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Prepared for the U.S. Department of Energy
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Uranium Metal Analysis via Selective Dissolution

CH Delegard
SI Sinkov
AJ Schmidt
JW Chenault

September 2008

Pacific Northwest
NATIONAL LABORATORY

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Summary

Uranium metal, which is present in sludge held in the Hanford Site K West Basin, can create hazardous hydrogen atmospheres during sludge handling, immobilization, or subsequent transport and storage operations by its oxidation/corrosion in water. A thorough knowledge of the uranium metal concentration in sludge therefore is essential to successful sludge management and waste process design.

The goal of this work was to establish a rapid routine analytical method to determine uranium metal concentrations as low as 0.03 wt% in sludge even in the presence of up to 1000-fold higher total uranium concentrations (i.e., up to 30 wt% and more uranium) for samples to be taken during the upcoming sludge characterization campaign and in future analyses for sludge handling and processing. This report describes the experiments and results obtained in developing the selective dissolution technique to determine uranium metal concentration in K Basin sludge. The work described in this report:

- provides a technical underpinning of the validity of the selective dissolution method, including the influence of various sludge components, in five test series using simulated and genuine sludges of widely varying composition
- establishes analytical parameters (concentrations, quantities, temperatures, and times) necessary to develop the selective dissolution sludge-digestion analytical procedure.

The uranium metal detection limit is estimated to be about 0.004 wt% based on the testing performed with actual sludge, thus meeting the goal detection limit of 0.03 wt%. The detection limit largely is established by the trace residual uranium carryover that exists in the leached and rinsed sludge. In the final series of method validation tests using actual K Basin sludge, spiked with uranium metal at concentrations ranging from 0.025 to 1.29 wt%, uranium metal recoveries averaged 99.4% with a standard deviation of 3.3%.

Based on the favorable testing results, an analytical method has been developed, extensively reviewed, and approved for routine use under the Pacific Northwest National Laboratory Analytical Support Operations Quality Assurance Plan, and this is compliant with the *Hanford Analytical Services Quality Assurance Requirements Document*, HASQARD.

Acronyms

BDL	below detection limit
HASQARD	*Hanford Analytical Services Quality Assurance Requirements Document*
ICP	inductively coupled plasma
IXM	inorganic ion exchange material
KPA	kinetic phosphorescence analysis
MWD	megawatt day
MTU	metric ton of uranium
NLOP	North Load-Out Pit
NR	not reported
OIER	organic ion exchange resin
PNNL	Pacific Northwest National Laboratory
PVT	pressure-volume-temperature measurements (gas)
QAPjP	*Quality Assurance Project Plan*
STP	Sludge Treatment Project
WIPP	Waste Isolation Pilot Plant
XRD	X-ray diffraction

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1.0 Introduction

Uranium metal, which is present in sludge held in the Hanford Site K West Basin, can create hazardous hydrogen atmospheres during sludge handling, immobilization, or subsequent transport and storage operations by its oxidation/corrosion in water. A thorough knowledge of the uranium metal concentration in sludge therefore is essential to successful sludge management and waste process design.

The goal of this work was to establish a rapid routine analytical method to determine uranium metal concentrations as low as 0.03 wt% in sludge even in the presence of up to 1000-fold higher total uranium concentrations (i.e., up to 30 wt% and more uranium) for samples to be taken during the upcoming sludge characterization campaign and in future analyses for sludge handling and processing. This report describes the experiments and results obtained in developing the selective dissolution technique to determine uranium metal concentration in K Basin sludge. The work described in this report:

- provides a technical underpinning of the validity of the selective dissolution method, including the influence of various sludge components, in five test series using simulated and genuine sludges of widely varying composition
- establishes analytical parameters (concentrations, quantities, temperatures, and times) necessary to develop the selective dissolution sludge digestion analytical procedure.

In previous sludge characterization efforts, uranium metal concentrations in K Basin sludge have been determined by the research method of gas-generation testing and, with much less sensitivity, a calorimetric method. In the calorimetric method, the heat evolved in the reaction of sludge with nitric acid is measured. Contributions to heat evolution include dilution of the acid by the water contained in the sludge, the dissolution of uranium oxides and aluminum and iron hydroxides, and the dissolution of uranium metal. The calorimetric technique is successful only if the concentrations of uranium metal are high (~10 wt% or more), and good estimates are available of water, iron, aluminum, and total uranium concentrations.

In the gas-generation technique, the reaction of uranium metal with water is monitored by the evolution of the hydrogen gas reaction product and the accompanying release of fission product (krypton and xenon) gases. The total gas quantities and individual gas concentrations are determined by gas pressure-volume-temperature (PVT) measurements and by mass spectrometric analyses of gas compositions. The amounts of uranium metal are determined by chemical (hydrogen) and burn-up (krypton and xenon) correlations. Uranium metal concentrations as low as 0.005 wt% in settled sludge have been determined by measuring the amount of released xenon fission product gas (Bryan et al. 2004). Determining uranium metal concentration by hydrogen gas evolution is less reliable at low levels because it is complicated by the suspected disappearance of hydrogen by its reaction with oxidized uranium or iron compounds or by its creation by other means (corrosion of other metals such as aluminum and by radiolysis).

The gas-generation testing to determine uranium metal concentrations is performed in sealed vessels held thermostatically at 80 to 95°C for several thousand hours (up to 4 months). To measure uranium metal concentrations by fission-product gas release requires knowledge or assumptions of the parent fuel burnup. With multiple gas samples, knowledge of uranium metal particle size also can be obtained based on the reaction kinetics. In contrast, with selective dissolution, the uranium metal concentrations in sludge can be determined more quickly (within 1 to 2 weeks), but no information on uranium metal particle-size distribution in the sample is acquired. However, some information on uranium metal particle size can be obtained by sieving the sample and performing selective dissolution on the size-fractionated sub-samples.

Laboratory tests of selective dissolution were conducted from December 2007 to June 2008 using a simulated sludge and several types of genuine sludge. In both test types, known quantities of sub-millimeter-diameter uranium metal beads were added. The simulated sludge tests were performed with a comprehensive chemical surrogate that included iron and aluminum hydroxides, organic and inorganic ion exchange media of the same types used at the K Basins, Hanford blow sand, and uranium dioxide prepared by corroding uranium metal in water. Spiked uranium metal concentrations ranged from 0.03 to 0.4 wt% with respect to total wet settled sludge. Blank tests (without U metal) also were conducted. Uranium metal recoveries of 75 to 119% were achieved. The analytical background was about 0.01 wt% uranium metal as determined from the blank tests.

Testing with four types of actual sludge spiked with 0.006 to 0.026 wt% uranium metal beads (with respect to settled sludge) achieved recoveries ranging from 106 to 179%. The high recoveries are at least partly due to the high relative contributions of the analytical background uranium compared with the small amounts of added uranium metal used in these tests. The analytical background was about 0.004 wt% as determined by blank tests.

Further tests were conducted with one of the four K Basin sludge types using 0.025- to 1.29-wt% added uranium metal as well as two blank tests. The average uranium metal recovery was 99.4 wt% with a standard deviation of 3.3 wt% with the blank tests again showing 0.004 wt% analytical background.

Because the origin of the uranium in the analytical background cannot distinguish between oxidized uranium and uranium metal, the analytical background is interpreted as the threshold below which uranium metal may be present in the sludge. It is noted that all chemical or radiochemical analyses experience this same phenomenon in that the lower analytical limit of the analyte in question, if reached for any sample, constitutes an estimate of the analyte's highest concentration.

The uranium metal detection limit is estimated to be about 0.004 wt% based on the testing performed with actual sludge, thus meeting the goal detection limit of 0.03 wt%. In the final series of method validation tests using actual K Basin sludge, spiked with uranium metal at concentrations ranging from 0.025 to 1.29 wt%, uranium metal recoveries averaged 99.4% with a standard deviation of 3.3%. The detection limit largely is established by the trace residual uranium carryover that exists in the leached and rinsed sludge. The potential contamination of selective dissolutions in the hot cell environment, where work with K Basin sludge, N Reactor fuel, and other uranium-rich materials has been conducted over prior decades, also can contribute to an increase in the detection limit if strict measures to maintain sample purity are not observed.

Based on the favorable testing results, an analytical digestion method has been developed, extensively reviewed, and approved for use under the Pacific Northwest National Laboratory (PNNL) Analytical Support Operations Quality Assurance Plan (i.e., compliant with the *Hanford Analytical Services Quality Assurance Requirements Document*, HASQARD; DOE 2007) for routine analytical use in PNNL's Radiochemical Processing Laboratory. The procedure is "Sample Preparation for Determination of Uranium Metal Concentrations in Sludge," RPG-CMC-107.

A technical data package supporting this work is maintained in the PNNL project records and has been provided to CH2M Hill Plateau Remediation Company (CHPRC): STP Records and STP Engineering (JP Sloughter, STP/BTR). The technical data package contains the approved PNNL Technical Procedure, "Sample Preparation for Determination of Uranium Metal Concentrations in Sludge," RPG-CMC-107, Rev 0; completed test instructions; supporting calculations; and supporting analytical data.

This report was prepared in accordance with the Statement of Work under PNNL Project 53451 (Contract 27647, Release 242) and the *Quality Assurance Project Plan* (QAPjP 2007).

2.0 Method Summary

The alternative technique of staged or selective dissolution of uranium oxides to determine the concentration of uranium metal in K Basin sludge has been tested with both simulated K Basin sludge and actual sludge containing known amounts of added uranium metal. The technique relies on the relatively rapid dissolution of oxidized uranium compounds in concentrated phosphoric acid (H_3PO_4; also containing 0.14 M Na_2SO_4) compared with the slow attack of uranium metal under the same conditions.

In selective dissolution, 3 to 5 grams of sludge is treated with 30 mL of Na_2SO_4-bearing H_3PO_4 for ~2 hours at 80°C to dissolve the oxidized uranium compounds. The work is performed in shielded cells (hot cells) for radiological safety. Some sludge compounds, such as the iron and aluminum (hydr)oxides [e.g., $FeOOH$, $Al(OH)_3$], also dissolve, but silica sand, zirconium cladding, organic and inorganic ion exchange media, and uranium metal do not dissolve under these conditions. A second contact with 10 mL of fresh Na_2SO_4-bearing H_3PO_4 is performed for 1 to 2 hours to improve dissolution and removal of the oxidized uranium compounds. Intermittent vortex mixing (about 4 times per hour) is used to improve the oxidized uranium phase dissolution.(a) The Na_2SO_4/H_3PO_4 solution may be analyzed spectrophotometrically to determine the oxidation state distribution of the oxidized uranium compounds (Sinkov et al. 2008) or may be discarded.

