

## STUDIES OF CHEMICAL PROCESSING OF K BASINS SLUDGE

PR Bredt, CD Carlson, CH Delegard,\* KH Pool, AJ Schmidt  
*Pacific Northwest National Laboratory*  
P.O. Box 999; MSIN P7-25  
Richland, Washington 99352 USA

DB Bechtold, J Bourges, DA Dodd, TA Flament  
*Numatec Hanford Corporation*  
P.O. Box 1300  
Richland, Washington 99352 USA

NN Krot, AB Yusov  
*Institute of Physical Chemistry, Russian Academy of Sciences*  
31 Leninsky Prospekt  
117915 Moscow, Russia

### ABSTRACT

Two water-filled concrete pools (K Basins) in the 100-K Area of the U.S. Department of Energy's Hanford Site in Washington State contain about 2100 metric tons of irradiated metallic uranium fuel elements and about 52 cubic meters of heterogeneous radioactive sludge. In the D&D of this facility, chemical processing of the sludge is being considered as a means to decrease the sludge's chemical reactivity, dispose the radioactivity onsite to existing facilities, and ensure criticality safety. Laboratory testing of

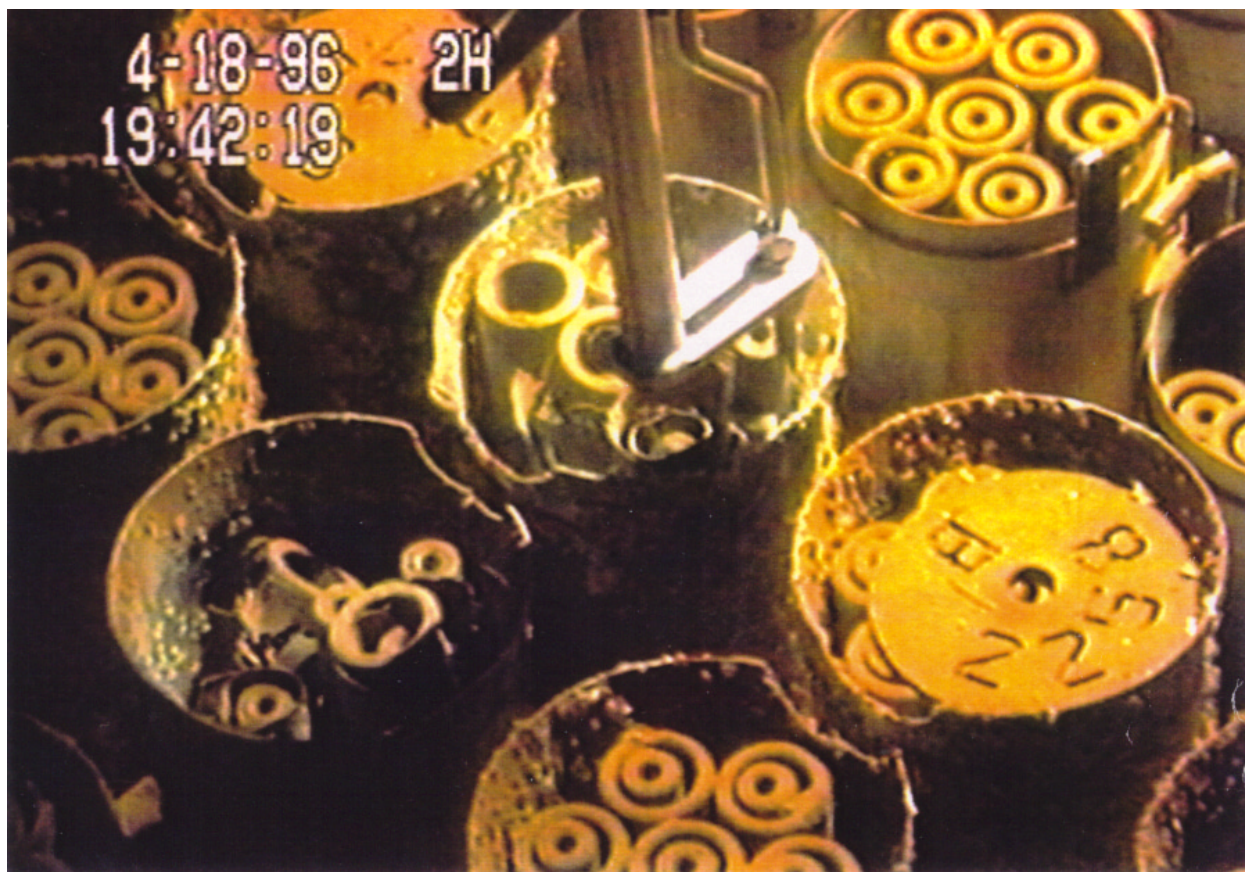
- sludge dissolution in nitric acid
- residual solids decontamination [to allow their onsite landfill disposal at the Environmental Restoration Disposal Facility (ERDF)]
- alkali treatment of the dissolver solution (to allow its disposal to onsite waste storage tanks)
- the stability of the alkali-formed precipitated solids to tank waste solutions

was conducted using actual K Basin sludge and simulated dissolver solutions. The test results confirmed the feasibility of chemical processing and were used to develop and verify the process flow diagrams and identify required areas for further studies.

### INTRODUCTION

The K East (KE) and K West (KW) fuel storage basins (K Basins) are concrete-lined pools, each with a ~4.9-million liter capacity. The K Basins were originally designed and used to decay short-lived fission products from irradiated, aluminum-clad uranium metal fuel elements discharged from DOE's 100-KE and 100-KW reactors on the Hanford Site before reprocessing the fuels. The K Basins are about 420 m from the Columbia River in the 100-K Area. The pools later were refit to accept zirconium/1.5 wt% tin-clad metallic uranium fuel from the 100-N reactor with the fuel held in double-barreled open (KE) or closed (KW) canisters containing up to 14 elements each. Only limited cooling times were envisioned in the original fuel design to allow decay of short-lived fission and activation products before fuels were reprocessed in Hanford's plutonium-uranium extraction (PUREX) plant. To enhance the rate of the fuel cladding dissolution step during reprocessing, the cladding was not very thick. Because planned cooling times were short, the incidental cracks that occurred in irradiated fuel discharge and handling and the resulting limited uranium metal corrosion were of little concern. However, with suspension of PUREX operations from 1972 to 1983 and plant shutdown in 1994, the designed outlet for the remaining 2100

metric tons of fuel (~115,000 fuel elements primarily from the 100-N reactor) was blocked. Storage times now approach 30 years for some elements, and extensive corrosion of many elements has been observed (Figure 1). It is planned for the fuel to be removed, cleaned, dried, and stored onsite in hermetically sealed, welded steel containers until it is ultimately disposed in a national nuclear waste repository. The K Basin facility will be decontaminated and decommissioned (D&D) once the fuel is removed.



