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Pacific Northwest National Laboratory
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Prepared for the U.S. Department of Energy
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Executive Summary

Five bench-scale tests (~50 ml each) were conducted in sealed, un-agitated reaction vessels using sludge samples collected from the K East Basin and particles/coupons of irradiated N Reactor fuel (also from the K Basins). These tests were designed to evaluate and understand the chemical changes that may be occurring under the hydrothermal conditions (e.g., 7 to 72 h at 185°C) of the Sludge Treatment Project (STP) corrosion process and the effects that any changes would have on sludge rheological properties. The two sludge formulations used in these tests were selected to represent nominal (vs. bounding) compositions of the two major sludge feed streams to the STP process. The scoping tests were not designed to evaluate engineering aspects of the process.

The hydrothermal treatment affected the chemical and physical properties of the sludge. In each test, significant uranium compound phase changes were identified, resulting from dehydration and chemical oxidation and reduction reactions. Physical properties of the sludge were significantly altered from their initial, as-settled, sludge values including, shear strength, settled density, weight percent water, and gas retention.

The high uranium content sludge (~70 wt% uranium) set up to form a very stiff solid that exhibited very high shear strength (120,000 to 170,000 Pa) after hydrothermal treatment at 185°C for 7 to 10 hours under static (unstirred) conditions. Shear strengths of untreated sludge range from about 270 to 8100 Pa. Also, the hydrothermal treatment reduced the water content in the settled sludge by about 20 wt%. The treated sludge was difficult to remove from the Teflon test vessels, with sludge firmly adhering to the Teflon vessel surfaces. The strength of the treated sludge was further evaluated by agitation in water. In a 600-ml beaker, with 400 ml water at ~30°C, the diameters of agglomerates were reduced by about 40 to 50% after 1 hour of agitation with a 5.08-cm (2-in.) diameter impeller rotated at a tip speed of 80 cm/s.

Further static tests with lower uranium-content sludges (~16 wt% uranium) run 72 h at 185°C produced softer solids with 9,000 to 16,000 Pa shear strengths. While some sludge adhered to the Teflon liner, it was not tenaciously bound. The agglomerates from these tests were relatively weak and, in some cases, were disintegrated with a gentle stream of water. The water content in the settled sludge was not significantly affected by the hydrothermal treatment.

Chemical phase alteration, observed by X-ray diffraction, scanning electron microscopy, and energy dispersive spectrometry, gave evidence that solids dissolution followed by precipitation was responsible for the increased strengths of the sludge products. The presence of organic ion exchange resin (OIER) and polymer flocculent (constituents known to be in K Basin sludge) in the lower uranium-content sludge did not appear to have a significant impact on the physical behavior of the post-treated sludge.

Four irradiated uranium metal fuel coupons were included in one test, and no residual uranium metal was found after hydrothermal treatment. This observation increases the confidence that uranium metal will react in accordance with the design basis rate laws at STP process corrosion conditions.

Summary and Key Findings

Problem Statement and Objectives

Irradiated metallic uranium fuel from the N Reactor was stored in two water-filled concrete pools, 105-K East Basin (KE Basin) and 105-K West Basin (KW Basin), at the United States Department of Energy's (U. S. DOE) Hanford Site. Radioactive sludges from the storage and corrosion of this fuel are present in the K Basins. The sludge is a mix of fuel corrosion products (including metallic uranium and metal oxidation products), iron and aluminum hydroxides/oxides, concrete grit, sand, infiltrated soil, and operational and biological debris. By definition, within the K Basin Closure (KBC) Project, sludge encompasses any material from the K Basins that will pass through a screen with 0.25 inch (6350 μm) openings. Because of its high concentrations of transuranics and high radioactivity, the K Basin sludge is destined for disposal as remote-handled transuranic waste at the Waste Isolation Pilot Plant (WIPP). To meet shipping requirements and WIPP waste acceptance criteria, the uranium metal, which reacts with water to form hydrogen gas, must be oxidized or removed.

The K Basins sludge is being managed as three distinct sludge streams: Container sludge, Settler Tank (Settler) sludge, and Knock-out Pot (KOP) sludge. The majority of the sludge, Container sludge (~41 m^3) is being consolidated in the basins into large rectangular and box-shaped containers, typically holding 8 to 25 m^3 of sludge. Container sludge consists of sludge from the KE and KW Basin floors and pits, along with smaller volumes of sludge from the KE fuel storage canisters and sludge from fuel washing. All KE and KW fuel (and fuel storage canisters) were washed in the Primary Clean Machine (PCM) located in the KW Basin. In addition to fuel washing, canister cleaning and scrap sorting operations occurred in the KW Basin. Sludge generated from these operations was vacuumed into the Integrated Water Treatment System (IWTS). In the IWTS, pieces of material larger than 0.25 in. are removed in strainers (i.e., because of its particle size, strainer material is not considered sludge). Next, larger sludge particles (~500 to 600 μm up to 6350 μm) are retained in Knock-out pots (KOPs), which include internal or external filters (total KOP sludge volume, ~ 0.26 m^3). After passing through the KOPs, the IWTS sludge stream enters the settler tanks (ten 20-in. diameter, 16-ft long tanks, operated in parallel), where the finer particulate sludge (<500/600 μm) is allowed to settle (total Settler sludge volume, ~5.4 m^3).