The solid residue is washed quickly seven times by 10-mL aliquots of cell-temperature 0.5 M nitric acid (HNO_3) to rinse out the dissolved uranium compound solution. The first, third, fifth, and seventh contacts are performed with vortex mixing to improve rinsing and to wash down the vessel walls. The residual rinsed solid heel then is treated with 10 mL of 105°C 10 M HNO_3 for about 2 hours to dissolve the uranium metal. The solutions from the last two 0.5-M HNO_3 rinses may be analyzed for uranium concentrations to determine the thoroughness of the washing step. The solution from the 10-M HNO_3 metal dissolution step with a contained sludge heel and vessel is weighed and the solution decanted and analyzed for uranium concentration to determine the amount of uranium metal contained in the sludge. The sludge heel is dried in the tare-weighed digestion vessel and vessel plus dried sludge heel weighed to determine the sludge heel weight and, by difference, the weight of 10-M HNO_3 digestate. The HNO_3 used in the rinse and metal dissolution steps is “Ultrex” grade prepared and contained in plastic vessels.

All leaching contacts and solution samples within the procedure are held in plastic vessels to minimize uranium contamination leached from glassware. The steps in the selective dissolution technique are diagrammed in Figure 2.1.

(a) Some of the early testing only used a single contact with Na_2SO_4-bearing H_3PO_4 and was done without vortex mixing.

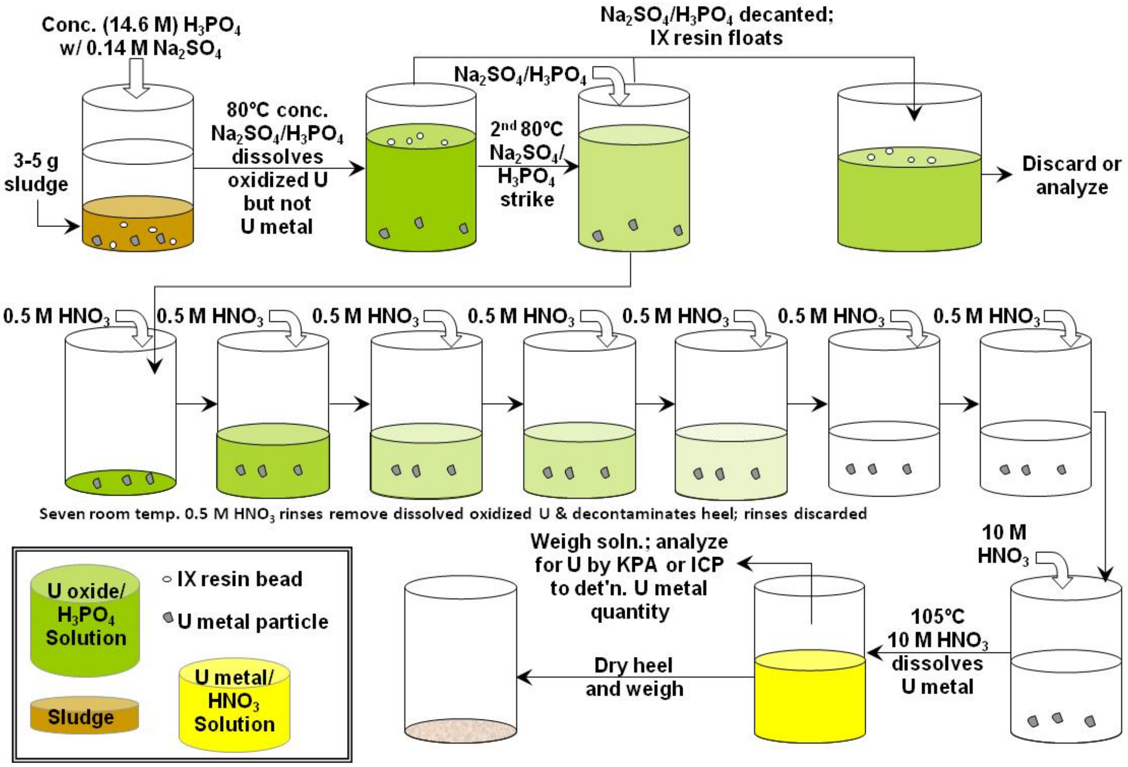

Figure 2.1. Block Flow Diagram for Selective Dissolution Analysis of Uranium Metal in Sludge

1) Uranium oxide dissolution in 80°C concentrated H_3PO_4 with 0.14 M Na_2SO_4; U metal does not dissolve. Intermittent vortex mixing used to improve acid/solid contact and dissolution.
2) Rinsing of dissolved oxidized uranium from remaining solids with room temperature 0.5 M HNO_3. Vortex mixing was used in the 1st, 3rd, 5th, and 7th contacts to improve solids leaching and rinse vessel walls.
3) Dissolution of uranium metal in 105°C 10 M HNO_3.

3.0 Technical Challenges Identified for Implementing the Selective Dissolution Approach

The proposed analysis must successfully address several technical challenges to attain the goal sensitivity of measuring 0.03 wt% uranium metal in the sludge. This measurement target is driven by flammable gas-generation limits in an RH-72B transuranic waste transportation container during transit to the Waste Isolation Pilot Plant (WIPP). The uranium metal concentration in the sludge will also affect sludge processing strategies and approaches to onsite storage and shipment of grouted sludge.

- The analysis must be capable of measuring uranium metal concentrations of 0.03 wt% (or lower; i.e., order of magnitude less than design-basis KE Floor sludge of 0.26 wt%). This uranium metal concentration is at least 1000 times lower than the total uranium concentration in some sludge (i.e., some sludge may contain >30 wt% total uranium).
- To detect the small amounts of uranium metal in many sludges, essentially all of the oxidized uranium compounds (e.g., uraninite, UO_2; metaschoepite, $UO_3 \cdot 2H_2O$) must first be dissolved and removed before dissolving the uranium metal.
- The oxidized uranium removal must be achieved with minimal dissolution of the uranium metal.
- Organic ion exchange resin (OIER) beads and the mordenite inorganic ion exchange material (IXM) also present in the sludge may sorb dissolved uranium. Neither the OIER beads nor the mordenite are visibly attacked by acid digestion, but either may release or sorb uranium during the 10-M HNO_3 treatment used to dissolve the uranium metal. Therefore, the effects of these ion exchangers must be determined.

An additional challenge in implementing the selective dissolution technique is in attaining low detection limits in the presence of high and ubiquitous uranium contamination levels in the analytical and process hot cells. As will be shown, testing also indicated that a difficult-to-dissolve precipitate formed upon adding the Na_2SO_4-bearing H_3PO_4 solution to the sludge. Subsequent testing showed that this precipitate could be dissolved but required vigorous mixing and a second Na_2SO_4/H_3PO_4 strike.

3.1 Dissolution of Uranium, Iron, and Aluminum Phases in Phosphoric Acid

The ratio of sludge to Na_2SO_4/H_3PO_4 must be as great as possible to improve method sensitivity but not so great that iron, aluminum, and particularly the uranium-phase dissolution cannot be achieved. For example, if 3 mL (~6 g) of the most uranium-rich sludge in the sludge archive inventory, KC-1 M500 (46.3 wt% U and 2.05 g/cm^3 density as-settled[a]), were to be dissolved in concentrated (14.6 M) H_3PO_4 to

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(a) CH Delegard, AJ Schmidt, and JW Chenault. 2007. *Characteristics of KE Basin Sludge Samples Archived in the RPL – 2007*, Letter Report 53451-RPT01, PNNL-17078 (limited distribution) Pacific Northwest National Laboratory, Richland, WA.

~35 mL total volume, the uranium concentration would be ~0.35 M. Settled sludge is typically ~75 vol% water, which will dilute the H_3PO_4 concentration about 10%.

The solubility of U(VI) in 12.7 M H_3PO_4 is at least 0.48 M at 25°C, and the U(IV) solubility in 14 M H_3PO_4 is ~1 M with both solubilities increasing with increasing temperature (Thamer et al. 1956). Therefore, the selected dissolution conditions are sufficient to dissolve all of the U(IV) and U(VI) phases even for the high uranium KC-1 M500 sludge. Complete dissolution of all U(IV) and U(VI) phases is necessary in light of the selective dissolution technique goal to leave uranium metal as the only uranium source in the H_3PO_4-leached sludge. For the KC-2/3 sludge used in the present testing, 34.8 wt% of the sludge is U on an as-settled (wet) basis, and the density is 2.03 g/cm^3 to give a projected ~0.23-M uranium concentration in the H_3PO_4 solution.

At the same time, uranium metal should not be significantly dissolved by the same treatment with the mixed Na_2SO_4/H_3PO_4 reagent. Preliminary tests showed that sub-millimeter-diameter uranium metal beads required 11 days to dissolve in 130°C concentrated H_3PO_4 for a penetration rate of <2 µm/hour. Even lower metal penetration rates are expected at the ~80°C temperatures to be used in the sludge dissolution with Na_2SO_4/H_3PO_4. Uranium metal penetration rates under sludge dissolution conditions were measured in the present testing.

Iron is the metallic element found in greatest molar concentrations in both FE-5 and KE Floc Comp test sludges used in the present tests. The dissolution of the precipitated iron (hydr)oxide phases (such as FeOOH), which may occlude or coprecipitate uranium present in the sludge aliquots, is essential in removing all oxidized uranium phases from the sludge before the later dissolution of the H_3PO_4-resistant uranium metal from the heel. Dissolving 3 mL of the iron-rich (~31 wt%, dry basis) FE-5 sludge to ~35 mL total volume will produce an ~0.46-M iron solution. Prior tests show that iron(III) in strong H_3PO_4 solution will be saturated at ~0.75 M. Therefore, the dissolution conditions should be adequate to dissolve the iron (hydr)oxide sludge phases present in any sludge tested in the present experiments.

Because aluminum concentrations in the sludge are lower, and aluminum is more soluble in H_3PO_4 than is iron (Brosheer et al. 1954), aluminum (hydr)oxide phases also should dissolve completely. Both aluminum and iron phosphates show increased solubility in H_3PO_4 with increasing temperature. Although some attack of accompanying soil minerals (e.g., basalt sand, anorthite) by Na_2SO_4/H_3PO_4 is expected, the dissolution of aluminum and iron phases present from these minerals is not required as the minerals native to Hanford and the sand introduced intentionally to the Basins for depth filters have negligible associated uranium.

3.2 Ion Exchange Behavior of K Basin Sludge Solids

Solids, including inorganic minerals and metals (e.g., silica, Zircaloy), the inorganic ion exchanger sodium mordenite [$(Ca,Na_2,K_2)Al_2Si_{10}\cdot 7H_2O$; Norton Zeolon 900] used in the K Basins to decrease ^{137}Cs concentrations, and the mixed strong-acid/strong-base OIER (Purolite NRW-37) also used in Basin water-quality operations are not expected to be dissolved by Na_2SO_4/H_3PO_4 or the succeeding dilute HNO_3 rinses.

