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Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System

Kenneth Czerwinski
University of Nevada, Las Vegas, czerwin2@unlv.nevada.edu

Byron Bennett
University of Nevada, Las Vegas

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Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System
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Professor Ken Czerwinski   E-mail: czerwin2@unlv.nevada.edu
Department of Chemistry and Harry Reid Center
Professor Byron Bennett
Department of Chemistry
University of Nevada, Las Vegas

Student: Inna Bashta, Incoming Radiochemistry Graduate Student
Graduate student to be determined
DOE Collaborator: Dr. George Vandegrift, ANL
Technical Focus Area: Separations

Abstract
        The speciation of hexavalent U and tetravalent Pu will be examined in the TBP-dodecane-nitric acid systems. This topic is chosen based on data needs for separation modeling identified by the AFCI. Emphasis will be placed on studying the influence of nitrate and acetohydroxamic acid on U and Pu speciation as well as conditions where a third phase forms in the organic phase. The organic phase will be 30 % TBP in dodecane. Equal volumes of aqueous and organic phase will be used. The speciation of the actinides in the aqueous and organic phase will be determined by a number of different spectroscopic and radiochemical techniques. Additionally the actinide distribution between the phases as a function of conditions will be determined. The project data will be incorporated into models to evaluate separations under a variety of conditions.

1. Background and Rational

1.1. Project Rational

The extraction of tetravalent Pu in nitric acid solution by tributylphosphate (TBP) is well known and has been the basis of Pu purification for a number of decades. The extraction is based on the formation of an organic phase neutral complexes such as $Pu(NO_3)_4 \cdot 2TBP$. Upon reduction, the trivalent Pu species is back extracted into an aqueous phase. However, the data needed for detailed modeling of Pu extraction is not available for all conditions of concern to the AFCI. Based on the direction from Dr. George Vandegrift of ANL, this proposal was developed to obtain the necessary data for Pu extraction modeling.

Understanding the role of nitrate in Pu speciation is important for determining the necessary data for Pu extraction modeling. Data indicates the dinitrate complex of Pu is strong and may account for difficulties in modeling Pu extraction under some nitrate conditions. The formation of hydrolysis products may also form an extractable species that will need to be included in modeling. In the UREX process, acetohydroxamic acid (AHA) is expected to be used (Figure 1). The interaction of AHA with tetravalent Pu decreases extraction into the organic phase by either complex formation or reduction of Pu to the trivalent state. For the separation of Pu in a solvent extraction system using acetohydroxamic acid, it is necessary to determine the complexation kinetics and thermodynamics [1]. In addition, since Pu is a redox sensitive element, the change in speciation due to oxidation-reduction reactions upon complexation needs to be evaluated. This project will experimentally 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 at high nitric and metal ion conditions. Experiments on the AHA systems will be conducted in collaboration with the and with input from AFCI separations group.

Figure 1. Acetohydroxamic acid
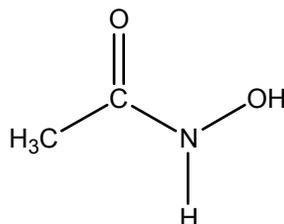
1.2. Pu Nitrate Data and Third Phase Formation