**Figure 1.** View of Intact and Broken Fuel in Open Storage Canisters During KE Basin Sludge Sampling

During the time the fuel has been stored, approximately 52 m<sup>3</sup> of heterogeneous solid materials have accumulated in the fuel canisters and the K Basins' floors. This material, described as sludge, must be properly disposed through the K Basins' D&D activities. Chemical and physical characterization shows that the sludge contains uranium metal fuel pieces (some with zirconium cladding still attached), uranium corrosion products, organic and inorganic ion exchange material (IXM), graphite-based gasket materials, iron and aluminum metal corrosion products, sand, infiltrated soil, biological debris, and trace polychlorinated biphenyls (PCBs). Additional sludge, rich in uranium and cladding, will be created during fuel element handling for cleaning and storage because of fracturing and crumbling of the corroded and friable fuel elements.

X-ray diffractometry (XRD) was used to identify many of the sludge solid phases. Uranium metal was not found by XRD because it was shielded by oxide layers on the metal surface. Uranium metal was indicated by the high densities of some sludges (up to 15 g/mL), hydrogen gas production (from reaction of uranium metal with water), xenon and krypton fission gas release, and up to 94 wt% uranium concentrations. Uranium metal corrosion products found include uranium hydride (UH<sub>3</sub>), various uraninites (UO<sub>2</sub>, U<sub>4</sub>O<sub>9</sub>, U<sub>3</sub>O<sub>7</sub>, U<sub>3</sub>O<sub>8</sub>), schoepites (UO<sub>3</sub>·2H<sub>2</sub>O, UO<sub>2.86</sub>·1.5H<sub>2</sub>O), uranates (Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·6H<sub>2</sub>O,

$K_2UO_4$ ,  $CaU_6O_{19} \cdot 12H_2O$ ), and a uranyl peroxide ( $UO_4 \cdot 4H_2O$ ). These phases are evidence of the progressive and ultimately complete oxidation of uranium metal to U(VI) compounds in the K Basins. Iron and aluminum corrosion products from K Basin structural items found by XRD include hematite ( $Fe_2O_3$ ), lepidocrocite and goethite (both  $FeOOH$ ), magnetite ( $Fe_3O_4$ ), and gibbsite, bayerite, and nordstrandite [all  $Al(OH)_3$ ]. Sand and infiltrated airborne native soil materials include quartz ( $SiO_2$ ), calcite ( $CaCO_3$ ), albite ( $NaAlSi_3O_8$ ), anorthite ( $CaAl_2Si_2O_8 \cdot 4H_2O$ ), and mica [ $Mg_3Si_4O_{10}(OH)_2$ ]. Ion exchange materials (IXMs) were used in pool water decontamination, and some was inadvertently lost in the basins. The IXMs include an inorganic zeolitic ion exchanger, Zeolon 900 (confirmed by XRD), and mixed organic strong-acid/strong-base resins (confirmed by electron microscopy). Zeolon 900 is composed of the mineral mordenite [ $(Ca,Na_2,K_2)Al_2Si_{10}O_{24} \cdot 7H_2O$ ].

Extensive sampling and characterization show that the sludges are heterogeneous. High uranium concentrations are observed in and near the open canisters of the KE Basin and in the closed canisters of the KW Basin. Lower uranium concentrations are found in the open floor and loadout pit areas of the KE Basin (1,2,3). Sludge sampling and analysis have not yet been performed for the KW Basin floor and loadout pit areas. Composite canister and floor and loadout pit area sludges created from KE Basin samples, an average KW canister sludge, and an IXM-rich sample are shown in Table I. The radioelement concentrations in the various sludges and in the IXM do not allow their direct onsite disposal to the ERDF, as shown by the respective criteria.

**Table I.** Concentrations of Key Radionuclides<sup>(a)</sup> and Chemical Constituents of K Basin Sludges and Comparison with ERDF Disposal Criteria

Analyte	Composition (dry basis)				
	KE Canister Sludge	KE Floor and Loadout Pit Area Sludge	KW Canister Sludge	IXM <sup>(b)</sup>	ERDF <sup>(c)</sup>
U; wt%	68.5	5.40	65.7	0.218	0.13
Fe; wt%	1.20	29.9	6.59	0.763	--
Al; wt%	1.84	4.66	2.04	2.36	--
Si; wt%	0.760	6.05	Not analyzed	8.62	--
Ca; wt%	0.118	1.22	<0.9	2.01	--
<sup>137</sup> Cs; $\mu Ci/g$	809	825	1900	103	16
<sup>239,240</sup> Pu; $\mu Ci/g$	121	14.1	147	0.168	0.022
<sup>241</sup> Am; $\mu Ci/g$	95.3	55.2	142	0.148	0.025

(a) Other radioactive fission and activation products are present in sludge (<sup>60</sup>Co, <sup>90</sup>Sr, <sup>154</sup>Eu, <sup>238</sup>Pu, <sup>243,244</sup>Cm).  
 (b) This IXM sample is about 65 wt% organic resin and 35 wt% mordenite.  
 (c) The constituents of most regulatory concern (4) in discharging treated solid residues to the ERDF onsite landfill are <sup>137</sup>Cs, U, <sup>239,240</sup>Pu, <sup>241</sup>Am, and the transuranic radionuclides (TRU; 0.100 $\mu Ci/g$ ), represented chiefly by <sup>239,240</sup>Pu and <sup>241</sup>Am (5).