The Sludge Treatment Project (STP), managed for the U. S. DOE by Fluor Hanford (FH), was created to design and operate a process to eliminate uranium metal from the sludge prior to packaging for WIPP. The STP will use high temperature liquid water to accelerate the reaction, produce uranium dioxide from the uranium metal, and safely discharge the hydrogen. Under nominal process conditions, the sludge will be heated in pressurized water at 185°C for as long as 72 hours to assure the complete reaction (corrosion) of up to 0.25-inch diameter uranium metal pieces. Prior tests with uranium metal-bearing K Basin sludge materials have been conducted at less than 100°C; however, no data are available on the behavior of the K Basin sludge under the proposed process conditions. An independent review panel identified several concerns with the STP corrosion process including retrieval, transfer, and sludge corrosion vessel operations (Heywood 2006).

A number of the panel concerns could be investigated by laboratory chemistry testing and through more complex prototype system testing. Concerns and data gaps were prioritized and used to formulate specific test objectives and a testing approach through collaborations between PNNL and FH engineers and scientists. The objectives were documented in a detailed test plan (Schmidt et al. 2006). The key objectives identified for the current testing are:

- Evaluate the changes (if any) in the chemical and rheological behavior of K Basin sludge resulting from the proposed 185°C hydrothermal processing using a simple test system (i.e., will chemical changes significantly impact the physical behavior of sludge?).
- Evaluate the impacts of organic flocculating agent (added to sludge during retrieval at the K Basins) and organic ion exchange resin (present at high concentration within some KE floor sludge) on sludge behavior during hydrothermal processing.
- Obtain general validation of the design basis rate equation for the reaction of uranium metal in water in the presence of other sludge components and at the proposed hydrothermal processing temperature (i.e., will other sludge constituents suppress the expected reaction rate?).

These tests were designed to evaluate and understand the chemical changes that may be occurring under the hydrothermal conditions of the STP corrosion process and the effects that any changes would have on sludge rheological properties. Because chemistry is not size dependant, the testing was conducted with relatively small sludge volumes (e.g., 50 ml). The current tests were not designed to test engineering aspects of the process, which are typically performed at a pilot scale and require larger sample volumes and more complex test apparatus. To address the data gaps and specific concerns, bench-scale testing with actual K Basin sludge samples and particles/coupons of irradiated N Reactor fuel were conducted by the Pacific Northwest National Laboratory (PNNL) in November and December 2006 under contract to FH/STP. Results from this testing are summarized in this report.

Approach and Specific Test Objectives

Five tests were conducted in sealed, un-agitated, reaction vessels using existing fragments of N Reactor fuel from K Basins and samples and sample mixtures of KE Canister sludge and KE Floor sludge. The tests were performed using two sludge formulations created from samples retrieved in FY1999 from the K Basins. The first formulation was a uranium-rich KE Basin Canister sludge of composition similar to that expected for Settler sludge. The second sludge formulation was a composite of KE Basin floor, pit, and canister sludges with a composition similar to nominal Container sludge. Because of the high radioactivity arising from the irradiated N Reactor fuel and K Basins sludge, the laboratory testing was performed in a shielded hot cell within the 325 Building. Sludge samples used were taken from selected samples archived from past characterization sampling campaigns performed by the KBC Project and stored at the hot cells. Before initiating the testing with radioactive materials, several tests were conducted with non-radioactive simulated K Basin sludges to evaluate the proposed test apparatus and protocols. For the bench-scale testing, ~125-ml capacity Teflon-lined 304 stainless steel vessels (Parr Model 4748) were used. The Parr Model 4748 test apparatus is designed as an isolated, closed reaction system, and is equipped with the safety feature of an overpressure rupture disk. After loading with predetermined quantities of sludge, fuel, and water, the contents of each Teflon liner were blanketed with nitrogen gas before closing. The vessels were loaded into a convection oven and heated at controlled rates and durations to match those of the STP corrosion process, or to satisfy specific test objectives. Temperature was monitored continuously for each of the test vessels via a thermocouple mounted on the outside vessel wall.

After the hydrothermal treatment, detailed examinations, measurements, and analyses were performed, including measurements of mass, volume, weight percent (%) water, and unconfined compressive strengths (to determine shear strength) of the product sludge. As appropriate, sieving was performed (for evidence of agglomeration) and the durability/erodibility of agglomerates were evaluated by mixing the agglomerates in water (at ~30°C) at various mixing rates. X-ray diffraction (XRD) analyses and scanning electron microscopy were performed on the initial and post-treated sludge to identify changes in crystalline chemical phases and particle shape. Table S.1 and the following describe specific parameters tested.