Although uranium solution concentrations are low in the K Basins sludge, some absorption onto solids could have occurred. However, in the acid dissolution steps, uranium solution concentrations will be much greater, with a greater likelihood of absorption onto solids including the mordenite and OIER. In strong H_3PO_4, the dissolved uranium potentially is present as anionic, cationic, or neutral U(IV) and U(VI) complexes of the form $U(HPO_4)_x^{(2x-4)-}$ and $UO_2(HPO_4)_x^{(2x-2)-}$, respectively. In strong HNO_3, any U(IV) is oxidized to U(VI) and cationic, neutral, or anionic nitrate U(VI) complexes of the form $UO_2(NO_3)_x^{(x-2)-}$ exist. As potentially charged species, the dissolved uranium may sorb on the solid surfaces, particularly the IXM, and affect the outcome of the uranium metal concentration determination. Therefore, this uranium must be removed from the solids during the sludge dissolution in concentrated H_3PO_4 solution and in succeeding rinse steps in dilute HNO_3.

Information on the distribution of uranium onto mordenite from HNO_3 or other acid solution is limited but points to low sorption from acid solution. The K_d of U(VI) onto mordenite as a function of pH decreases with decreasing pH as shown in Figure 3.1 (Reddy and Cai 1996, pp. 1173–1179). The K_ds for divalent strontium (Sr) and cobalt (Co) and trivalent cerium (Ce), europium (Eu), terbium (Tb), and iron (Fe) on Zeolon 900 (mordenite), also plotted in Figure 3.1, show similarly decreasing K_ds with decreasing pH (Kanno and Mimura 1985, pp. 237–247). Over the same pH 1 to 5 range, the K_d for cesium (Cs) onto mordenite is high (~10,000 mL/g) and relatively invariant. Mordenite is selective for cesium ion because the diameter within mordenite's zeolitic channel structure is suited to cesium's ionic diameter. The data in Figure 3.1 for the seven metals, including those of uranium, all trend to decreasing absorption as pH decreases. As a result, the sorption of uranium onto mordenite in HNO_3 solution is expected to be low.

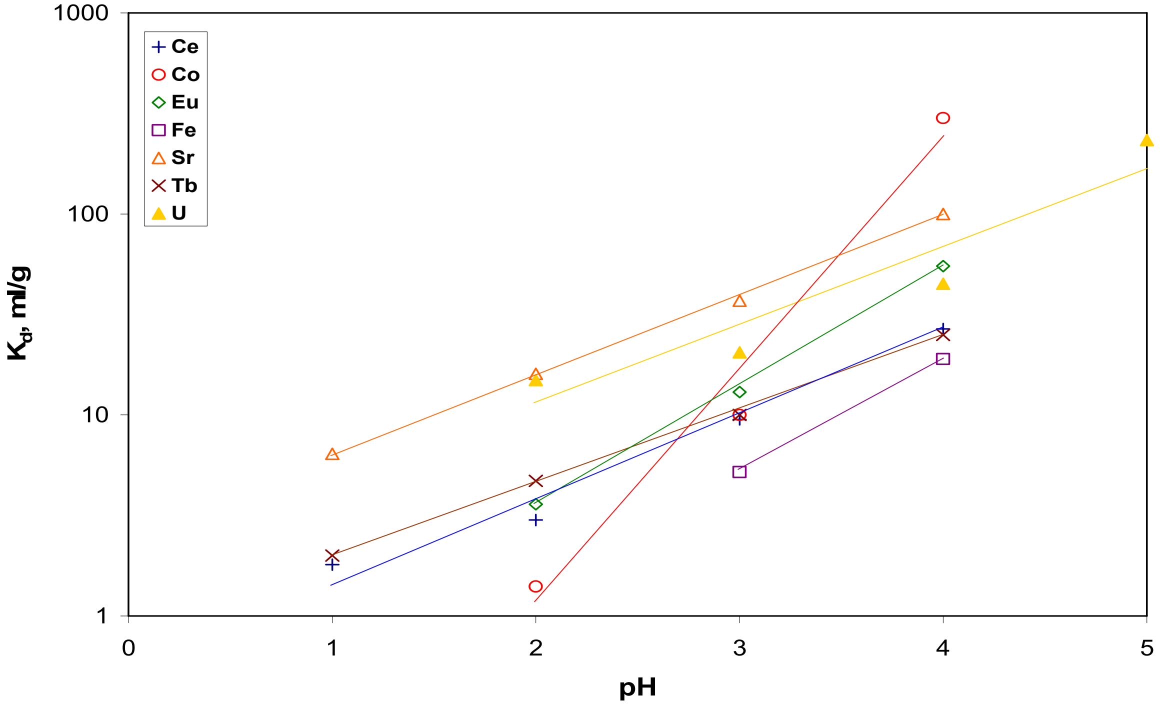

Figure 3.1. Distribution Coefficients, K_ds, for Various Metals onto Mordenite as Functions of pH

Uranium uptake from HNO_3 solution onto mordenite and other sorbents was examined (Marsh et al. 1994). In the mordenite tests, an acidified aliquot of Hanford tank 102-SY simulant (containing 0.5 M HNO_3, 0.65 M sodium, 0.43 M aluminum, 0.36 M iron, 0.023 M uranium, and others) was contacted with beads of polyacrylonitrile-bound synthetic mordenite powder at a ratio of 6-mL solution to 0.25 g of solid. The synthetic mordenite comprised 93% of the total bead weight. The uranium K_d values were 0.4, 0.6, and 0.4 mL/g after 0.5-, 2-, and 6-hours contact, respectively. Of the 14 elements whose uptakes were studied, only cesium and zirconium showed significant sorption.

Because of their high exchange capacities, the OIER are of most concern for uranium uptake and have been shown, in tests with genuine K Basin sludge containing both OIER and OIER with mordenite, to retain uranium to a limited degree (Schmidt et al. 1999; Delegard and Rinehart 1998; Delegard et al. 1998). The distribution coefficients (K_d) calculated for uranium in one of these studies were about 0.1 mL/g on mordenite and about 0.5 mL/g on the mixed organic resin in HNO_3 solutions of K Basin sludge also containing ~0.52 M iron and ~0.16 M aluminum in ~4 M HNO_3. Under less competitive conditions (i.e., with lower or negligible concentrations of other metals, such as iron and aluminum, to compete with the uranium for ion exchange sites), the K_ds for the undifferentiated (mixed) inorganic and organic IXM did not change appreciably with difference in acid composition and were about 4 mL/g in 6 M HNO_3/0.4 M $Ce(NO_3)_4$, 5 to 6 mL/g in 4 M HNO_3, and 3 to 6 mL/g in 0.1 M HNO_3/0.2 M $H_2C_2O_4$. In comparison, the K_d of U(VI) onto strong-base anion exchange resin is 3.9 mL/g at 7 M HNO_3 (Weigel et al. 1986).

These data show that uranium sorption onto the IXM present in many of the K Basins sludges is low and that the two Na_2SO_4/H_3PO_4 sludge dissolution contacts followed by seven dilute HNO_3 rinses will further decrease the uranium retention.(a) Under the envisioned sequence of sludge dissolution by strong H_3PO_4 followed by rinsing of the heels with dilute HNO_3, the IXM residues should retain little of the oxidized uranium. However, the IXM also could absorb some of the uranium dissolved from the metal in the final strong HNO_3 dissolution step and complicate the interpretation of the uranium concentration data. Fortunately, the OIER will float in the dense concentrated Na_2SO_4/H_3PO_4 solution and thus may be readily separated from the remaining denser solids heels (sand, Zircaloy cladding, mordenite, U metal) when the Na_2SO_4/H_3PO_4 solutions are decanted. The retention of uranium on mordenite must be tested.

3.3 Uranium Metal Dissolution in Nitric Acid

In the selective dissolution technique, uranium metal and other heel solids are rinsed with cell temperature 0.5 M HNO_3 to remove interstitial solutions from oxidized uranium dissolution in Na_2SO_4/H_3PO_4. The rinsed solids then are treated with 105°C 10 M HNO_3 to dissolve the uranium metal in preparation for analysis. The selection of these HNO_3 concentrations and temperatures arises from consideration of the uranium metal dissolution rate under these widely differing conditions. Optimally, no uranium metal dissolution should occur in the 0.5-M HNO_3 rinse while the metal completely dissolves in the 10-M HNO_3 treatment.

(a) For example, at a nominal K_d of 0.5 mL/g and 0.5 g of solids being washed with 10 mL of solution, each contact would remove ~97.6% of the uranium. Three such contacts would remove ~99.999% of the uranium. If the K_d were 5 mL/g, 99.2% would be removed in three contacts, and ~99.999% would be removed in seven contacts. Seven 0.5-M HNO_3 rinse contacts are used in the present testing.

The uranium metal dissolution rate in nitric acid solution increases with increasing temperature. The rate also increases with increasing nitric acid, or total nitrate, concentrations. The dissolution rate of uranium metal in 3 M to 12 M HNO_3 at 25°C was studied (Lacher et al. 1961). The rate decreases by a factor of ~300,000 per decade decrease in HNO_3 concentration in this range and is about 5×10^{-4} µm/hour in 3 M HNO_3. Even for a 1-µm-diameter uranium metal particle, which has a mass of $\sim10^{-11}$ grams, uranium dissolution would be negligible (i.e., the initial 1.000 µm diameter would decrease to 0.999 µm) in 3 M HNO_3 in the estimated 1 hour time needed to accomplish the seven 0.5 M HNO_3 rinses. Therefore, treatment of uranium metal particles in the sludge heel with the even more dilute 0.5 M HNO_3 should have a negligible effect on uranium metal recovery.

The dissolution rates of uranium metal in boiling HNO_3 solutions as a function of total nitrate concentration (HNO_3 plus uranyl nitrate and other metal nitrates) are shown in Figure 3.2. It is seen that the dissolution rate of uranium metal in 10 M HNO_3 is about 500 µm/hour. Two hours of treatment with near boiling 10 M HNO_3 should dissolve a 2000-µm-diameter uranium particle and thus dissolve most uranium metal particles expected in bulk floor and canister sludge.(a) Larger particles of uranium metal, such as from KOP sludge, would be readily observed in handling the sludge heel after the Na_2SO_4/H_3PO_4 and subsequent 0.5 M HNO_3 treatments and would require special treatment. Sludge is defined as material from the K Basins passing a ¼-inch screen. A ¼-inch-diameter uranium metal sphere weighs about 2.6 grams and thus would constitute a significant portion of the 3- to 5-gram sludge sample weight.