Interim transport and storage of the sludge in Hanford's T Plant canyon, without chemical treatment, became the reference sludge disposition alternative in mid-1999. However, until that time, chemical processing was considered the reference approach to treating the sludge in D&D of the K Basins. Through chemical processing, the sludge's chemical reactivity would be decreased, the radioactive solution and partially decontaminated solid fractions could be disposed onsite to existing facilities (the waste tanks and ERDF, respectively), and the criticality safety of the overall course of action could be ensured. To this end, bench-scale laboratory testing of the chemical processing option was performed in our laboratories. Experimental approaches and results for the chemical processing alternative are presented in this paper and described more fully in the cited references. Issues related to PCB treatment and disposal from K Basin sludge will not be addressed in this paper.

## BENCH-SCALE TESTING OF CHEMICAL PROCESSING

Bench-scale chemical testing was undertaken to help define process parameters and to evaluate process performance. The conceptual process flowsheet, given in Figure 2, indicates by shading the chemical steps that were investigated:

- sludge dissolution by nitric acid ( $\text{HNO}_3$ )
- further decontamination of the sludge residues following acid treatment to allow their disposal with other solid residues to the ERDF in a grout-immobilized waste form
- decontamination of the IXM (separated from the sludge by physical means prior to acid treatment) to allow its disposal to ERDF
- treatment of the acidic dissolver solution and leachates with added depleted uranium (DU) and iron (Fe) nitrate salts for criticality safety and with added sodium hydroxide and sodium nitrate ( $\text{NaOH}$  and  $\text{NaNO}_2$ ) to allow its disposal as an alkaline slurry to the Hanford waste tanks
- blending of the alkaline slurry with existing double-shell tank (DST) wastes.

The acid dissolution and IXM leaching tests were performed in shielded cell facilities (hot cells) with materials taken from the K Basins. The residue solids leaching tests were performed in fume hoods with residues generated from K Basin sludge. To investigate the effects of process solution variability, the adjustment/neutralization and waste blending tests were performed with simulated waste compositions.

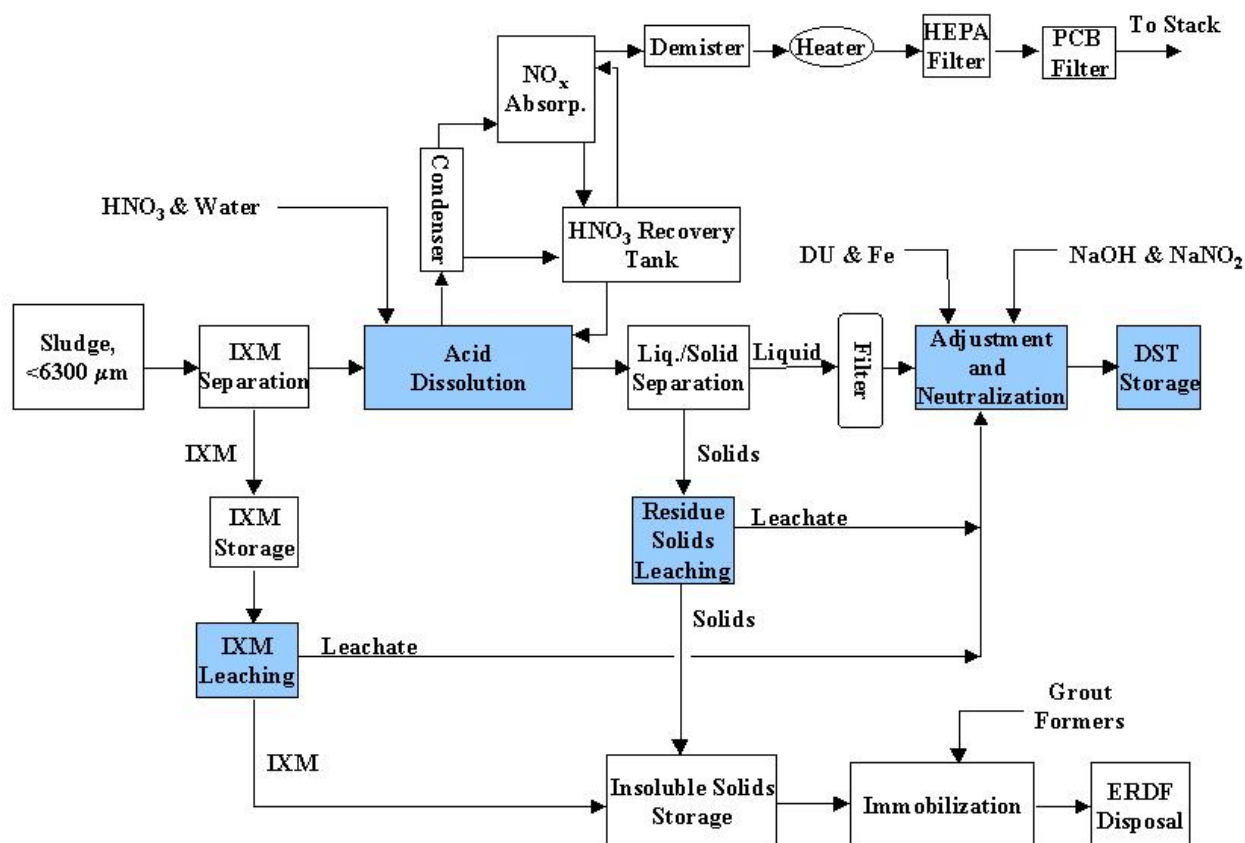


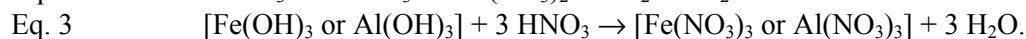
Figure 2. Conceptual Flowsheet for K Basin Sludge Treatment and Disposal

### Acid Dissolution

Initial batch sludge dissolution studies investigated the effects of process temperature (25°C to boiling) and acid concentration (2- to 10-M HNO<sub>3</sub>) on the rate and extent of sludge dissolution (6,7,8). The studies showed that gels, likely amorphous silica, formed during the hot acid digestion. Gel formation in acid digestion of certain silicate minerals is attributed to the release of low-order (monomeric or dimeric) silicate units during mineral dissolution followed by the precipitation of amorphous silica gel (9) when the ~10<sup>-3</sup>-M amorphous silica solubility in HNO<sub>3</sub> (10) is exceeded. The gels retard solid/liquid separations by filter blinding; retention of dissolved radioactive constituents in gels also effectively decreases the solids decontamination necessary for ERDF disposal. The scoping studies showed that solids decontamination increased with leaching time. Highest decontamination was achieved at around 6 M HNO<sub>3</sub>, and reaction rates increased with temperature. Based on these findings and to ensure excess acidity to prevent plutonium polymerization and maximize process rates, nominal 95°C, 6-M HNO<sub>3</sub> dissolver conditions were selected for the reference flowsheet and subsequent semicontinuous sludge dissolution validation tests.