Recent efforts on evaluating the role of nitrate in Pu speciation during extraction has been directed at understanding the formation of a third phase in the extraction process. Third phase occurs at high metal ion and high nitric acid concentration. Under the correct conditions, the organic phase will split into two separate phases (Figure 2). Historically, the study of third phase formation in solvent extraction systems has exclusively focused on defining the boundaries where it may occur. Typically, results are reported as limiting organic concentrations (LOC), which is the maximum concentration of metal found in the organic phase prior to a visual observation of phase splitting. The effects of several variables, including nitric acid concentrations, temperature, diluent and ionic strength, have been studied on the formation boundaries [2- 5], However, the lack of a complete, fundamental understanding has resulting in considerable confusion in the literature on the exact boundaries for a given system as illustrated in Figure 3.
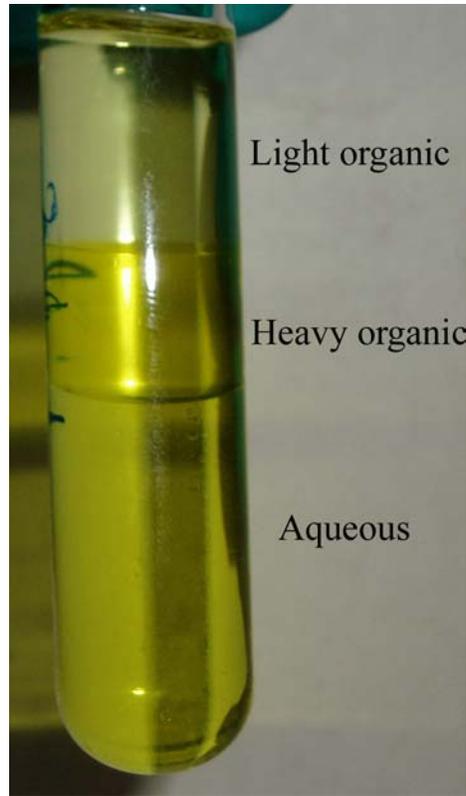
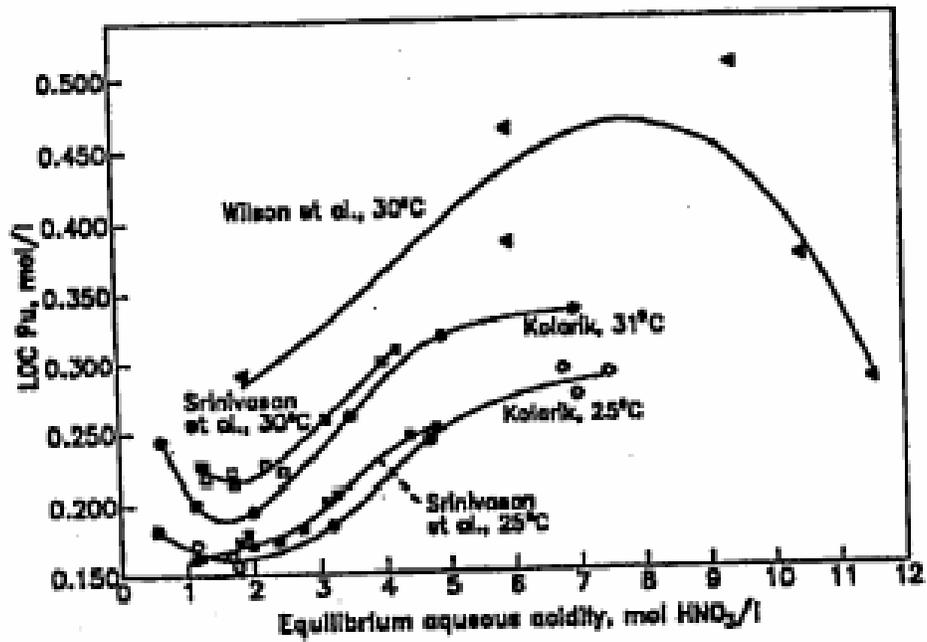Figure 2. TBP-HNO$_3$-UO$_2^{2+}$ third phase appearance

Figure 3: Comparison of LOCs in literature reviewed by Rao [2].

Recent advances in the study of third phase formation have led to greater insights on the mechanism of formation and the role of nitrate in the speciation of the extracted nitrate species. A model for the mechanism based upon mass balances of metal, HNO_3, and TBP has been developed In line with studies on uranium third phase characteristics [6], it was proposed the third phase as an extended solvate ($Pu(NO_3)_4 \cdot 2TBP \cdot HNO_3$) of the normal metal adduct ($Pu(NO_3)_4 \cdot 2TBP$). The reaction system was thus represented as:

$$Pu(NO_3)_4 \cdot 2TBP + HNO_3 \cdot TBP \leftrightarrow Pu(NO_3)_4 \cdot 2TBP \cdot HNO_3 + TBP$$

$$H_2O + TBP \leftrightarrow H_2O \cdot TBP$$
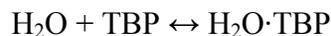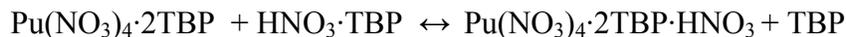
Using experimental values found in the literature, an equilibrium expression and corresponding value for the equilibrium constant were determined

$$K = \frac{\left[Pu(NO_3)_4 \bullet 2TBP \bullet HNO_3\right]}{\left[Pu(NO_3)_4 \bullet 2TBP\right]\left[HNO_3 \bullet TBP\right]}$$

$$K = 5.6910e^{\left(-1.5103[HNO_3]_{tot}\right)}$$

This constant is based upon only three data points in a 30% TBP-n-dodecane-HNO_3 system. The mechanism did hold well in the Th(IV) and U(VI) systems where substantially more data were available and indicates an existing variation in the presumed Pu nitrate chemistry.