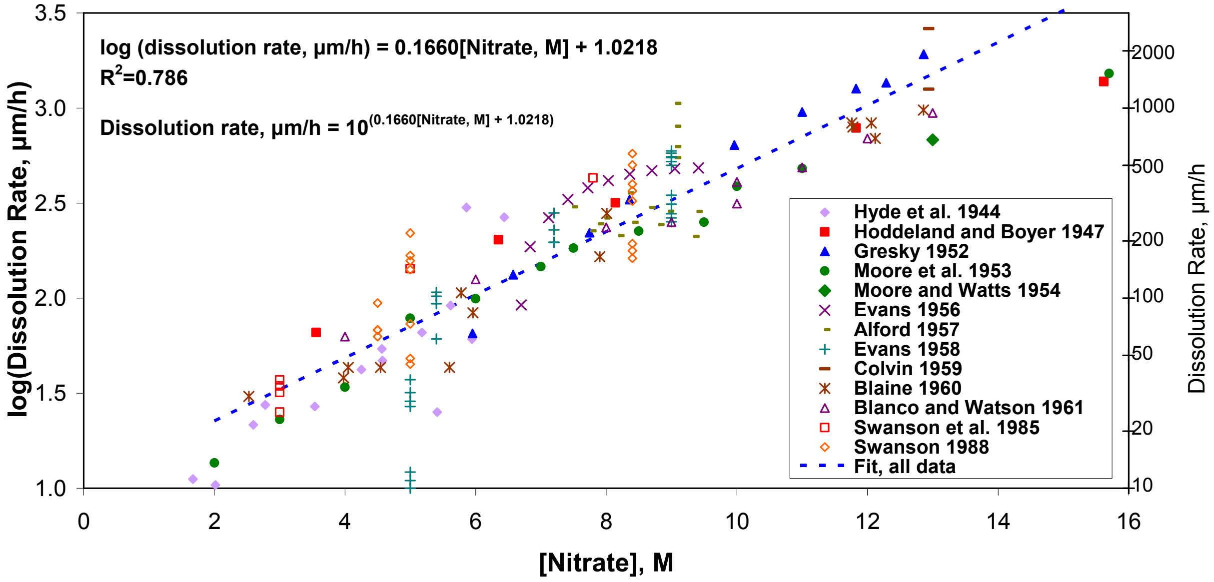

Figure 3.2. Dependence of Uranium Metal Dissolution Rate on Total Nitrate Concentration at Boiling

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(a) The nominal diameter of uranium metal observed in KC-2/3 P250 sludge is ~800 µm (Delegard et al. 2000). The kinetic data from that study have been re-analyzed using the STP rate equation (Appendix G of Plys and Schmidt 2006) to show that the nominal uranium metal diameter is ~560±28 µm.

The capacity of 10 mL of 10 M HNO_3 is sufficient to dissolve 4 grams of uranium metal based on the least effective reaction stoichiometry to form NO_2 from HNO_3 chemical reduction:

$$U + 8\ HNO_3 \rightarrow UO_2(NO_3)_2 + 6\ NO_2 + 4\ H_2O$$

Therefore, HNO_3 is available in at least a 10-fold stoichiometric excess for metal dissolution from a 4-gram sample of settled sludge containing 10 wt% uranium metal (or ~20 wt% uranium metal on a dry sludge basis). Most sludge, except for knock-out pot (KOP) sludge, is expected to have much lower uranium metal concentrations.

4.0 Experiments for Uranium Metal Dissolution Rate and Analysis of Uranium Metal Concentration in Simulated Sludge

In the initial development of the selective dissolution technique for actual K Basin sludge, laboratory work was conducted to determine the rate of uranium metal dissolution in concentrated H_3PO_4 solution at 80°C. Samples were taken periodically over 24 hours of reaction to determine the rate of dissolution of uranium metal present as sub-millimeter-diameter beads.

Testing with simulated sludge was performed to determine the efficacy of the rinses from sludge residues and to investigate the effects of ion exchange materials on the method sensitivity. The dry simulated sludge contained uranium dioxide (UO_2 at 22 wt%), sand (blow sand from the Arid Lands Ecology, ALE, reserve adjacent to the Hanford Site, at ~21 wt%), aluminum hydroxide [$Al(OH)_3$, gibbsite, at 17 wt%], iron hydroxide [FeOOH added as $Fe_5O_7(OH)\cdot 4H_2O$, ferrihydrite, equivalent to $FeOOH\cdot 0.4H_2O$, at 40 wt%], and 0, 1, or 4 carefully weighed U metal beads. The UO_2 was prepared separately by the corrosion of uranium metal in anoxic liquid water at 60°C (Sinkov et al. 2008). These summed dry weights were complemented by a matching weight of added water (i.e., the simulated sludge was 50 wt% water). The composition of the simulated sludge is shown in Table 4.1.

Table 4.1. Composition of Simulated Sludge

Component	Weight, g	Weight %
$Al(OH)_3$	12.751	8.498
FeOOH	30.002	19.996
ALE Blow Sand	15.756	10.501
UO_2	16.502	10.998
Water	75.028	50.006

Selected tests were run with mixed-bed, strong acid/strong base OIER. The OIER used was Purolite NRW-37, the same as has been used in the K Basins. Powdered inorganic sodium mordenite IXM also was added to the simulated sludge. The original mordenite IXM used in the K Basins water treatment was granular Norton Zeolon 900. Because Zeolon 900 was no longer available, (UOP LLC) molecular sieve LZM-5, a sodium mordenite in powder form, was used. The amounts of IXM added were relatively high, corresponding to about 0.1 g of each of the organic and inorganic IXM per ~3 g of wet simulated sludge or about 3 wt% for each type of IXM. The simulated sludge compositions, including added uranium metal, OIER, and mordenite, are presented in Table 4.2.

Table 4.2. Compositions of Test Items Prepared with Simulant Sludge, Uranium Metal, and IXM

Test Identification	Component Weight, g			
	Sludge[a]	Uranium Metal	OIER	Mordenite
S-Blank	3.129	0.0	0.0	0.0
S-1	3.092	0.00094	0.0	0.0
S-1 Dup	3.130	0.00078	0.0	0.0
S-4	3.168	0.00769	0.0	0.0
SX-Blank	2.919	0.0	0.100	0.103
SX-1	3.156	0.00195	0.102	0.102
SX-1 Dup	3.194	0.00252	0.101	0.103
SX-4	3.093	0.01246	0.100	0.102
(a) Sludge composition given in Table 4.1.				

The tests were completed under an approved test instruction.(b) The dissolutions were performed according to the sequence identified in Figure 2.1 (although with only one Na_2SO_4/H_3PO_4 contact) with plastic vessels used throughout to eliminate uranium leaching from glass as a contamination source. The uranium concentration analyses were performed using kinetic phosphorescence analysis (KPA) under an approved analytical procedure.(c)

(b) CH Delegard. 2007. "Development of Alternative Method to Determine Uranium Metal Concentration in Sludge in Support of the K Basin Sludge Treatment Project," 53451 TI04, Rev. 0, Pacific Northwest National Laboratory, Richland, WA.

(c) C Soderquist. 2001. "Uranium by Kinetic Phosphorescence Analysis," RPG-CMC-4014, Rev. 1, Pacific Northwest National Laboratory, Richland, WA.

5.0 Results for Uranium Metal Dissolution Rate and Analysis in Simulated Sludge

The uranium metal linear penetration dissolution rate in 80°C Na_2SO_4-bearing H_3PO_4 is 0.08 µm/hour according to KPA measurements of the solution as a function of contact time. The corrosion rate plot is shown in Figure 5.1.

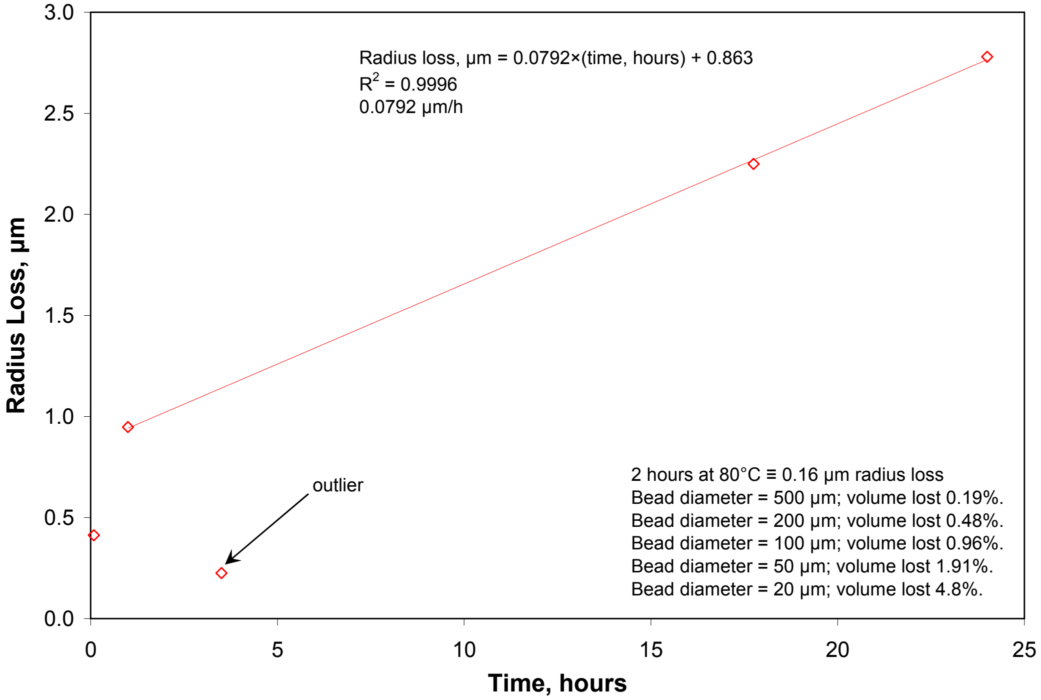

Figure 5.1. Uranium Metal Corrosion Rate in Concentrated H_3PO_4

As shown in Figure 5.1, this rate is sufficiently low to allow reliable uranium metal concentration determination even for 20-µm-diameter particles, well below the uranium metal particle sizes identified in prior gas-generation testing of the KC-2/3 P250 sludge (Delegard et al. 2000).

Analyses of the uranium concentrations found in the sixth and seventh 0.5-M HNO_3 rinses and in the subsequent metal dissolution step with 10 M HNO_3 are shown in Table 5.1. The sixth and seventh rinses are the last two in the rinse sequence and were analyzed to determine the completeness of oxidized uranium removal.

Table 5.1. Uranium Concentrations in 0.5 M Nitric Acid Rinses and in 10-M Nitric Acid Digestions for Simulated Sludge

Sludge Type	Sample	µg U/mL (ppm)		
		0.5 M HNO_3		10 M HNO_3
		6th Rinse	7th Rinse	
Without IXM	S-Blank	0.209	0.335	22.8
	S-1	0.217	1.87	113
	S-1 Dup	0.359	0.347	104
	S-4	0.306	0.424	778
With IXM	SX-Blank	0.412	0.448	35.5
	SX-1	0.834	0.931	214
	SX-1 Dup	0.450	0.541	251
	SX-4	0.501	0.758	1110

It is seen that the single Na_2SO_4/H_3PO_4 dissolution contact and seven subsequent dilute HNO_3 rinses efficiently removed the oxidized uranium and generally decreased the uranium concentration to less than 1 ppm (µg of uranium per mL) under conditions in which the initial Na_2SO_4/H_3PO_4 solution would have had uranium concentrations of about 8,000 ppm. The uranium concentrations in the two 10-M HNO_3 blank test solutions were about 80 times higher than the prior 0.5-M HNO_3 rinses for the test without added IXM and the test with added IXM. Although the OIER was largely removed by flotation in the Na_2SO_4-bearing H_3PO_4 contact, the inorganic IXM (mordenite) was not removed. Overall, however, as shown by comparing the data with and without IXM, the presence of IXM did not markedly affect uranium retention in the uranium metal-free simulated sludge solids.