The 95°C, 6-M HNO<sub>3</sub> sludge dissolution step was validated in three bench-scale process tests (5). The tests used the uranium-rich KE canister sludge (Table I), the KE canister sludge with uranium metal fuel pieces, and the mineral-rich KE floor and loadout pit area sludge (Table I). The latter test included a stainless steel mesh bag containing several grams of IXM (Table I) to determine radionuclide uptake and leaching on the IXM during the acid-treatment step. Process operations examined in these tests were semicontinuous sludge feed (frozen sludge pellets were used to guarantee complete addition of the sticky sludge fractions), make-up acid additions, solution/slurry sampling for analysis of reaction progress, and real-time reaction progress monitoring by measuring product gases and solution electrical conductivity.

Gases are produced in the reaction of HNO<sub>3</sub> with many of the sludge constituents. Some sludge components (primarily the reduced uranium compounds) are oxidized by HNO<sub>3</sub> and produce NO<sub>2</sub>, NO, and N<sub>2</sub>O gaseous nitrate reduction products (Eq. 1). Carbonates undergo acid-base reactions to produce CO<sub>2</sub> gas (Eq. 2), while some metal oxides or hydroxides consume acid but yield no product gases (Eq. 3). Some components (e.g., crystalline quartz) are largely unreactive.

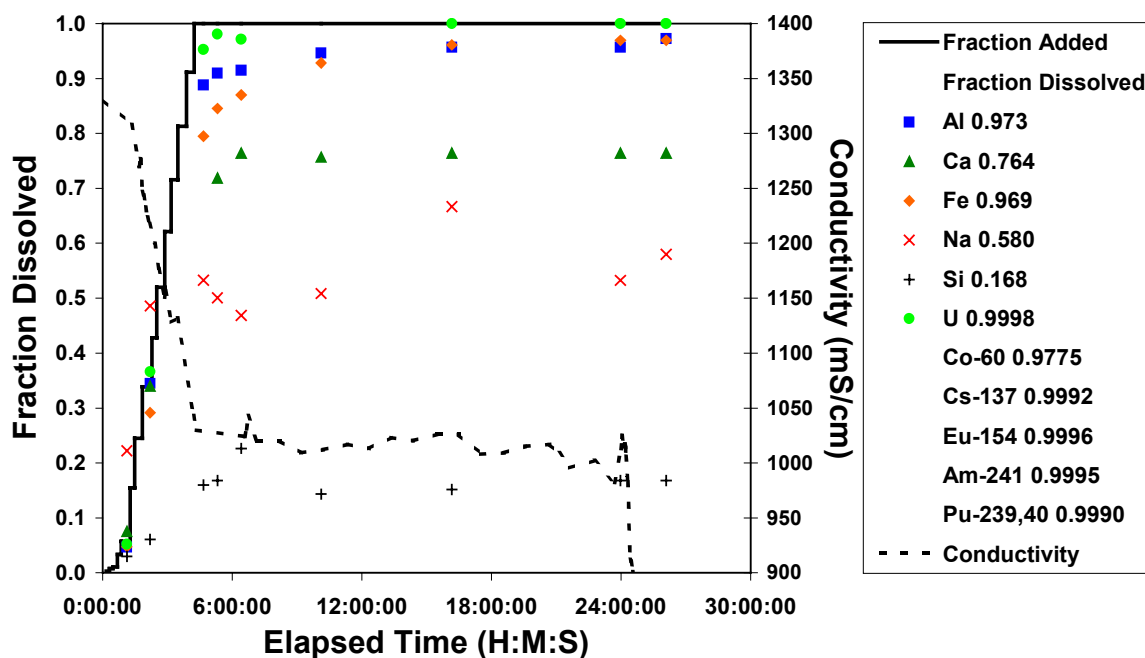


The uranium metal reaction (Eq. 1) is the one observed in fuel dissolution at the PUREX plant (11). Trace N<sub>2</sub>O also is found in this reaction. The same oxides of nitrogen (NO<sub>x</sub>) are formed in dissolution of UO<sub>2</sub>; it is found that the NO/NO<sub>2</sub> distributions produced by oxidations in HNO<sub>3</sub> do not depend on the material being oxidized but rely only on the acid concentration and temperature (12). The CO<sub>2</sub> evolution from CaCO<sub>3</sub> dissolution (Eq. 2) is instantaneous. The production of gas by sludge dissolution reactions means that measurements of offgas quantities and rates can be used to determine reaction stoichiometry and follow reaction progress.

Solution electrical conductivity is another means to measure reaction progress in HNO<sub>3</sub> dissolutions. The primary conducting species in HNO<sub>3</sub> solution is the hydrogen ion, H<sup>+</sup>. As seen in the representative sludge dissolution reactions, H<sup>+</sup> is consumed in the acid-base and redox reactions, and H<sup>+</sup> chemical activity decreases accordingly. Hydrogen ion activity also decreases by inhibition of HNO<sub>3</sub> dissociation through the nitrate common ion effect of the product dissolved metal nitrate salts [e.g., UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, Al(NO<sub>3</sub>)<sub>3</sub>]. The effects of dissolved salts on conductivity diminish at lower HNO<sub>3</sub> concentrations [e.g., 0.5-M Fe(NO<sub>3</sub>)<sub>3</sub> decreases the conductivity of 4-M HNO<sub>3</sub> about 20% but decreases the conductivity of 1-M HNO<sub>3</sub> less than 2%]. Thus, as acid becomes depleted, electrical conductivity

becomes a direct measure of remaining HNO<sub>3</sub> concentration (5,13,14,15). As such, electrical conductivity is an effective indicator not only of reaction progress but also of impending acid deficiency (and risk of plutonium precipitation) for plant process control.