Several recent studies have examined the structure of the third phase in U(VI) and Th(IV) systems [6,7]. Through a combination of chemical analysis, FTIR, UV-Visible Spectroscopy, EXAFS, and SANS, it was demonstrated that the composition of U(VI) third phase to be $UO_2(NO_3)_2 \cdot 2TBP \cdot HNO_3$. Additional SANS and FTIR work [8,9] supported similar nitric acid binding in Th(IV) third phase species. It has been proposed that this aggregation is responsible for the observed phase splitting. However, an abrupt change in UV-Visible spectra for the phases has been observed, suggesting that third phase formation is not a molecular aggregation phenomenon but rather the formation of separate chemical specie [6].

1.3. Acetohydroxamic acid

The deprotonation of acetohydroxamic acid has been examined and a $pK_a=8.70$ was evaluated. It was found that the deprotonation occurs over the alcohol proton rather than the amine [10]. Complexation studies have been performed with UO_2^{2+} [11] and lanthanides [12,13]. Both kinetics and thermodynamics were evaluated. Comparison studies of acetohydroxamic acid with desferrioxamine B have been performed, with similarities found for the complexation [14]. The complexation of desferrioxamine B with lanthanides and actinides has been evaluated by the PI [15]. Spectrophotometric titration was used to examine the complexation constants of UO_2^{2+} species from pH 4 to pH 9 (Figure 4). XAFS studies were also used to correlate the changes in speciation with changes in constants, mainly due to the formation of mixed hydroxyl species at high pH. Both UV-spectroscopy with titration and XAFS will be used to evaluate U and Pu interaction with acetohydroxamic acid. However, the high pH range may not accessible for tetravalent Pu due to precipitation from hydrolysis.

Figure 4. Absorbance spectra from the titration of UO_2^{2+} with desferrioxamine B. The ligand and metal concentrations are 1 mmol/L
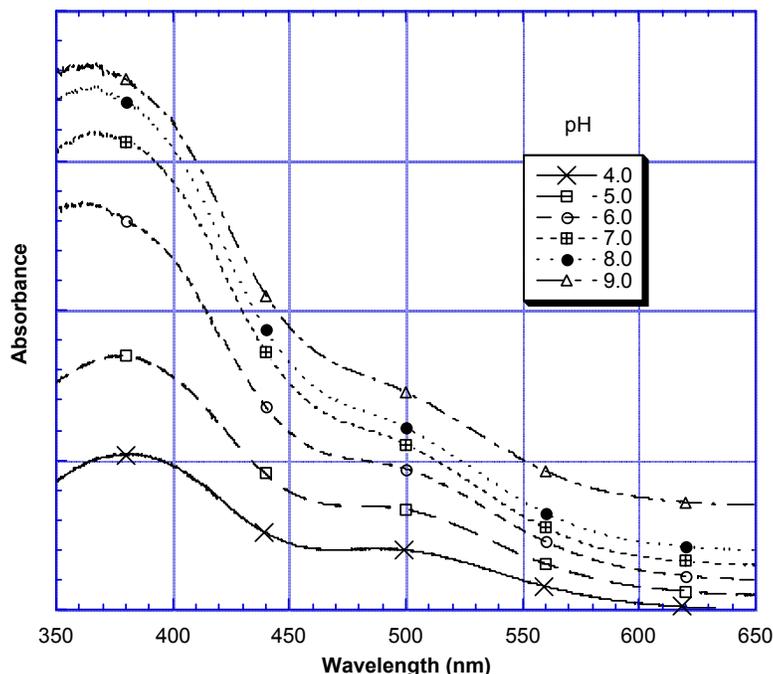
1.4. Evaluation of Chemical Thermodynamic and Kinetic Data