The concentrations of uranium metal measured in the simulated sludge tests with and without added uranium metal and IXM are shown in Table 5.2 and in Figure 5.2. Analyses of the blank tests with no added metal were assayed to contain 0.0065- and 0.0103-wt% uranium metal, respectively, for simulated sludge without and with added IXM. Based on these values, the lower detection limits for uranium metal in the blank tests were around 0.01 wt% of the sludge. The uranium recoveries obtained for tests to which ~0.03 to 0.40 wt% of uranium metal were added were found to range from 80 to 119%. Overall, recoveries were somewhat greater for the three tests without IXM (103±20%) than for the three tests containing IXM (90±10%), but the differences between these two data sets are not statistically significant. Hence, there was no discernable effect of the presence of IXM on the uranium recovery.

Table 5.2. Uranium Metal Analysis Results in U-Metal Spiked and Unspiked K Basin Sludge Simulant

Sludge Type	U Metal Concentration in Settled Sludge, wt%										
	Blank		Test 1			Test 2			Test 3		
	Added	Found	Added	Found	% Rec.	Added	Found	% Rec.	Added	Found	% Rec.
Without IXM	0.0000	0.0065	0.0303	0.0329	109	0.0250	0.0297	119	0.242	0.197	81
With IXM	0.0000	0.0103	0.0580	0.0578	100	0.0741	0.0672	91	0.377	0.301	80

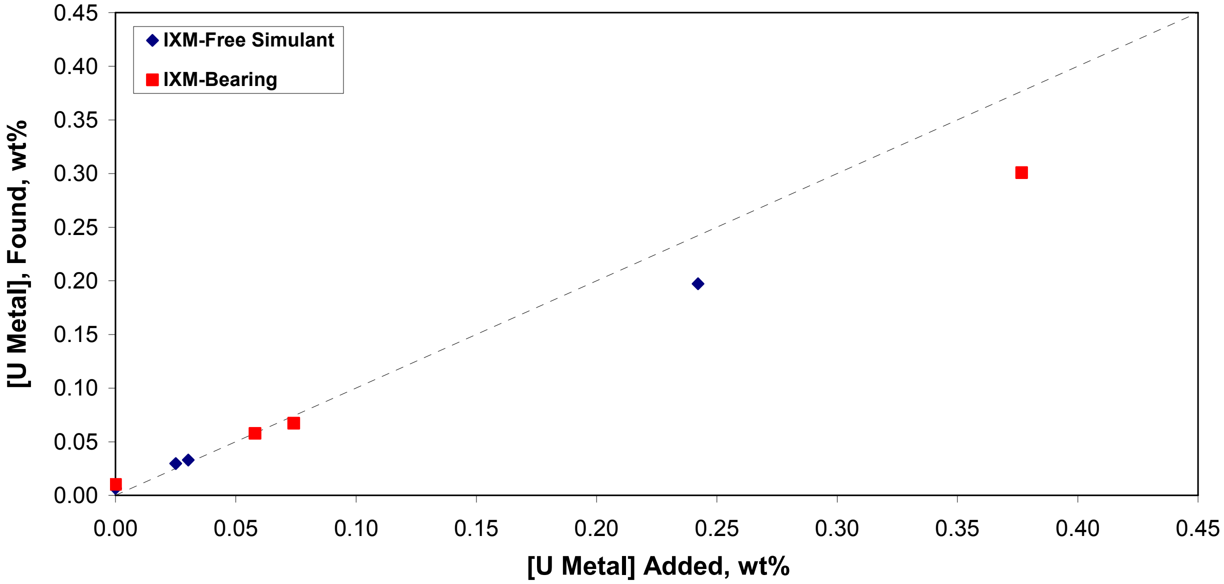

Figure 5.2. Uranium Metal Analysis Recoveries in Simulated Sludge

Analyses to quantify ~0.03 to 0.24 wt% uranium metal in settled sludge simulant without IXM showed uranium metal recoveries of about 86±7% when corrected for the blank analyses of the uranium metal-free simulated sludge. For sludge simulants containing both organic ion exchange resin and inorganic mordenite having ~0.07 to 0.40 wt% uranium metal, ~80±3% uranium metal recovery, blank-corrected, was found.

Design basis KE Floor sludge contains 0.26 wt% uranium metal. The results for the testing with simulated sludge showed that the proposed uranium metal measurement procedure method gave satisfactory results. On this basis, testing with actual K Basin sludge spiked with known amounts of uranium metal was performed.

6.0 Experiments for Uranium Metal Analysis in K Basin Sludge

Based on the promising findings with simulated sludge, tests of selective dissolution were performed for actual K Basin sludge containing known amounts of added uranium metal. The work was conducted under approved test instructions.(a)

A broad range of representative sludge compositions was tested. The FE-5 sludge, which originated from the KE Weasel Pit and South Loadout Pit, was tested because about one quarter of the total K Basin sludge volume is composed of the Weasel and South Loadout Pit sludge. The most uranium-rich sludge is that collected in Settler Tubes during fuel washing operations. However, because no sample of Settler Tube sludge exists in the laboratory, the Settler Tube sludge was represented by the uranium-rich KC-2/3 sludge. Most of the KE and KW sludge has been collected in five large containers located in the KW Basin. The KE Basin was the larger contributor to the volume of the containerized sludge. The KE Floc Comp sludge, a composite of floor, pit, and canister sludge retrieved from the KE Basin, was used to represent the entire containerized K Basin sludge inventory. This composite sludge also has been mixed with the same flocculating agent (Nalco Optimer 7194 Plus) and dosages as were used in K Basin sludge process transfers. The KE Floc Comp sludge is a blend of four sludges, including FE-5, plus three from canisters, including a small contribution from a composite of three canister sludges. The IXM materials (organic resin and mordenite) are potentially problematic sludge components. Therefore, a fourth sludge, KC-6, visibly rich in OIER and likely containing significant mordenite based on its sampling location, was added to KE Floc Comp sludge to determine the effects of IXM. The identities and properties of the four archived KE Basin sludge samples used in the testing are listed in Table 6.1. Further details on the sludge properties are provided in Table 6.2.

As shown in Table 6.1, the FE-5, KC-6, and KE Floc Comp sludges had 0.05 wt% or lower uranium metal concentrations when they were analyzed in 1999 or 2000. These low uranium metal concentrations can only have decreased, likely to zero, by storage in the HLRF since their analyses ~8 years ago. However, the KC-2/3 sludge, which contained ~3.2 wt% uranium metal (dry basis) when analyzed in 1999, may still contain uranium metal.

Tests were performed both with and without known amounts of added uranium metal beads. The quantities of added uranium ranged from ~0.006 to 0.015 wt%, settled sludge basis, for all sludge types. These tests were conducted according to the sequence shown in Figure 2.1 with a single 2-hour, 80°C contact with Na_2SO_4/H_3PO_4. As will be seen, the tests with sludge KC-2/3 were repeated using two 2-hour/80°C contacts with Na_2SO_4/H_3PO_4 to improve oxidized uranium compound dissolution. Vortex agitation of the heated sludge mixtures with Na_2SO_4/H_3PO_4 was performed about every 15 minutes to

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(a) CH Delegard. 2008. "Uranium Metal Analysis Testing for K East Basin Sludge Composites," 53451-TI06, Rev. 0, Pacific Northwest National Laboratory, Richland, WA.
CH Delegard. 2008. "Uranium Metal Analysis Testing for Higher Uranium Metal Concentrations in K East Basin Sludge Composite," 53451-TI09, Rev. 0, Pacific Northwest National Laboratory, Richland, WA.

break up sludge agglomerates and enhance dissolution. Vortex mixing (rather than simple shaking) also was introduced to improve the 0.5-M HNO_3 rinse contacts.

Table 6.1. KE Basin Samples Used in Testing

Sample ID	**Source**	**Vol. Jar/ Sludge, mL**	**Dry Wt.%**				**Wet Density, g/cm^3**
			Al	**Fe**	**U**	**U_{metal}[(a)]**	
FE-5	KE Weasel Pit and South Loadout Pit	500/260	2.66	30.6	5.32	0.05	1.66
KC-2/3	Consolidated samples from fuel storage canisters with moderate and highly damaged fuel	1000/425	5.16	1.84	59.0	3.22	2.03
KE Floc Comp	Flocculated composite of KC-4 M250, KC-5, FE-5, KC Can Comp	500/260	7.70	24.2	10.3	0.02	1.25
KC-6	Consolidated sample from floor area in west bay known to be high in OIER	250/140	1.87[(b)]	1.51[(b)]	0.314[(b)]	<0.01	1.31

(a) Estimated uranium metal concentration based on xenon fission product gas release analyses of constituent sludges (Bryan et al. 2004 for FE-5 and KC-6, Delegard et al. 2000 for KC-2/3, and both Bryan et al. 2004 and Schmidt et al. 2004 for KE Floc Comp).

(b) No analytical data are available for KC-6, which contains high concentrations of organic ion exchange resin beads. Data are from the similar sample KES-H-08. The acid-insoluble residue concentration for KES-H-08 is 97.3 wt% on a dry basis. The acid insoluble residue is OIER and mordenite inorganic exchange media (Schmidt et al. 1999).

Nine additional tests with greater amounts of added uranium metal (0.025 to 1.29 wt%, settled basis) as well as two blank tests (no added uranium metal) were run for sludge KE Floc Comp according to the sequence shown in Figure 2.1. In these later tests, two 2-hour/80°C contacts with Na_2SO_4/H_3PO_4 again were used with intermittent vortex mixing.

As part of the testing, spectrophotometric analyses of the Na_2SO_4/H_3PO_4 digestion solution from the various genuine sludges were completed to identify the oxidation states of the dissolved uranium.