Reactions of the finely particulate sludge materials were found to be rapid. Therefore, sludge feed rates were used to control the reaction rates in the process validation tests and can be used to control the reaction rates in full-scale processing. Electrical conductivity mirrored the uranium-rich canister sludge addition and reached steady values within five minutes (Figure 3). However, the iron-rich floor and loadout pit area sludge required ~60 minutes to reach steady electrical conductivity. Dissolution rates from the canister sludge, proceeding in the order uranium>aluminum>iron, showed ~12 hours were required to reach steady iron concentrations (Figure 3). Uranium, <sup>137</sup>Cs, <sup>239,240</sup>Pu, and <sup>241</sup>Am dissolutions at the test end were >99.9% for the canister sludge (Figure 3); total dissolutions at test end were 98.9% for <sup>137</sup>Cs and >99.5% for uranium, <sup>239,240</sup>Pu, and <sup>241</sup>Am for the bulkier floor and loadout pit area sludge. In agreement with batch test results (6,7), the KE canister sludge left about 2 wt% residue (with respect to initial sludge weight) and KE floor and loadout pit area sludge left about 17 wt% residue. The dissolver residues contained quartz and anorthite in all tests, mica and zirconium metal needles in the tests with KE canister sludge, and zirconium cladding shards in the test to which fuel metal pieces were added.



**Figure 3.** Chemical and Radiochemical Behaviors and Solution Electrical Conductivity in KE Canister Sludge Dissolution Bench-Scale Process Validation Test in 95°C, 6-M HNO<sub>3</sub> (the fraction of element or radionuclide dissolved at the end of each test is shown in the legend; the conductivity decrease after 24 hours was caused by solution cooling from shutdown of the heater)

Offgas measurements were conducted for the second and third validation tests. Spikes observed in NO<sub>x</sub> and CO<sub>2</sub> production corresponded to the sludge and metal addition events, but slow subsequent release of NO<sub>x</sub> from the solution obscured direct observation of sludge oxidation kinetics by offgas monitoring. The NO<sub>x</sub> quantities ranged from 50 to 90% of the predicted quantities based on sludge inventories. The gas product shortfall probably arose because of NO<sub>x</sub> retention in the dissolver and condenser solutions. The NO<sub>2</sub>:NO mole ratio was about 1:3 in the test with uranium metal fuel pieces and KE canister sludge; the ratio was about 1:0.9 for the test with KE floor and loadout pit area sludge. Based on these findings,



about 600 kg each of NO<sub>2</sub> and NO would be generated in processing the estimated inventory of 21.5 tonnes of KE floor and loadout pit area sludge, 4.3 tonnes of KE canister sludge, and 1.6 tonnes of uranium fuel fragments (dry sludge basis). In practice, lower NO<sub>x</sub> discharge could be attained with air oxidation, reflux, and scrubbing of product gases.

Gels were observed to form in all three tests. The gels adhered to the dissolver vessel walls and to the temperature and conductivity probes but could be easily removed by a distilled water rinse. Blinding was observed in filtration of solutions from both KE canister sludge tests through polymer filters. Blinding did not occur in the test with KE floor and loadout pit-area sludge despite higher gel quantities.

Though the sludge dissolution reactions were relatively rapid, uranium metal fuel piece dissolution was slow. Estimated dissolution rates were consistent with the ~0.22 mm/hr linear penetration expected based on previous Hanford studies (e.g., 11). This rate implies that the nominal 6300-μm-diameter metal pieces that define the upper range of the sludge stream (Figure 2) would require about 14 hours to dissolve in 95°C, 6-M HNO<sub>3</sub>.

The radioactive acidic dissolver solution generated in processing KE floor and loadout pit area sludge in the third bench-scale test desorbed <sup>137</sup>Cs from the IXM (held in the stainless steel mesh bag and processed with the sludge) to give a decontamination factor of ~100. However, contact with the dissolver solution left uranium IXM concentrations unchanged and increased <sup>241</sup>Am IXM concentrations about six-fold and <sup>239,240</sup>Pu concentrations about 100-fold.

Important distinctions were found in the behaviors of the inorganic (mordenite) and organic IXM (Table II). Most significantly, <sup>239,240</sup>Pu concentrations, a factor of 5 above direct ERDF discard limits in the initial organic resin, increased to about 1400-times the limit after acid processing with sludge. Cesium concentrations, a factor of 30 above the ERDF limit in the initial mordenite, decreased to about 0.3-times the limit after acid sludge processing. Americium concentrations were similar in the original resin and mordenite fractions. After dissolver solution contact, the <sup>241</sup>Am concentration in the resin increased about 10-fold, while the inorganic fraction remained unchanged. Uranium concentrations in both fractions were relatively unaffected by exposure to dissolver solution. The high plutonium uptake in the organic resin underscores the need to remove IXM before the acid dissolution step.