The goal of our Pu and U speciation studies will be to obtain data for modeling the behavior of the actinides under a range of extraction conditions, including acid concentration, metal ion concentration, and temperature. Speciation calculations can be performed if the stability and solubility constants for the chemical species formed under the examined conditions are known. For the extraction system under study precipitation is not expected, therefore solubility data can be neglected. If conditions under which precipitation of the actinide occurs, solubility studies of the precipitated species will be included. A general chemical reaction is described as:

$$aM^{z+} + bL^{x-} \Leftrightarrow M_aL_b^{(az-bx)} \qquad \text{Eq. 1}$$
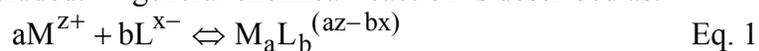
for complexation where M is the metal ion and L is a ligand. In the case of the extraction system under investigation, two ligands may be considered, namely nitrate and TBP. The kinetics of the reaction can be measured to establish conditions needed for equilibrium. For the extraction system under study the kinetics are expected to be rapid. However, kinetic evaluation of third phase formation may be needed. The change in actinide and ligand concentration can drive the formation of various chemical species.

From Eq. 1, the stability constant to describe speciation at equilibrium can be written as:

$$\beta_{MaLb} = \frac{[M_aL_b^{(az-bx)}]}{[M^{z+}]^a[L^{x-}]^b} \qquad \text{Eq. 2}$$

In actuality, the constants should include activity coefficients. If the constant is measured as a function of ionic strength, the specific ion interaction theory or the Pitzer equation can be used to evaluate constants at different ionic strengths. Temperature variations are explained by second law extrapolations with Gibbs free energy. Enthalpy and entropy will be investigated by

evaluating the stability constant as a function of temperature through the following equations (using standard nomenclature) [16]:

$$\Delta G = -RT \ln ß \qquad \text{Eq. 3}$$

$$R \ln ß = -\frac{\Delta H}{T} + \Delta S \qquad \text{Eq. 4}$$

For a system with different species, if the stability constants are known, then all the species can be calculated at any given pH by:

$$[M]_{total} = 10^{-pM} + \sum 10^{-(apM-bpL-\log ß_{MaLb})} \qquad \text{Eq. 5}$$

where pM is -log[M] and pL is -log[L]. The thermodynamic data can also easily be incorporated into existing codes such as AMUSE or the geochemical code CHESS.

2. Research Objectives and Goals

- Influence of nitrate on the speciation of U and Pu in the TBP-dodecane-nitric acid system (Task 1)
    - o The aqueous and organic speciation of U and Pu will be examined as a function of the following conditions
        - ▪ nitric acid concentration
        - ▪ nitrate concentration (by the addition of $NaNO_3$)
        - ▪ actinide ion concentration
        - ▪ temperature
        - ▪ time
- Speciation of U and Pu with AHA in the presence and absence of TBP-dodecane organic phase(Task 2)
    - o The aqueous and organic speciation of U and Pu will be evaluated under the following conditions
        - ▪ AHA concentration
        - ▪ Metal ion concentration
        - ▪ Metal ion redox state
        - ▪ pH
        - ▪ temperature
            - • experiment will initially examine the aqueous phase then examine the two phase system
- Modeling (Task 3)
    - o Incorporation of thermodynamic and kinetic data into existing codes
- Experimental techniques
    - o The following experimental techniques will be used in the evaluation of U and Pu speciation
        - ▪ UV-Visible spectroscopy
        - ▪ Time resolved laser fluorescence spectroscopy
        - ▪ NMR spectroscopy
        - ▪ IR spectroscopy
        - ▪ Raman spectroscopy
        - ▪ Titrations
        - ▪ ICP-MS
        - ▪ ICP-AES
        - ▪ XAFS

- Electrochemical

3. Technical Impact

The research will address an important area within AFCI by providing data useful for modeling the extraction of Pu. The data will expand the utility of existing codes and provide fundamental data on the chemical behavior of Pu in nitric acid. This will permit the modeling of novel extractions under a variety of TBP-nitric acid conditions as well as evaluate the influence of AHA. Furthermore, the formation of third phase will be understood based on speciation data. An understanding of third phase formation is of importance in accessing the safety of nuclear solvent extraction systems. While basic data on the third phase formation boundaries exists for certain specific PUREX flowsheets, no data is available for the proposed AFCI system. In addition, historically the study of third phase formation in solvent extraction systems has exclusively focused on defining the boundaries where it may occur. Although the effects of several variables have been studied, very little progress had been made on the formation mechanism or characterization of third phase species. It is expected the results will provide the data necessary to describe the role of nitrate in Pu extraction, particularly in the presence of AHA.

