO for the purposes of metal uptake [10,11]. Correlations between solvent extraction chemistry, batch mode extraction and column separations are compared to previous work in this area and with each other.

2. Experimental section

2.1. Materials and instrumentation

All aqueous solutions were prepared from analytical grade reagents and ultrapure (18 M Ω) deionized H_2O . Solution density was determined by using a calibrated one mL pipette and weighing the aliquot at room temperature. Nitric acid solutions were prepared by mass using Fischer Scientific concentrated (15.8 M) HNO_3 solution. Sodium hydroxide solutions were prepared from dilutions of 50% w/w NaOH (Alfa Aesar) and standardized by titration of potassium hydrogen phthalate to a phenolphthalein end point. Solutions of K_2CrO_4 and $\text{Al}(\text{NO}_3)_3$ were prepared by mass using analytical grade J.T. Baker solids. The L-ascorbic and 1-hydroxyethane 1,1-diphosphonic acid (HEDPA) solutions were prepared by mass from Fisher Scientific ACS certified reagents and Alfa Aesar, respectively. TOPO (> 99%, Sigma Aldrich) was used without further purification and was diluted volumetrically using methanol. Amberlite XAD-7 (Rohm & Hass) was treated as described in the following section.

Experiments using $^{152/154}\text{Eu}$, ^{237}Np , $^{233}\text{UO}_2$, $^{238}\text{UO}_2$, ^{238}Pu , and ^{232}Th nitrates were conducted by dilution of standardized stocks from the Washington State University (WSU) radioisotope inventory. Experiments using stable $\text{Eu}(\text{NO}_3)_3$ were prepared by dilution of standardized stocks. Radioactive $^{152/154}\text{Eu}$ was created by neutron activation of 99.999% Eu_2O_3 (Arris International) using a Teaching, Research, Isotopes General Atomics (TRIGA) reactor with a neutron flux of 5×10^{12} n/cm 2 s at the Nuclear Radiation Center at WSU. Radiotracer experiments using $^{152/154}\text{Eu}$ were analyzed on a NaI(Tl) solid scintillation counter (Packard Cobra-II auto gamma) for gross gamma counting. Radiotracer experiments using ^{233}U , ^{237}Np and ^{238}Pu were analyzed using a Beckman LS6500 liquid scintillation counter for alpha detection with 5 mL of EcoScint $^{\text{®}}$ scintillation fluid. Light metals analysis (Cr, Al) and heavy metal analysis (^{238}U , ^{232}Th) was done using a Perkin Elmer Optima 3200 RL ICP-OES instrument and an Agilent 4500 + ICP-MS, respectively. Mixing was done using a VWR mini vortexer and mass measurements were obtained using a Mettler Toledo

XS105 Dual Range series analytical balance.

2.2. Resin preparation

Amberlite XAD7 resin is a polyacrylic resin with a 20–60 mesh particle size and a surface area of 450 m 2 /g. Acidic impurities were removed with a DI water rinse until a neutral pH was obtained. Resin drying was expedited by methanol (MeOH) addition and removal, followed by placement in an oven at 80 $^{\circ}\text{C}$ for at least an hour. Dried resin was removed from the oven, allowed to cool in a vacuum desiccator, weighed and contacted for 15 min by vigorous shaking with 1 M TOPO in MeOH with excess coating solution. Excess solution after contact was removed and the coated resin was dried at 80 $^{\circ}\text{C}$ overnight. The amount of extractant loading to the resin is defined in this work as the ratio of mass of organic extractant present to the total final mass of the extractant loaded resin. This coating process provided 58 wt%. For 38 wt % resin, dried resin was contacted in a ratio of 1.05 g XAD7 : 1.75 g TOPO in excess methanol.

The rate of metal uptake onto TOPO-XAD7 resin was determined to be significantly slower than comparable solvent extraction systems. To encourage faster metal uptake kinetics, the TOPO-XAD7 resin was wetted with *n*-dodecane (abbreviated TOPO-XAD7n) using a 50% v/v chloroform/*n*-dodecane solution [12]. The 58% and 38% TOPO-XAD7 resins were wetted with 100 and 160 μL of the chloroform/*n*-dodecane mixture providing dissolution of 30% and 53% of TOPO on the resin surface, respectively. Wetting ratios were selected to minimize the presence of excess *n*-dodecane and potential loss of TOPO from the resin during the wetting process. Wetting the chromatographic material produced 46% and 24% TOPO-XAD7n resins. Assuming a density of 1 g/mL, which is generally consistent with the literature [13], the concentration of TOPO for the 46% and 24% wetted resin is 1.33 and 0.75 M, respectively.

2.3. Batch experiments

All batch extractions were performed in triplicate and the errors presented denote a $\pm 1\sigma$ standard deviation of the triplicate analysis. The weight distribution ratio of the analyte, D_w (mL \cdot g $^{-1}$), was calculated according to the following equation:

$$D_w = \left(\frac{A_o - A_s}{A_s} \right) \times \frac{V}{m} \quad (1)$$

where A_o and A_s are the aqueous phase activity (counts per minute) before and after equilibration, m the mass of resin (g) and V the volume of the aqueous phase (mL). For radiotracer experiments, triplicate experiments showed the reproducibility of the distribution measurements was generally within 10%, although the uncertainty interval was somewhat higher for the highest distribution values ($D_w \geq 10^3$) due to a lack of discernible activity in the aqueous phase. When possible, weight distribution values (D_w) were corrected for nitrate complexation in the aqueous phase, as done previously, to provide the corrected weight distribution ratio, D_{w_0} [7,8]. The ratio of solution volume to resin was kept at 10 mL/g.

2.3.1. Eu^{3+} partitioning

For $^{152/154}\text{Eu}$ extraction experiments with TOPO-XAD7, the aqueous phase contained various amounts of HNO_3 , $\text{Al}(\text{NO}_3)_3$, Cr(III/VI), and Eu (III). Chromium and ascorbic acid concentrations were maintained at 1 mM and 3 mM, respectively. Europium uptake from varying HNO_3 in the presence of constant $\text{Al}(\text{NO}_3)_3$ and constant HNO_3 with varying Al (NO_3) $_3$ was studied. Non-radiotracer europium was present at 1 mM to highlight the macroscale uptake capabilities of the TOPO resin. Phases were contacted for 20 min by vigorous shaking and aliquots of the aqueous phase were obtained. Analysis for $^{152/154}\text{Eu}$ in the aqueous phase was performed as described previously.

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