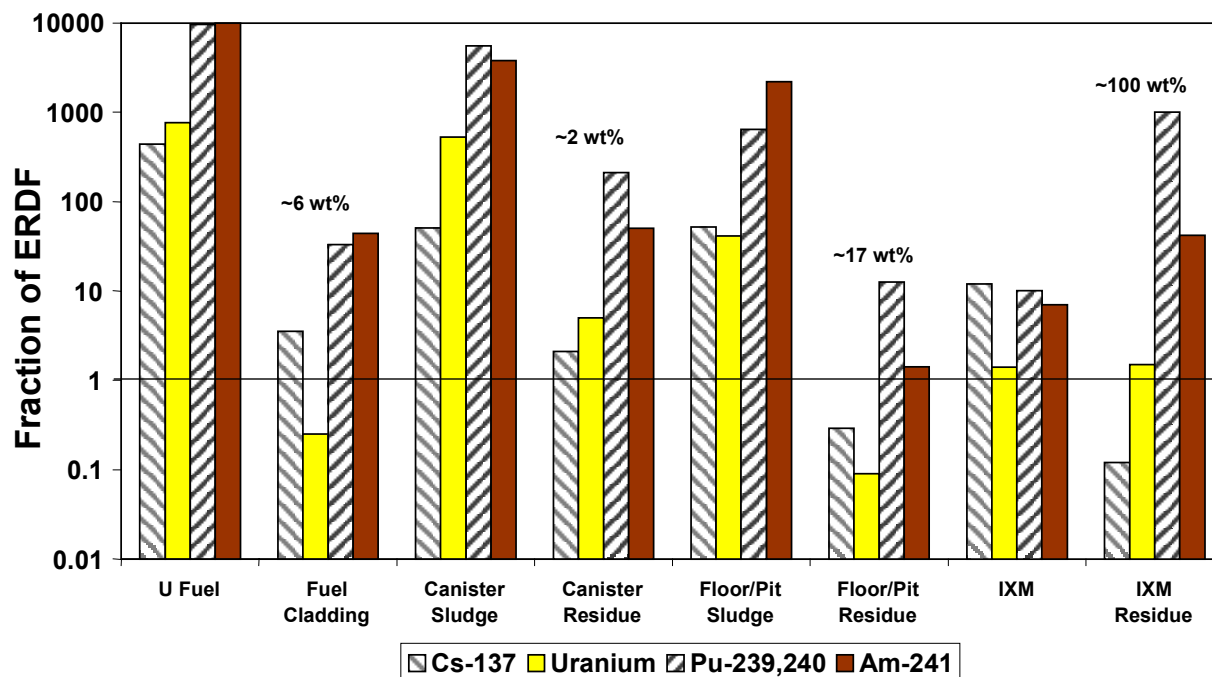
**Table II.** Radioelement Concentrations in Ion Exchange Materials Before and After Contact with Dissolver Solution

Solid	Radioelement Concentration			
	<sup>137</sup> Cs (μCi/g)	U (wt%)	<sup>241</sup> Am (μCi/g)	<sup>239,240</sup> Pu (μCi/g)
Before - Organic	7.34	0.249	0.149	0.107
Before - Inorganic	496	0.0571	0.258	0.450
Before - Combined	186	0.176	0.179	0.231
After - Organic	1.01	0.266	1.41	31.1
After - Inorganic	4.09	0.0514	0.263	3.95
After - Combined	1.93	0.200	1.06	22.7

### Residues Requiring Further Decontamination

The batch and flowsheet-validation acid dissolution tests showed that HNO<sub>3</sub> dissolves uranium solid phases. However, zirconium cladding (found as shards and needles in the residues) from the fuel dissolution, some soil minerals (quartz, anorthite, and muscovite as well as the silica-rich gels) from the canister and floor and load-out pit area sludges, and the IXM remain undissolved. All three of these solid residue types are contaminated with <sup>137</sup>Cs, uranium, <sup>239,240</sup>Pu, and/or <sup>241</sup>Am above ERDF direct disposal limits (Figure 4). Although immobilization of the residue solids by grouting is required prior to ERDF

disposal (Figure 2) and will decrease the effective radioelement concentrations in the disposed waste form, further decontamination of the solids to meet ERDF disposal criteria was found to be necessary.



**Figure 4.** Fuel, Sludge (KE Canister and Floor and Loadout Pit Area), and IXM Radioelement Concentrations with Respect to ERDF Direct Disposal Criteria Before and After HNO<sub>3</sub> Processing (percentages show quantities of residues remaining after acid treatment relative to starting materials)

### IXM Decontamination

The unacceptably high plutonium uptake that occurred by processing the IXM through the reference acid dissolution conditions demonstrated that physical separation of the IXM from the bulk sludge (e.g., by elutriation and screening) would be required before the acid dissolution step. Chemical processing to decontaminate the separated IXM then would be necessary (see Figure 2). Initial scoping tests showed that aggressive acid treatment failed to defunctionalize or destroy the IXM. The mordenite survived six hours in 90°C, 10-M HNO<sub>3</sub> with structure intact. Though the organic resins underwent some nitration by 24 hours' treatment in 95°C, 15.7-M HNO<sub>3</sub>, both cation and anion resins retained their ion exchange capacities (16).

Three alternative leachants were tested for IXM (composition given in Table I). Decontaminating the mixed organic resins of plutonium was particularly challenging because of plutonium's strong sorption on cation resin at low HNO<sub>3</sub> concentrations and strong sorption on anion resin at high HNO<sub>3</sub> concentrations. A single-step treatment using cerium(IV) in 6-M HNO<sub>3</sub> was tested to remove plutonium from cation resin by H<sup>+</sup> displacement and from anion resin by mass action competition of the Ce(NO<sub>3</sub>)<sub>6</sub><sup>2-</sup> complex with the analogous Pu(NO<sub>3</sub>)<sub>6</sub><sup>2-</sup> complex and oxidation of plutonium(IV) by cerium(IV) to the less strongly bound plutonium(VI) nitrate complex. The Ce(IV)/HNO<sub>3</sub> treatment was compared with two-contact treatments. The first contact, using 4-M HNO<sub>3</sub> or 6-M HNO<sub>3</sub>/0.3-M HF, was designed to remove plutonium from the cation resin; HF would aid in dissolving any accompanying sludge. The second contact, oxalic acid in dilute HNO<sub>3</sub>, was designed to remove plutonium from both resins by formation of the charge-neutral Pu(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub><sup>0</sup> complex. The initial strong acid treatment also was expected to remove the <sup>137</sup>Cs<sup>+</sup>, UO<sub>2</sub><sup>2+</sup>, and <sup>241</sup>Am<sup>3+</sup> sorbed species from the mordenite and organic ion exchange resins. The two-contact process



with HF proved most effective overall, especially in removing plutonium (17,18). Results of IXM decontamination are summarized in Table III.

**Table III.** IXM Decontamination Treatment Results

Treatment	Fraction of ERDF Disposal Criterion <sup>(a)</sup>			
	<sup>137</sup> Cs	Uranium	<sup>239,240</sup> Pu	<sup>241</sup> Am
<i>Starting IXM</i>	12	1.4	10	7
0.4-M Ce(IV)/6-M HNO <sub>3</sub>	1.9	1.5	5	2.4
1 <sup>st</sup> 4-M HNO <sub>3</sub> ; 2 <sup>nd</sup> 0.2-M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> /0.1-M HNO <sub>3</sub>	2.4	0.8	1	3.4
1 <sup>st</sup> 0.3-M HF/6-M HNO <sub>3</sub> ; 2 <sup>nd</sup> 0.2-M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> /0.1-M HNO <sub>3</sub>	2.1	0.4	0.6	2.8

(a) Concentration in IXM/concentration given in ERDF direct-disposal acceptance criterion (Table I).