4. Research Approach

Initial experiments will be performed with UO_2^{2+}. The initial results obtained with UO_2^{2+} will be the basis for further experiments with Pu. In extraction experiments, the aqueous and organic phases will be equal volumes and range from 0.5 mL to 5.0 mL. The actinide ion concentration will be varied from μmol/L to the mmol/L range. Nitrate concentrate will be varied from the concentration due to nitric acid by the addition of $NaNO_3$. The nitric acid concentration will be varied from 14 M to the pH range in experiments with AHA. The temperature will be varied from 20 °C to 80 °C. The results will be used to determine Gibbs free energy (see section 1.4).

4.1. Task 1. Influence of nitrate on the speciation of U and Pu in the TBP-dodecane-nitric acid system

In Task 1 the influence of nitrate on the speciation of hexavalent U and tetravalent Pu in the TBP-dodecane-nitric acid system will be examined. The TBP concentration in the organic phase will be 30 % and the TBP will be purified by washing with carbonate prior to use. The following parameters will be varied:

Nitric acid: 2-14 M
Metal ion concentration: 1 μmol/L to 500 mmol/L
Nitrate: 2.5-14 M, increased by the addition of $NaNO_3$
Temperature: 20-80 °C

Kinetics will be measured in conditions were third phase forms by collecting UV-Visible spectra and evaluating change in spectra as a function of time. The distribution of the actinide will be determined to permit comparison with existing data. The chemical form for the actinide in the aqueous and organic phase will be examined by UV-Visible spectroscopy, time resolved laser fluorescence spectroscopy (for hexavalent U), and with indicator dyes or chromatography at lower concentrations. XAFS spectroscopy will be used to determine oxidation state and coordination environment around the metal center. The nitrate in the organic phase will be evaluated by Raman spectroscopy. The TBP speciation will be examined by ^{31}P NMR. The

concentration of the acid in the organic phase will be determined by titration with base and the addition of ammonium oxalate to complex metal ion from an organic sample back extracted with an aqueous phase. We expect to obtain data to describe the formation of actinide-nitrate-TBP species and determine complexation constants based on the equations in section 1.4.

4.2. Task 2. Speciation of U and Pu with AHA in the presence and absence of TBP-dodecane organic phase

The initial experiments in task 2 will examine the speciation of hexavalent U and Pu with AHA in a nitrate aqueous phase. The effect of AHA concentration, metal ion concentration, nitrate, pH and temperature on actinide speciation will be evaluated. The acid range will be from slightly basic to 10 M nitric acid with most effort focused on range where AHA will complex the actinides based on the pKa of AHA . Nitrate concentration will be varied from 0.1 M to 8 M. The temperature range will be from 10 ºC to 80 ºC. The Pu oxidation states will be 3+, 4+, and 6+ with a focus on the tetravalent state. The preparation of the different Pu oxidation states will be performed according to the literature [17]. Kinetics will be evaluated by collecting UV-Visible spectra over time; including spectrophotometric titrations (see Figure 4). Changes in the absorption peaks for the free and complexed U and Pu will be examined as a function of time, yielding kinetic rate constants. Equilibrium will be identified by a consistent absorption spectrum. The complexation constants can be determined from spectrophotometric data with the program SQUAD or OPIUM [18]. Deconstruction of the equilibrium data will allow a determination of stability constants under the given experimental conditions based on the generalized equation given in section 1.4. Once the initial aqueous phase experiments are complete studies on the 2 phase systems will be performed. The two phase experiments will be based on and compared to results from task 1. This will permit an evaluation of the impact AHA has on U and Pu speciation, distribution, and third phase formation.

