



Abstract

A study will be performed on the speciation of U and Pu in a TBP (tributylphosphate)-dodecane-nitric acid extraction system. The influence of nitrate concentration on U distribution and speciation will be the main focus of this work. The aqueous phase will consist of uranyl nitrate, nitric acid, and lithium nitrate. The organic phase will be a 30% TBP in dodecane solution, and equal volumes of the two phases will be contacted. These studies will be used to obtain data for modeling the behavior of actinides under a range of conditions encountered in separations, including acid concentration, metal ion concentration and temperature. The procedures developed will be applied to further studies of Pu.

Introduction

The PUREX process is well known and is the basis of the UREX process. For these separations spent nuclear fuel is dissolved in nitric acid and contacted with an organic extractor. In PUREX, U and Pu are separated from the rest of the spent fuel with Pu being separated from U by reduction to the trivalent state. The separation of Pu is a proliferation concern, and so the process has evolved into the UREX process. In the UREX process the interaction of AHA (acetohydroxamic acid) with Pu is exploited to achieve the separation of U and Tc from the Pu and other radionuclides in spent fuel by maintaining Pu in the aqueous phase. While the extraction is functional, more data is needed in order to achieve detailed modeling. Understanding the role of nitrate in speciation is important for determining the necessary data for extraction modeling since nitrate is the main counter anion in the extraction process. This project will evaluate the fundamental speciation of Pu and U in the TBP-dodecane-nitric acid system, with the main emphasis on nitrate speciation and subsequent third phase formation. These studies will be used to obtain data needed for modeling the behavior of the actinides under a range of extraction conditions, including acid concentration, metal ion concentration and temperature.

Experimental

Sample Generation

- aqueous phase
 - concentrations of nitric acid from 0 M to 12 M
 - concentrations of nitrate vary by addition of LiNO_3
 - concentrations of uranium are 0.1 M and 0.05 M $\text{UO}_2(\text{NO}_3)_2$
- organic phase
 - pre-equilibrated 30% TBP(tributylphosphate) in dodecane
- contact 0.75 mL of each phase
- phases mix for 2 minutes
- centrifuge for 3 minutes to separate
- extract phases for analysis

Determining Concentration

- decide on best methods to measure:
 - [U]
 - [H⁺]
 - [NO₃⁻]
- use the data to calculate distribution and stability constants to predict speciation

Spectroscopy

- use available spectroscopic methods to prove the predicted speciation
 - UV-Visible
 - NMR
 - IR
 - EXAFS
 - Laser Fluorescence

Method Development

Measuring Nitrate Concentration:

- Investigated three methods
 - ISE (ion selective electrode)- linear range of about 1×10^{-4} M to 1×10^{-1} M, problems at higher acid concentrations, and the results were not reproducible
 - HPLC (high performance liquid chromatography)- linear range of about 1×10^{-6} M to 1×10^{-2} M, minimal acid effects, and the results were reproducible
 - IC (ion chromatography)- linear range was the same as HPLC, the acid effects were minimized, and the results were reproducible

Measuring Uranium Concentration:

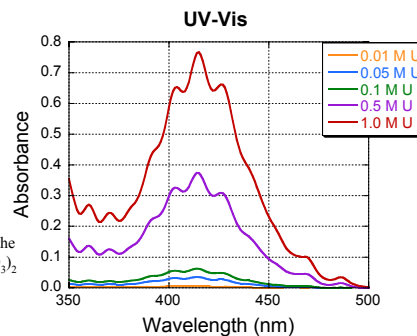
- Investigated two methods
 - ICP-AES (inductively coupled plasma-atomic emission spectroscopy)
 - LSC (liquid scintillation counting)- large range of detection, and also reproducible and dependent results

Measuring Acid Concentration:

- Only used titration with a Metrohm automated titrator

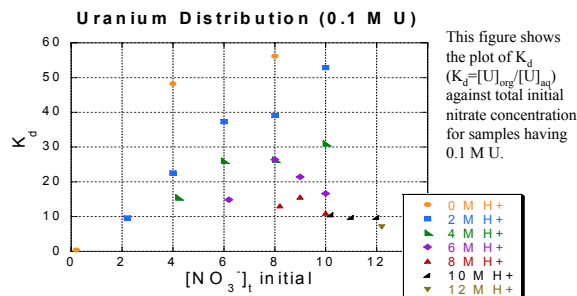
Spectroscopy

The current methods available are UV-Visible spectroscopy and EXAFS (Extended X-Ray Absorption Fine-Structure spectroscopy). The following methods will soon be used: NMR spectroscopy, IR spectroscopy, Raman spectroscopy, and Laser fluorescence spectroscopy.



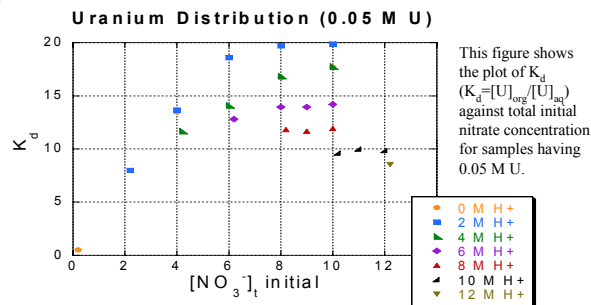
This figure shows the spectra of $\text{UO}_2(\text{NO}_3)_2$

Distribution



This figure shows the plot of K_d ($K_d = \frac{[U]_{org}}{[U]_{aq}}$) against total initial nitrate concentration for samples having 0.1 M U.

Distribution



This figure shows the plot of K_d ($K_d = \frac{[U]_{org}}{[U]_{aq}}$) against total initial nitrate concentration for samples having 0.05 M U.

Results and Conclusions

- We have investigated the various methods for the detection of nitrate and uranium
 - Found the best way for measuring nitrate ion concentration is by IC (ion chromatography)
 - Found that the simplest way for measuring uranium concentration is LSC (liquid scintillation counting)
- The results of the first set of extractions show that the amount of U extracted into the organic phase increases with increasing nitrate concentrations until it reaches a plateau around 8 M [NO₃⁻].
- Future work
 - perform the same experiment with a smaller range of concentrations to narrow in on an area of interest
 - spectroscopic methods that have recently become available (IR, NMR, and Laser fluorescence) will be utilized in order to help determine the exact speciation in each phase
 - Once this system is understood, then work can begin with PU. The future research will provide fundamental data on the chemical behavior of Pu. This will permit the modeling of novel extraction under a variety of TBP-nitric acid conditions as well as evaluate the influence of AHA.

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