### Zirconium Cladding Decontamination

Cladding samples taken from the validation test conducted with uranium metal fuel pieces were about 3 times the direct ERDF disposal limit in <sup>137</sup>Cs, 0.3 times the uranium limit, 33 times the <sup>239,240</sup>Pu limit, and 44 times the <sup>241</sup>Am limit (Figure 4). Technical literature was surveyed to identify zirconium cladding decontamination methods to help achieve ERDF disposal limits. Previous tests with 100-N reactor fuel cladding showed that surface leaching of cladding by extended HNO<sub>3</sub> treatment did not attain appreciable decontamination. The lack of an effect, proposed to have been due to interdiffusion of uranium into the cladding metal during fabrication and subsequent retention of the irradiation products in the cladding (11), indicated leaching could not be successful. However, the cladding could, if necessary, be dissolved using a mixed NH<sub>4</sub>NO<sub>3</sub>/NH<sub>4</sub>F solution (the Zirflex process used in the PUREX plant); the solution could be made alkaline and be disposed to the waste tanks (19). For these reasons, and because of the expected low relative quantity of cladding in the total residue inventory, no tests of cladding decontamination were performed in the present study.

### Mineral Solids Decontamination

Nitric acid-based leachants containing various additives [Ag(I)/persulfate, Ce(IV), HCl, and HF] were tested for their efficacy in decontaminating mineral residues from the KE floor and loadout pit area sludge dissolution scoping tests. The highly oxidizing Ag(I)/persulfate and Ce(IV) leachants targeted PuO<sub>2</sub> by oxidative dissolution to form Pu(VI), the HNO<sub>3</sub>/HCl targeted iron-rich minerals, and the HNO<sub>3</sub>/HF was selected for silicate and PuO<sub>2</sub> attack. The HNO<sub>3</sub>/HF leachant achieved the greatest decontamination from americium, plutonium, and uranium (20). This leachant subsequently was tested with residues from KE canister sludge dissolution scoping tests (21). Results of the mineral residue leach testing presented in Table IV show the relative efficacy of the HNO<sub>3</sub>/HF leachant.

**Table IV.** Mineral Residue Decontamination Treatment Results

Treatment	Fraction of ERDF Disposal Criterion <sup>(a)</sup>			
	<sup>137</sup> Cs	Uranium	<sup>239,240</sup> Pu	<sup>241</sup> Am
<i>Starting KE floor and loadout pit area sludge residue</i>	0.29	0.092	12	1.4
0.2-M Ag(I)/0.5-M K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> /4-M HNO <sub>3</sub>	0.20	0.026	2.8	0.97
0.4-M Ce(IV)/6-M HNO <sub>3</sub>	0.089	0.016	2.1	0.70
0.3-M HCl/6-M HNO <sub>3</sub>	0.075	0.017	2.7	0.87
0.3-M HF/6-M HNO <sub>3</sub>	0.10	0.0088	1.6	0.12
<i>Starting KE canister sludge residue</i>	2.1	5.0	210	50
0.3-M HF/6-M HNO <sub>3</sub>	0.45	0.37	8.3	3.1

(a) Concentration in residue/concentration in ERDF direct-disposal acceptance criterion (Table I).

### Residue Disposition

The inventories of the insoluble residues were estimated to be about 190 kg from cladding, 7400 kg from minerals in the floor and pit areas, 340 kg from canister sludge minerals, and 1880 kg from the IXM. The solid residues from the acid dissolution and decontamination steps will be blended and physically stabilized in a grouted matrix (Figure 2). The testing showed that the final grout-stabilized solids (cladding shards, leached floor and loadout pit area and canister sludge residues, and leached IXM) could meet the ERDF criteria for all four radioelements of interest— $^{137}\text{Cs}$ , uranium,  $^{239,240}\text{Pu}$ , and  $^{241}\text{Am}$ .

### Dissolver Solution Adjustment, Neutralization, and Product Slurry Stability

The acidic dissolver solutions must be made alkaline with NaOH prior to storage in Hanford double shell tanks (DSTs). This treatment step was studied as a function of solution composition, excess NaOH concentration (pH 12 to 1-M NaOH), direction of mixing (acid $\leftrightarrow$ base), and process temperature (40 or 80°C). Iron and uranium have low solubilities in alkaline solution and will precipitate as solid phases. The product solids particle size, solids settling rate, and uranium, plutonium, and americium solution concentrations were measured to assess the effects of the process variables. The solid/solution slurries from processing the K Basins sludge will be blended in the DSTs with other waste slurries, some of which contain significant concentrations of carbonate and organic complexing agents (such as ethylenediamine tetraacetate, EDTA) which can significantly increase actinide (uranium, plutonium, americium) solubilities in alkaline media. Therefore, the resistance of the precipitated solids to leaching by alkaline carbonate and EDTA model tank waste solutions also was tested (22).

The dissolver solution compositions reflected the additions of depleted uranium (for uranium fissile isotope dilution) and iron (as a neutron poison primarily for plutonium). These additions were required to achieve criticality safety for disposal of the NaOH-treated dissolver solution to the Hanford DSTs. The nominal adjusted dissolver solution composition was 22.8 g U/L, 13.7 g Fe/L, and 0.9 g Al/L in 1- to 4-M  $\text{HNO}_3$ . The simulated adjusted dissolver solutions also contained dissolved silica, oxalate, and fluoride based on the sludge dissolution processing. The NaOH-treated solutions are required to be pH  $\geq 12$  for tank farm corrosion acceptance, and the precipitated solids are required to have less than 10- $\mu\text{m}$  particle size for waste tank criticality safety.