Table 6.2. Chemical and Radiochemical Compositions of Sludge Used in Selective Dissolution Tests

Sludge	**FE-5**	**KC-2/3**	**KC-6(a)**	**KE Floc Comp(b)**
Dry Basis				
Element	**Concentration, Wt%**			
Al	2.66	5.16	1.87	7.70
Ca	1.2	0.134	1.22	0.945
Fe	30.6	1.84	1.51	24.2
Mg	0.146	0.0462	0.225	0.230
Na	BDL(c)	0.24	3.26	0.365
Si	0.330	0.752	NR(d)	3.57
U(e)	5.32	59.0	0.314	10.3
Compound(f)	77.1	94.8	16.9	92.6
Radionuclide	**Concentration, µCi/g**			
^{60}Co	0.875	0.441	0.185	1.02
^{137}Cs	170	860	144	783
^{154}Eu	0.985	8.14	BDL	1.68
^{238}Pu	2.06	16.2	0.0618	3.22
$^{239/240}$Pu	13.1	114	0.403	23.9
^{241}Am	10.4	90.5	0.397	18.9
Settled Sludge Basis				
Element / H_2O	**Concentration, Wt%(7)**			
Al	1.56	3.04	0.802	2.53
Ca	0.704	0.0791	0.523	0.310
Fe	18.0	1.09	0.648	7.92
Mg	0.0857	0.0273	0.0965	0.0755
Na	BDL	0.142	1.40	0.120
Si	0.194	0.444	NR	1.17
U	3.12	34.8	0.135	3.37
H_2O	41.3	41.0	57.1	67.2
Radionuclide	**Concentration, µCi/g(g)**			
^{60}Co	0.514	0.260	0.0794	0.334
^{137}Cs	100	507	61.8	257
^{154}Eu	0.578	4.80	BDL	0.552
^{238}Pu	1.21	9.56	0.0265	1.06
$^{239/240}$Pu	7.69	67.3	0.173	7.84
^{241}Am	6.10	53.4	0.170	6.20
Reference(h)	a	a	a, b, c	a, d

(a) No analytical data are available for KC-6, which contains high concentrations of organic ion exchange resin beads. Data are from the similar sample KES-H-08. The acid-insoluble residue concentration is 9.73×10^5 µg/g (on a dry basis) for KES-H-08.

(b) KE Floc Comp (flocculated KE Container Composite) is a composite of KC-4 M250 (50.6 wt%), KC-5 (29.6 wt%), FE-5 (19.4 wt%), and KC Canister Composite (0.35 wt%), all on a settled sludge basis. Composition calculated from the compositions of the constituent sludges (except KC Canister Composite) converted to a dry weight basis.

(c) BDL means below detection limit.

(d) NR means not reported.

(e) Uranium concentrations generally were those reported by phosphorescence, or by inductively coupled plasma (ICP) if phosphorescence values were not available.

(f) Based on assignment of the elements to the compounds $Al(OH)_3$, $CaCO_3$, $Fe(OH)_3$, $MgCO_3$, Na_2O, SiO_2, and $UO_{2.63}\cdot H_2O$. The compounds $Al(OH)_3$, $CaCO_3$, and SiO_2 have been observed in genuine sludge. The compound $Fe(OH)_3$ generally is X-ray indifferent but represents the likely state of the wet iron hydroxide solids present in sludge (though Fe_2O_3 and other crystalline iron compounds have been observed by X-ray diffraction [XRD]). The compound $MgCO_3$ is assigned based on its chemical similarity to $CaCO_3$; Mg is too scarce to have a phase identifiable by XRD. The hypothetical compound Na_2O represents the stoichiometry of sodium as oxide within more complex oxide minerals. The hypothetical compound $UO_{2.63}\cdot H_2O$ represents a 50:50 (moles of U basis) mixture of $UO_{2.25}$ and $UO_3\cdot 2H_2O$, the

Table 6.2. Chemical and Radiochemical Compositions of Sludge Used in Selective Dissolution Tests

<table>
<tr><th>Sludge</th><th>FE-5</th><th>KC-2/3</th><th>KC-6(a)</th><th>KE Floc Comp(b)</th></tr>
<tr><td colspan="5">uranium phases most frequently observed in sludge (see Schmidt and Delegard 2003). The material balance shortfall for KC-6 (KES-H-08) is because of the presence of OIER, which is composed largely of organic polymers, and mordenite (inorganic ion exchanger), both of which do not dissolve in the acid digestion done for this sample. All other sample analyses are based on fusion digests.
(g) Settled sludge analyses are calculated based on the water concentrations of the respective sludges. Note that drying and wetting in storage and during sample maintenance will alter these values and that water-concentration values should be determined upon use to re-establish the component concentrations.
(h) References: a—Baker and Welsh(a); b—Bredt et al. 1999; c—Makenas et al. 1996; d—Silvers et al. 2000.</td></tr>
</table>

(a) RB Baker, and TL Welsh. 2001. “Laboratory Data from the Consolidated and Single Pull Core Sludge Sampling Campaign.” Internal FH Memo, 01-SNF/RBB-004, May 10, 2001, Spent Nuclear Fuel Project, Fluor Hanford, Richland, WA.

7.0 Results for Uranium Metal Analysis in K Basin Sludge

Cemented agglomerates were observed when the Na_2SO_4-bearing H_3PO_4 was added to KC-2/3 canister sludge that is rich in uranium oxides. The solids, suspected to be U(VI) phosphates, yielded somewhat to shaking and crushing to improve the acid-sludge contact in the initial set of tests with this sludge. Despite these measures, however, undissolved oxidized uranium evidently remained. This was shown when the solids dissolved quickly when cell-temperature 10 M HNO_3 was added to the heel solids. A bright yellow color indicating dissolved uranium(VI) was observed. The uranium concentration analyses of the sixth and seventh 0.5-M HNO_3 rinses of the KC-2/3 sludge also were atypically high.

The rapid and intense yellow color developed in the 10 M HNO_3 contact, and the high-rinse values suggested that the source was not the added uranium metal. Preliminary KPA confirmed that the heel contained uranium concentrations well in excess of the amounts of uranium metal added. Because of these observations of undissolved sludge, tests with KC-2/3 were repeated under approved test instructions using more aggressive agitation supplied by a vortex mixer. A second Na_2SO_4/H_3PO_4 contact also was implemented to improve sludge solids dissolution.(e) Because these additional measures were found to be effective in dissolving the oxidized uranium phases, they have been adopted into the standard selective dissolution procedure as shown in Figure 2.1.

As part of the testing, spectrophotometric analyses of the Na_2SO_4/H_3PO_4 digestion solution from the various genuine sludges were completed to identify the oxidation states of the dissolved uranium. The analyses showed the presence of dissolved iron(III) and uranium(IV) and (VI).

A significant interference at low wavelengths also was observed. Filtration and centrifugation did not remove the interference. A spectrum of the solution generated by treating Hanford blow sand with Na_2SO_4/H_3PO_4 showed the same steeply increasing absorbance as the wavelength decreased. These findings indicate that the low wavelength interference may have been caused by light scattering by colloidal silica or by organic materials present in the blow sand. A sample of basalt rock (which would contain no organic material) was crushed and then treated with hot Na_2SO_4/H_3PO_4. The spectra of the blow sand and the crushed basalt (Figure 7.1) both showed the low wavelength interference, indicating that silica was responsible for at least part of the interference. Each spectrum also showed a broad peak at about 405 nm that is attributed to Fe(III) based on measurements of dissolved ferrihydrite. The attribution of the interference to silica particles is strengthened by knowledge that silica sol is made by treating soluble silicates with acid and that at a 400-nm wavelength, light absorbance increases with sol concentration and with sol particle size (Iler 1979, pp. 331–332 and 348–349). The sols have ~10- to 60-nm particle diameters.

(e) CH Delegard. 2008. "Uranium Metal Analysis Testing for K East Basin Canister Sludge," 53451-TI08, Pacific Northwest National Laboratory, Richland, WA.

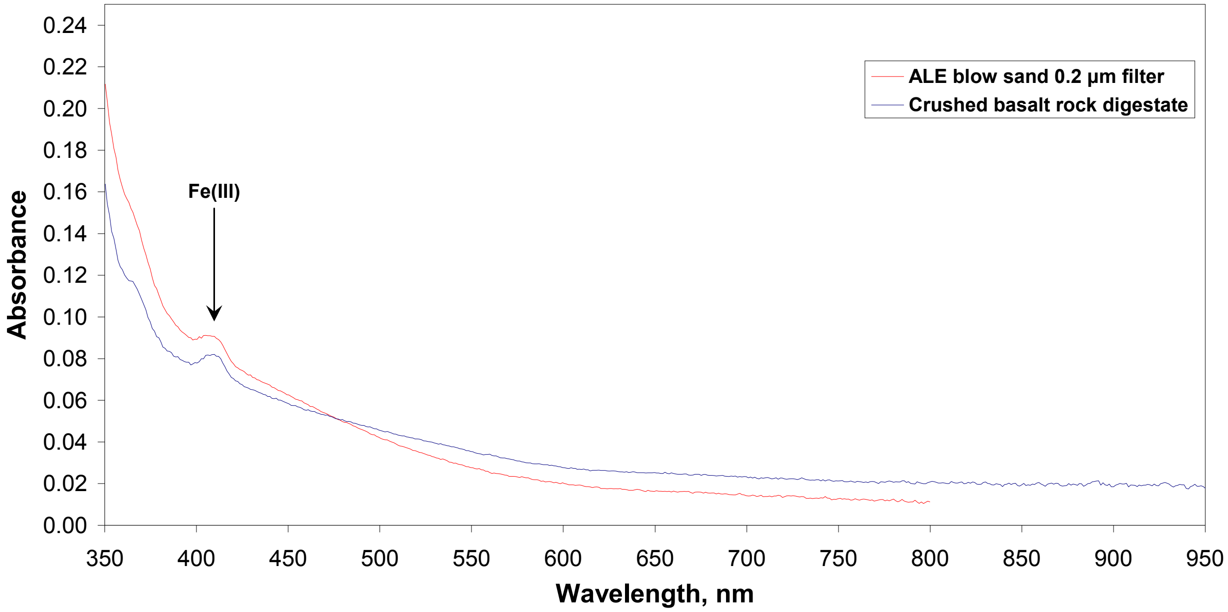

Figure 7.1. Absorbance Spectra of Solutions Produced by Na_2SO_4/H_3PO_4 Digestion of Blow Sand and Crushed Basalt

Figure 7.2 shows spectra for samples FE-5, which has a high interference at low wavelengths, which is likely due to silica sols, and sample KC-2/3, which contains relatively high uranium concentrations and had to be diluted by a factor of five to be measured accurately. Both spectra show peaks characteristic of U(IV), between 600 and 700 nm, and of U(VI), the multiplet centered at ~420 nm. The FE-5 sample also shows significant broad absorbance near 400 nm, which is indicative of Fe(III).

The sludge sample spectra were interpreted using silica background correction to show that uranium(IV) ranged from only about 2.3 to 20% of the total dissolved uranium (Table 7.1), confirming that significant uraninite (UO_2, U_4O_9, U_3O_7) oxidation has occurred during the hot cell storage of sludge for the past 9 to 10 years. The plutonium concentration in the KE canister sludge (KC-2/3) also was measured based on plutonium spectral data obtained in Na_2SO_4-bearing H_3PO_4 and its peak intensity relative to uranium. The plutonium concentration measured by spectrophotometry was fully consistent with that expected based on prior sludge analyses, attaining 95% recovery of the known value. Comparison of the data for the KE Floc Comp and the KE Floc Comp and KC-6 tests show that the presence of IXM (in KC-6) affects the relative amounts of U(IV) and U(VI) in the Na_2SO_4/H_3PO_4 solution by the apparent selective absorption of U(VI).

