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SPECIATION AND SURFACE INTERACTIONS OF
ACTINIDES ON AGED ION-EXCHANGED RESINS

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Speciation and Surface Interactions of Actinides on Aged Ion-Exchange Resins.

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Introduction

The United States Department of Energy is presently faced with the stabilization and safe disposition of hundreds of metric tons of residue materials resulting from 50+ years of nuclear weapons production activities. These residues encompass a broad range of substrates and radionuclides and include both solid and liquid materials. Combustible residues constitute a significant fraction of the total residue inventory, and an important constituent within the combustible category is spent anion ion-exchange resins. These resins are typically utilized for the separation of plutonium from other radionuclides under strongly acidic nitric or hydrochloric acid solution conditions which favor the formation and partitioning of anionic Pu(IV) nitrate or chloride species. The spent resins are usually rinsed prior to storage as residues to reduce both acid and radionuclide concentrations, but significant radionuclide concentrations remain in these resins, and the long-term effects of concentrated acid and radiolysis on the resin integrity are relatively unexplored. Thus, new research is needed to assess the stability of these resin residues and address the need for further treatment to ensure stability prior to long-term disposal.

There have been numerous previous spectroscopic studies of plutonium and uranium solution speciation under ion-exchange process-relevant conditions¹⁻⁴, and even some spectroscopic studies of plutonium speciation within the exchange sites of the anion-exchange resins⁵. However, similar speciation investigations on resins that have undergone aging effects as a result of chemical and radiolytic degradation have not been reported. In this study, we are examining the speciation and surface interactions of uranium and plutonium nitrate species on anion-exchange resins that have been "aged" under controlled conditions of elevated nitric acid concentration and temperature.

Experimental

Two anion exchange resins were selected for these studies; Dowex 11 which is a quarternary amine-derivatized polystyrene/divinylbenzene copolymer formulation, and Reillex HPQ which is a methylated 4-vinylpyridine/divinylbenzene copolymer formulation. These resins

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are typical of those used in actinide processing applications. The resins are artificially aged by storage at ~ 50 °C in nitric acid solutions ranging from 4 - 12 M for periods from several days to ~ 12 months. The effects of aging on the resins (in the absence of actinide species) is being assessed by Raman and luminescence spectroscopy. Aged and fresh resins are reacted with solutions of UO_2^{2+} or Pu(IV) in nitric acid of varying concentrations (0 - 12 M). Freshly loaded resins are also allowed to age in the presence of the actinide. The extent of loading and the speciation and interaction mechanism(s) of the actinide species on the resin are being determined using luminescence, photoacoustic, and Raman spectroscopies.

Results

The nitric-acid induced degradation of the anion-exchange resins is strongly dependent on the nitric acid concentration. At concentrations below 4 M, the resins appear to be indefinitely stable. At 12 M HNO_3 , essentially complete degradation is observed within ~ 100 days. At intermediate concentrations (notably those in the actinide processing regime) there are subtle changes in the vibrational spectroscopic data that clearly indicate a change in resin structure. However, the spectroscopic change suggests a quite specific, highly localized structural change. We do not observe changes in the nitrate stretching region of the vibrational spectra ($\sim 1350 - 1400 \text{ cm}^{-1}$) that would be consistent with nitration of the resin backbone.

Luminescence spectral data (continuous-wave and time-resolved) obtained for UO_2^{2+} on the resins as a function of nitric acid concentration (0 - 12 M) clearly indicate extensive uptake, even for nitric acid concentrations as low as 4 M. This suggests that anionic uranyl nitrate species exist even at these low HNO_3 levels in contrast to previously published interpretations of uranyl nitrate solution speciation results^{3,4}. The luminescence data are complicated by the presence of a luminescence signal from the resin itself. However, the resin signal is overwhelmed by the uranyl signal at sufficiently high uranyl loading levels. In addition, the two luminescent signals do not appear to be simply additive, suggesting that there is some degree of electronic interaction between the uranyl in the resin exchange site(s) and the resin chromophore(s). At liquid nitrogen temperatures, the signals from the resin and the uranyl species become very well resolved, and the uranyl spectrum acquires its characteristic vibronic structure. Time-resolved spectral data were acquired to search for multiple uranyl exchange complexes on the resins, but these results are somewhat ambiguous. Aging effects in this system are still being assessed. Preliminary data analyses suggest that there are not significant changes in the speciation or uranyl on the resin with time.

New experimental studies for the Pu(IV) system on the resins using photoacoustic spectroscopy are underway and the results will be discussed in detail as part of this report.

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