The initial process parameter scoping tests showed that particle size, centered at  $\sim 2\text{--}3$  nm, easily met the  $<10$   $\mu\text{m}$  limit. Particle size was measured by a small angle x-ray scattering technique. The solid phases invariably included  $\text{Na}_2\text{U}_2\text{O}_7$  identified by XRD (volumetric size distribution maximum at  $\sim 3.5$  nm) and amorphous  $\text{Fe}(\text{OH})_3$ , frequently with goethite and sometimes hematite also present (volumetric maximum at  $\sim 1.4$  nm). Thus, the particle size distributions often were bimodal. Increasing temperature increased precipitate settling rates and decreased settled solids volume but mixing direction (acid $\leftrightarrow$ base) exerted little influence. Uranium showed amphoteric behavior and increased in solubility from about  $2 \times 10^{-6}$  M to  $2 \times 10^{-5}$  M as excess NaOH increased from 0.01 to 1 M, in agreement with recently published data (23).

Further parametric tests were conducted with simulated criticality-adjusted (i.e., iron and uranium added) 1-4 M  $\text{HNO}_3$  dissolver solutions. The solutions contained 37.5 g/L of total metal (U, Fe, Al) of varying uranium/iron/aluminum ratios. Dissolver solution composition had little effect on uranium, plutonium, and americium solution concentrations in the NaOH-treated slurry (Table V). Plutonium concentrations decreased slightly with increasing NaOH concentration and americium concentrations decreased about 10-fold. Plutonium (at  $\sim 8 \times 10^{-9}$  M) was about 1000-fold below its TRU waste limit, and americium [at about  $(6\text{--}100) \times 10^{-12}$  M] was 1200- to 20,000-fold below its TRU limit.

**Table V.** Effects of Adjusted Dissolver Solution Composition and pH on Supernate Concentration<sup>(a)</sup>

Weight Fraction U/Fe/Al	pH 12			1-M NaOH		
	[U], $\mu$ M	[Pu], nM	[Am], pM	[U], $\mu$ M	[Pu], nM	[Am], pM
1.0/0/0	2.0	12	100	20	2.2	9.7
0.9/0.1/0	3.1	8	100	18	6.0	12
0.5/0.5/0	2.0	6	66	18	6.3	4.7
0.1/0.9/0	2.4	15	64	18	5.4	6.5
0.5/0/0.5	3.0	12	70	32	8.6	6.4
0.33 / 0.33 / 0.33	4.2	6	50	34	7.6	4.3

(a) Total metal concentration in the dissolver solution is 37.5 g/L.

Though the supernatant alkaline solutions prepared from the simulated dissolver solutions were easily non-TRU, the uranium, plutonium, and americium in the precipitated solids were susceptible to leaching by alkaline carbonate. The leaching of plutonium and particularly americium decreased strongly in the presence of iron (Table VI). Similarly, americium (but not uranium or plutonium) was leached by alkaline EDTA solution (Table VII). Iron sharply decreased americium leaching by EDTA. Though both plutonium and americium coprecipitated with uranium in alkaline solution, their association with iron (hydr)oxides evidently is stronger. This commends the planned use of additional iron as a neutron poison for plutonium, though the precipitate is bulky and difficult to settle. The interaction of plutonium with iron in alkaline coprecipitation was recently demonstrated by Mössbauer spectroscopy (24). This study also showed that the Mössbauer spectrum of amorphous Fe(OH)<sub>3</sub> is the same as that of goethite, suggesting that amorphous Fe(OH)<sub>3</sub> consists of small x-ray-indifferent crystallites of goethite and is a precursor to this compound. In contrast, Mössbauer spectroscopy in the present tests showed that essentially no chemical interaction exists between uranium and iron. Thus criticality control, if required for uranium, must occur by isotopic dilution.

**Table VI.** Effects of Adjusted Dissolver Solution Composition and pH on Leaching by Simulated High Carbonate Tank Waste Solution<sup>(a)</sup>

Weight Fraction U/Fe/Al	pH 12			1-M NaOH		
	[U], mM	[Pu], $\mu$ M	[Am], nM	[U], mM	[Pu], $\mu$ M	[Am], nM
1.0/0/0	14	<b>6.7</b> <sup>(b)</sup>	<b>550</b>	2.1	1.5	75
0.9/0.1/0	12	4.2	9.6	2.0	2.0	1.1
0.5/0.5/0	7.8	1.8	4.2	1.4	1.8	1.1
0.1/0.9/0	1.6	3.2	1.0	0.39	1.1	0.15
0.5/0/0.5	4.2	<b>11</b>	25	12	2.6	<b>210</b>
0.33/0.33/0.33	3.8	3.0	1.7	24	6.0	2.1

(a) 1-M Na<sub>2</sub>CO<sub>3</sub>/5-M NaNO<sub>3</sub>.  
(b) Numbers in **bold** are above the 100-nCi/g limit for TRU waste.

**Table VII.** Effects of Adjusted Dissolver Solution Composition and pH on Leaching by Simulated High Complexant Tank Waste Solution<sup>(a)</sup>

Weight Fraction U/Fe/Al	pH 12			1 M NaOH		
	[U], $\mu$ M	[Pu], nM	[Am], nM	[U], $\mu$ M	[Pu], nM	[Am], nM
1.0/0/0	16	3	6.8	25	66	26
0.9/0.1/0	12	5	7.4	15	38	7.6
0.5/0.5/0	9.0	8	0.87	22	35	1.6
0.1/0.9/0	10	21	0.28	15	65	0.39
0.5/0/0.5	8.4	14	<b>120<sup>(b)</sup></b>	26	140	18
0.33/0.33/0.33	12	18	1.4	34	48	1.7

(a) 0.1-M EDTA/1-M NaOH/5-M NaNO<sub>3</sub>.  
 (b) Numbers in **bold** are above the 100-nCi/g limit for TRU waste.

### CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER TESTING

Transport and onsite storage are considered a less-expensive near-term means to address the disposition of sludge from D&D of the K Basins. However, chemical processing, as described in this paper, was demonstrated to be technically feasible. If chemical processing is to be pursued based on the present studies, additional testing is advised in three key areas:

- increasing uranium metal dissolution rates
- enhancing solid/liquid separation in the presence of gels
- investigating alternative neutron poisons that coprecipitate well with plutonium, carry americium, and form denser, more easily settled precipitates.

Tests to confirm the expected distribution of PCBs to the residual solids destined for ERDF disposal, not addressed in the present studies, also are required.

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