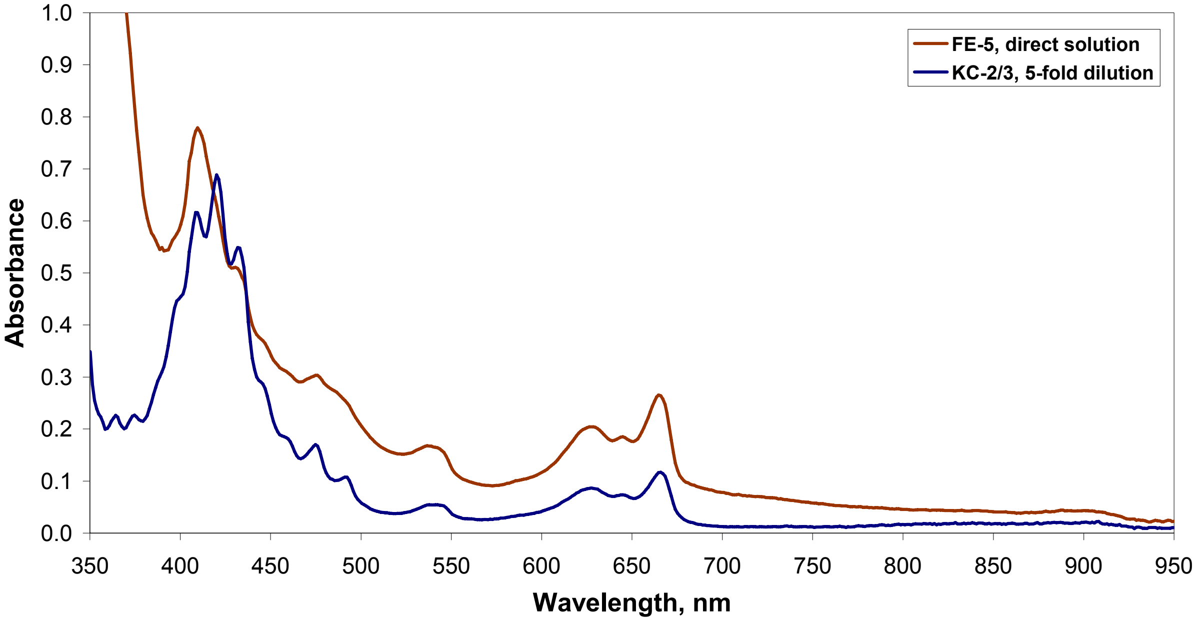

Figure 7.2. Spectra of Solutions Produced by Na_2SO_4/H_3PO_4 Digestion of Sludge Samples FE-5 and KC-2/3

Table 7.1. Uranium(IV) Percentages in Sludge Samples Dissolved in Na_2SO_4/H_3PO_4

Sludge	U(IV), % of Total Dissolved Uranium
FE-5	20.0
KC-2/3	3.9, 3.7, 4.6; 4.1 (avg.)
KE Floc Comp	2.3
KE Floc Comp & KC-6	10.8

Results of the uranium solution analyses in the sixth and seventh 0.5-M HNO_3 rinses and in the 10-M HNO_3 dissolution step are presented in Table 7.2. The results from the first set of tests for KC-2/3 are omitted from Table 7.2 because of the known incomplete oxidized uranium dissolution in the single Na_2SO_4/H_3PO_4 step. The concentrations in the sixth and seventh rinses for the original KC-2/3 test were approximately 100 to 1000 times greater than those reported in Table 7.2 for the re-run test.

The 0.5-M HNO_3 rinse concentrations ranged from about 0.25 to 10 ppm under conditions in which the initial Na_2SO_4/H_3PO_4 solution would have contained as much as 12,000 ppm of uranium. The uranium concentrations in the 10-M HNO_3 blank test solutions for the four different sludges were about 1 to 25 times higher than the rinse concentrations. This suggests that the higher acid concentration often led to enhanced uranium dissolution or displacement from the sludge heel. The lowest uranium concentrations observed in the 10-M HNO_3 blank test digestions occurred for the composite sludge (KE Floc Comp) selected to emulate the containerized sludge. The same sludge, but blended with the IXM-rich KC-6 sludge, had the second lowest uranium concentration.

Table 7.2. Uranium Concentrations in 0.5-M Nitric Acid Rinses and in 10-M Nitric Acid Digestions

Sludge Type Represented	Sludge Used	Number of Na_2SO_4/H_3PO_4 Contacts	Sample	µg U metal/mL (ppm)		
				0.5 M HNO_3		10 M HNO_3
				6th Rinse	7th Rinse	
Pit	FE-5	1	Blank—no U metal	8.84	9.69	44.8
			With U metal—Test 1	5.27	4.12	54.8
			With U metal—Test 2	4.21	4.59	59.9
Settler	KC-2/3	2	Blank—no U metal	2.23	0.854	17.4
			With U metal—Test 1	3.85	6.38	22.0
			With U metal—Test 2	1.26	0.717	157
Containerized	KE Floc Comp	1	Blank—no U metal	1.12	3.69	3.90
			With U metal—Test 1	1.65	4.17	29.6
			With U metal—Test 2	3.87	8.92	47.8
Containerized with IXM	KE Floc Comp & KC-6	1	Blank—no U metal	2.27	3.94	6.59
			With U metal—Test 1	1.31	1.91	44.4
			With U metal—Test 2	2.04	1.66	34.5
Containerized	KE Floc Comp	2	Blank—no U metal—1	0.254	0.468	6.45
			Blank—no U metal—2	2.53	1.99	32.6
			With U metal—Test 1	0.497	0.369	142
			With U metal—Test 2	1.82	1.23	289
			With U metal—Test 3	2.54	0.664	331
			With U metal—Test 4	0.412	4.68	691
			With U metal—Test 5	1.23	1.41	456
			With U metal—Test 6	1.24	1.82	1300
			With U metal—Test 7	0.901	0.558	2890
			With U metal—Test 8	0.748	1.25	6840
			With U metal—Test 9	1.43	2.89	7750

The uranium metal analysis recovery data for the tests with uranium metal spiked and unspiked K Basin sludge are shown in Table 7.3 and Figure 7.3.

The uranium concentrations found in the blank heels remaining after the Na_2SO_4/H_3PO_4 dissolution step and dilute HNO_3 rinses range from 0.0010 to 0.0099 wt% U. This indicates that no appreciable amounts of uranium metal remained in any of the tested sludges, including the KC-2/3 sludge, which originally contained about 3.2 wt% uranium when analyzed by gas-generation techniques in 2000.

The amounts of uranium metal added in the initial tests with the FE-5, KE Floc Comp, and KE Floc Comp with KC-6 sludge range from 0.0064 to 0.0085 wt% and thus are only about 2 to 3 times the 0.0037-wt% uranium metal average lower detection limit based on the blank analyses. The amounts of uranium metal added to the tests with the KC-2/3 sludge were 0.0121 and 0.0146 wt%, about 4 times the average lower detection limit. The uranium metal recoveries for seven of eight of these tests range from 106 to 179% with the high recoveries at least partly due to the high relative contributions of the analytical background uranium compared with the small amounts of added uranium metal. The uranium metal concentration for the eighth test, Test 1 of the KC-2/3 determination, was only 0.0030 wt%, or 25% of the amount added. Because of the low recovery, it is likely that the transfer of the miniscule uranium metal bead to the sludge did not occur for this test.

Table 7.3. Uranium Metal Analysis Results in Uranium Metal Unspiked and Spiked K Basin Sludge

Sludge Type Represented	Sludge Used	Number of Na_2SO_4/H_3PO_4 Contacts	Sample	$[U_{metal}]$, wt%			Recovery, %
				Added	Found	Diff. (Found-Added)	
Pit	FE-5	1	Blank—no U metal	0.00000	0.00994	0.00994	NA
			With U metal—1	0.00679	0.0107	0.00392	157.7
			With U metal—2	0.00670	0.0113	0.00458	168.2
Settler	KC-2/3	2	Blank—no U metal	0.00000	0.00286	0.00286	NA
			With U metal—1 (a)	0.0121	0.00300	-0.00907	24.8
			With U metal—2	0.0146	0.0262	0.0116	179.3
Containerized	KE Floc Comp	1	Blank—no U metal	0.00000	0.00096	0.00096	NA
			With U metal—1	0.00490	0.00783	0.00293	159.8
			With U metal—2	0.00941	0.0132	0.00382	140.6
Containerized with IXM	KE Floc Comp & KC-6	1	Blank—no U metal	0.00000	0.00140	0.00140	NA
			With U metal—1	0.00777	0.0118	0.00404	152.0
			With U metal—2	0.00808	0.00860	0.00052	106.4
Containerized	KE Floc Comp	2	Blank—no U metal—1	0.00000	0.00141	0.00141	NA
			Blank—no U metal—2	0.00000	0.00589	0.00589	NA
			With U metal—1	0.0250	0.0247	-0.00037	98.5
			With U metal—2	0.0592	0.0602	0.00109	101.8
			With U metal—3	0.0612	0.0641	0.00236	103.8
			With U metal—4	0.139	0.135	-0.00352	97.5
			With U metal—5	0.0812	0.0830	0.00171	102.1
			With U metal—6	0.275	0.280	0.00467	101.7
			With U metal—7	0.521	0.517	-0.00402	99.2
			With U metal—8	1.210	1.166	-0.0443	96.3
			With U metal—9	1.291	1.207	-0.0836	93.5
Blank only; 6 tests					Average	0.0037	
					Standard Dev.	0.0035	
<0.02 wt% added uranium metal (KC-2/3 Test 1 excluded); 13 tests					Average	0.0041	
					Standard Dev.	0.0033	
<1 wt% added uranium metal (KC-2/3 Test 1 excluded); 20 tests					Average	0.0028	
					Standard Dev.	0.0037	
(a) Data suspect; uranium metal bead apparently not added.							