4.3. Task 3. Complexation Modeling

This task will be coordinated with the ANL partner to facilitate data incorporation into the AMUSE code. The resulting kinetic and thermodynamic data will be used to model the affect of nitrate, temperature, metal ion, and AHA on U and Pu speciation and distribution under solvent extraction conditions. Complexation constants will be use to evaluate solution concentrations under equilibrium conditions. We expect the kinetics to be rapid and equilibrium conditions to be readily attainable. Additional calculations can be performed as describe in section 1.4 or with the modeling code CHESS. The program CHESS examines metal ion, colloid, and matrix chemistry [19]. The key attribute of CHESS is the ability to include surface complexation through the double layer theory. The main data base for CHESS is from the literature [20,21]. It contains around 700 species, over 600 minerals, over 50 redox couples, and 10 gases. Relevant data for the evaluated system can be introduced into the CHESS program for our work. We have used CHESS for evaluation actinide speciation in a number of different extraction, coolant, and environmental systems.

5. Capabilities

The PI has a transuranic chemistry laboratories for performing radiochemical and spectroscopic experiments. Laser and Raman spectroscopy will be performed in cooperation with the laboratory of Prof. Malcolm Nicol of the Chemistry and Physics Departments. Prof. Bennett will coordinate spectroscopic measurements using NMR and IR spectroscopy. To further

extend our capabilities we have initiated a cooperative program with Forschungszentrum Karlsruhe, Institut fuer Nukleare Entsorgungtechnik. They have agreed to provide laboratory experimental space for a visiting scientist to perform studies in their institute.

For determining actinide speciation and concentration, the main experimental methods can be divided into spectroscopic (see discussion in section 4) and separation followed by detection. XAFS (XANES and EXAFS) will also be used. XAFS experiments will be performed with DOE collaborators at ANL or SRTC. Separation/Detection experiments divide species based on size, charge, or a combination of the two. The amount of each species is quantified by radiation detection or analytical techniques. Speciation by spectroscopy relies upon the differences between the absorption or emission of different species. Through controlled experiments, spectra are collected and deconstructed to analyze the contribution from each species. We can also utilize electrochemical methods to evaluate the speciation of Pu with acetohydroxamic acid. Electrochemistry is a powerful tool for the determination of formal redox potentials, detection of chemical reactions that precede or follow the electrochemical reaction and the evaluation of electron transfer kinetics. XAFS experiments are to be performed at Stanford or ANL facilities with partners from ANL or SRTC. We have already used these XAFS facilities for examining actinide containing solutions and solid phases. XAFS is well suited to actinide speciation studies [22]. This is because X-ray absorption originates from an atomic process, and an element will always exhibit XAFS regardless of its speciation (i.e., species are never spectroscopically silent). Since XANES and EXAFS provide average local electronic and structural information about specific atomic species, they are well suited to the study of actinide ions in many forms (e.g. molecular ions, An^{3+}, An^{4+}, AnO_2^{2+}; complexes $AnO_2(OH)_2$, $An(CO_3)_4^{2}$; and solids AnO_2CO_3, AnO_s, where An=U or Pu).

6. Project Timeline

Reports will be produced as specified. It is anticipated that presentations at annual scientific meeting will result from this research. The project will be 3 years in length. The time frame and expected results for each task are below.

Task 1: Influence of nitrate on the speciation of U and Pu in the TBP-dodecane-nitric acid system (Project months 0-28)

- Speciation of U in the TBP-dodecane-nitric acid system as a function nitric acid concentration (finalized by month 12)
- Speciation of U in the TBP-dodecane-nitric acid system as a function nitrate concentration (finalized by month 16)
- Speciation of Pu in the TBP-dodecane-nitric acid system as a function nitric acid concentration (finalized by month 16)
- Speciation of Pu in the TBP-dodecane-nitric acid system as a function nitrate concentration (finalized by month 20)
- Kinetic data on third phase with U and Pu (finalized by month 20)
- Temperature effects on U and Pu speciation (finalized by month 26)

Task 2: Speciation of U and Pu with AHA in the presence and absence of TBP-dodecane organic phase (Project Months 6-32)

- Speciation of U in the presence of AHA as a function of nitric acid concentration (finalized by month 13)

- Speciation of U in the presence of AHA as a function of nitrate concentration (finalized by month 19)
- Speciation of Pu in the presence of AHA as a function of nitric acid concentration (finalized by month 17)
- Speciation of Pu in the presence of AHA as a function of nitrate concentration (finalized by month 23)
- Temperature effects on U and Pu speciation (finalized by month 30)
- Two phase experiments with U and Pu (finalized by month 31)

Task 3: Modeling (Project Months 24-36)
- Data incorporation into CHESS and AMUSE
- Evaluation of nitrate and AHA on U and Pu speciation

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