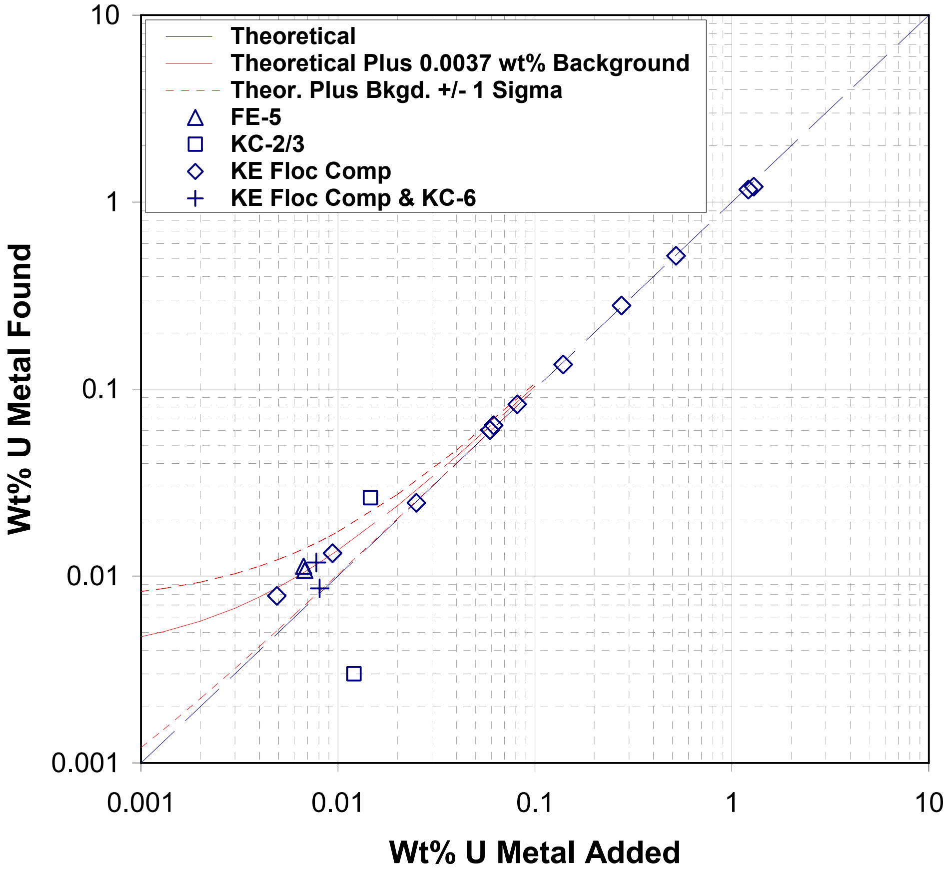

Figure 7.3. Uranium Metal Analysis Recoveries in Spiked and Unspiked K Basin Sludge

The average background for the six blank tests is 0.0037±0.0035 wt% (at one standard deviation). This level of background concentration appears to be the result of variable traces of residual oxidized uranium remaining in the insoluble residue after the Na_2SO_4/H_3PO_4 strike(s) and the dilute HNO_3 rinses and may also include uranium displaced from solids surfaces by the 10 M HNO_3. The uranium quantities leached from the blank heels with 10 M HNO_3 are lower, on average, than the 0.0065- and 0.0103-wt% values observed in tests with the simulated sludge (Table 5.2), but the differences are not statistically significant.

Because many of the tests were run with small amounts of added uranium metal, the average background also may be calculated as the difference between the amount of uranium metal found by analysis and the amount of uranium added. The differences between the as-found and added uranium concentrations are shown in Table 7.3. The average background calculated from the differences between the as-found and added uranium concentrations for the 13 tests run below 0.02 wt% added uranium (including the blank tests but excluding the anomalous first test of KC-2/3) is 0.0041±0.0033 wt%. These values are comparable to the values found for the six blank tests alone. Even for the 20 test runs below 1 wt% added uranium (again excluding the single outlying KC-2/3 result), the average background is 0.0028±0.0037 wt%. Based on these findings, the nominal background concentration is estimated to be ~0.004 wt%.

As shown in Table 7.3 and Figure 7.3, aside from Test 1 of the KC-2/3 experiment, the uranium metal concentrations found by the selective dissolution technique correspond well with the concentrations of added uranium metal if the average analytical background concentration is included. However, at uranium metal concentrations lower than about 0.01 wt%, the average background uranium concentration of ~0.004 wt% becomes an increasingly significant contributor to the total analyzed uranium concentration. The uranium metal recoveries for tests above 0.02 wt% uranium (Tests 1 through 9 for KE Floc Comp having two Na_2SO_4/H_3PO_4 contacts) average 99.4 wt% with a standard deviation of 3.3 wt%.

8.0 Uranium Metal Concentrations in Sludge Compared with Analysis Targets

The uranium metal concentration testing with unspiked simulated sludge and KE Basin sludge show analytical detection limits of ~0.004 wt%. This value is 8.5 times lower than the Safety Basis uranium metal content for KE North Loadout Pit (NLOP) sludge. The KE NLOP sludge has been successfully packaged (as contact handled transuranic waste) for disposal to WIPP. The 0.004-wt% detection limit is also a factor of 65 less than the current design basis uranium metal content for KE Floor sludge. Thus, deploying this method to characterize new sludge samples affords the Sludge Treatment Project the potential to measure a significantly lower uranium metal content than that given in current design/safety basis documents.

Further consideration of the target detection and quantitation limits is worthwhile. Some of the considerations are based on the uranium metal concentrations known or projected in various K Basin sludge streams as shown in Table 8.1.

Table 8.1. Uranium Metal Concentrations in Sludge and Considerations for Measurement Detection Limit

Stream	[U_{Metal}], wt% (settled sludge basis)	Reference/Assumptions
Design Bases		
KE NLOP Design Basis	0.0057	Schmidt 2006. Note that H_2 generation from KE NLOP (Safety Basis) is not a handling, shipping, or storage issue for grouted KE NLOP sludge (at ~20 liters of sludge per drum).
KE NLOP Safety Basis	0.034	
KE Floor Design Basis	0.26	Schmidt 2006.
KE Floor Safety Basis	1.5	
KE Canister Design Basis	2.1	
KE Canister Safety Basis	5	
93/7 Mix KE Floor/Can – Design	0.45	Calculation from KE Floor and Canister Design Basis.
Sludge Analyses (via gas-generation testing)		
Canister sludge, KC-2/3	1.9	Delegard et al. 2000 (meas'd. Oct. 1999–April 2000).
Weasel Pit sludge, FE-5	0.027	Bryan et al. 2004 (meas'd. July–Sept. 2000).
Shipping Limit		
U metal limit in 55-gal drum in RH-72B Cask, with 96.4 liters of as-settled sludge.	~0.01	Assumes: 3-drum 60 day & 60°C shipment (3.65×10^{-8} mol/s); 500-µm U metal particles, no particle consumption, no radiolysis, no matrix rate mitigation.
Analytical Detection Limits		
Detection limit by xenon fission product gas analysis based on Gas-Generation II testing.	~0.005	Bryan et al. 2004 (technique assumes knowledge of the burn-up of source fuel).
Projected detection limit from initial results of selective dissolution.	~0.004	Based on testing of selective dissolution with actual sludge samples (4 grams) spiked with U metal.

The uranium metal concentrations analyzed in sludge are compared in Table 8.1 with the projected ~0.004 wt% uranium metal detection limit obtained for the present selective dissolution technique using about 4 grams of sludge sample and requiring about 7 to 14 days of preparation and analysis time and the ~0.005 wt% uranium metal detection limit projected by xenon fission product gas release using about 20 grams of sludge and requiring about 2 months of preparation and analysis time. It is seen that the selective dissolution technique is about as sensitive and provides much more timely results than the alternative gas-generation-analysis technique. The gas-generation technique also must rely on estimates of uranium metal fuel exposure (typically, ~2900 MWD/MTU [megawatt day/metric ton of uranium]) to be applied.

The target measurement limits to meet Sludge Treatment Project (STP) goals may also be affected by the following considerations related to grouting sludge and preparing it for shipment to, and disposal at, WIPP:

- It is unlikely that individual drums will be loaded with the 96-liter upper limit of as-settled sludge. A decreased waste loading will permit an increase in the allowable uranium metal concentration (uranium metal surface area).
- Smaller drums of lower capacity likely will be used. These drums then will be overpacked in 55-gallon drums. This will result in less sludge per shipment, increasing the allowable uranium metal concentration within the sludge.
- Some reaction of uranium metal will occur before, during, and after grout processing. The hydrogen generation rate is greatest at the beginning of the anoxic reaction time when the uranium metal surface area is greatest. Taking credit for the burn-out occurring before the 60°C 60-day shipping window will effectively double the allowable mass per drum as compared with assuming the uranium metal surface area remains constant.
- Some decrease in the uranium metal corrosion rate may occur because of the influence of the grout matrix. Prior testing has shown marginal rate decreases for certain grouted sludge (Delegard et al. 2004).
- A shorter shipping duration of 10 days instead of 60 days for transporting the RH-72B from Hanford to WIPP may be permitted. This shorter duration would effectively increase the allowable uranium metal content by a factor of 6.
- The apportionment of hydrogen generation due to the uranium metal reaction with water and due to radiolysis will impact the allowable uranium metal content in the sludge during shipment.

9.0 Key Findings from Selective Dissolution Validation Testing

The following conclusions and observations are based on the results of selective dissolution testing with complex K Basin sludge simulants containing uranium metal and actual sludge spiked with uranium metal:

- The uranium metal detection limit of ~0.004 wt% U metal (settled sludge basis) for selective dissolution is essentially equivalent to the ~0.005 wt% U metal detection limit achieved with testing based on xenon fission product gas release.
- The demonstrated method sensitivity appears sufficient to meet STP testing needs.
- The experimental results provide a sufficient technical basis for an approved routine analytical procedure for this approach.
- Uranium metal can be measured with ~3 to 5 grams of sample in 1 to 2 weeks with the selective dissolution method. For gas-generation testing, uranium metal measurements require about 20 grams of sample and can require in excess of 2 months.
- While both selective dissolution and gas-generation testing can provide data on uranium metal concentration in the sludge, gas-generation testing can also estimate the uranium metal particle-size distribution provided that sufficient metal concentrations exist in the sludge, and multiple gas analysis samples are taken. Information on uranium metal particle-size distribution can be obtained by selective dissolution methods if the sludge samples are first size classified (for example, by sieving).
- To counter uranium interference background from labware and reagents, the selective dissolution analysis uses plastic labware to minimize uranium contamination that is present at low levels in ordinary glass and uses high-purity HNO_3 reagent prepared and held in plastic vessels.
- The quantification limit for selective dissolution can be affected by the ubiquitous uranium contamination in the hot cell and requires careful laboratory practices to minimize its influence.
- Beyond hot cell contamination, however, all selective dissolution preparations will contain a small quantity of oxidized uranium that is not removed from the sludge heel that remains after the Na_2SO_4/H_3PO_4 dissolution and subsequent serial 0.5 M HNO_3 rinses. The residual uranium may arise because of incomplete oxidized uranium dissolution, but more typically is due to sorption on the heel solids and potentially on the plastic digestion vessel. Part or all of the oxidized uranium is dissolved during the subsequent uranium metal dissolution step with 10 M HNO_3 where it adds to the uranium reporting to the solution as dissolved metal. The net effect of this tramp residual uranium is that it will be interpreted as uranium metal being present in the sludge even for sludge samples containing no uranium metal. Based on the tests performed to-date with actual sludge, this residual uranium is equivalent to a uranium metal background of about 0.004 wt%. Thus, the

selective-dissolution method will always predict the presence of a small threshold quantity of uranium metal.[a]

- Testing with actual sludge performed at the low end of the expected range of uranium metal concentration in the sludge (0.007 to 0.015 wt%, settled sludge basis) achieved uranium metal recoveries ranging from 106 to 179%.
- Testing at higher uranium metal levels (0.025 to 1.29 wt%, settled sludge basis), encompassing the design basis KE Floor sludge concentration of 0.26 wt%, achieved 99.4 wt% recovery with 3.3% uncertainty at one standard deviation.

(a) It is noted that all chemical or radiochemical analyses have a lower analytical limit that, if reached for any sample, constitutes an estimate of the highest potential concentration of the analyte in question.

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