Test 1: Fine KE Canister Sludge + Fine Uranium Metal Fuel Particles

Test 1 examined the behavior of a sludge estimated to be typical of K Basin Settler sludge composition. The corresponding primary focus of Test 1 was to understand the product rheology after heating finely particulate sludge having high uranium oxide content with fine particles of irradiated metallic uranium fuel. For this test, a composite of fine (<250 μm) KE Canister sludge was mixed with fine (<500 μm but >250 μm) uranium fuel particles from irradiated N Reactor fuel. Because the Settler tanks contain only fine particulate (less than ~500-600 μm), the baseline STP process hold time is 6.8 h at 185°C. Consequently, the corresponding test hold time at 185°C was 7 h.

The KE Canister sludge used in this test (sample KC-2/3 M250) emulates the expected properties of the Settler tank sludge (~75% of settler tank sludge is derived from processing KE fuel/canisters). Sample KC-2/3 sludge is a composite of sludge collected from 11 fuel storage canister locations in the KE Basin. The KC-2/3 whole sludge sample (all particulate material less than ¼-inch, 6350 μm) was sieved in 1999 at 250 μm to provide a “plus (P250)” and “minus (M250)” fraction and the M250 fraction was used in Test 1. The KC-2/3 M250 sludge is 68.3 wt% uranium on a dry weight basis.

Test 2: Fine KE Canister Sludge Composite + Uranium Metal Coupons

Test 2 was designed to provide rheological information on high uranium content sludge held at the STP process temperature for a longer period of time (compared to Test 1) and to provide confirmatory information on the reaction rate of uranium metal immersed in the sludge at 185°C. For this test, four uranium metal coupons from irradiated N Reactor fuel were immersed in finely particulate KE Canister sludge (KC-2/3 M250). Before the test, the axial dimensions (height, length, width less than 6350 μm, but greater than 4000 μm) and weights of the coupons were measured. Based on the coupon dimensions and the KBC Project design Databook (Schmidt 2006) rate equation, the time at temperature (185°C) to corrode ~80 wt% of the coupons was calculated (10 h) and used to establish the target test run time. For this test, the reactor vessel was placed in the oven after the oven had first been heated to 185°C to provide a simple time/temperature profile for the uranium metal corrosion rate evaluation.

Test 3: KE Container Sludge + Flocculent + Fuel Particles

This test was designed to examine the effects of flocculent and uranium metal fuel particles on the physical behavior and rheology of K Basin Container sludge in the STP corrosion process. During sludge retrieval and containerization in the KE Basin and the subsequent transfer and containerization of sludge in the KW Basin containers, it is anticipated that flocculent (specifically Optimer 7194 Plus, Nalco) will be added to all Container sludge. The use of flocculent will add approximately 1,300 μg (0.0013 g) of total organic carbon (TOC) per cm^3 of settled sludge, or ~5.5 ml of neat flocculent per liter of sludge. The flocculent addition will almost double the TOC concentration of KE Floor and Weasel Pit sludge, whose average TOC concentration is ~1,400 $\mu g/cm^3$ before flocculent addition.

This test also examined the effects of uranium metal corrosion on Container sludge rheology. In prior testing at 60°C for 1100 hours followed by ~70 h at 80°C and ~48 h at 95°C, a similar mixture of KE Floor sludge and uranium metal particles, but without flocculent, was found to be difficult to remove from its stainless steel reaction vessel and found to adhere to the vessel bottom and walls [Test SNF + Can 60L in Schmidt et al. (2003)].

The KE Container sludge composite was formulated from archived sludge samples to resemble a 93/7 volume percent mixture of (93 vol%) KE Floor and (7 vol%) KE Canister sludge. The composite contains moderate concentrations of iron (20 wt%), aluminum (8 wt%), and uranium (16 wt%). The uranium metal particle sizes ranged from 500 to 1000 µm. This range is consistent with the size range of fuel particles previously determined to be present in typical KE Canister sludge during gas generation testing (Delegard et al. 2000).

Test 4: KE Container Sludge + Flocculent

The primary objective of Test 4 was to examine the effects of the STP process conditions and flocculent on the sludge product rheology. This test is similar to Test 3, with the exception that it did not include added uranium metal particles. It is likely that a significant fraction of the Container sludge batches processed through the STP corrosion vessel will have very little uranium metal and thus will be similar to the Test 4 composition. However, all Container sludge is expected to contain some flocculent. Therefore, Test 4 serves, in part, as a control test for comparing and interpreting the results of Test 3 and Test 5.

Test 5: KE Container Sludge + Organic Ion Exchange Resin (OIER) Beads

Test 5 was conducted to examine the propensity for the OIER beads found in some of the sludge to soften and potentially contribute to sludge agglomeration at STP process conditions. OIER from spilled ion exchange material is a significant component of the floor sludge from the KE Basin. The OIER in the K Basins, Purolite NRW-37, is a mixed bed material consisting of strong acid cation exchange resin and strong base anion exchange resin. Both resin types are composed of polystyrene divinylbenzene polymers; the cation resin has sulfonate and the anion resin has quaternary ammonium functional groups. Approximately 15 vol% of the sludge material in this test consisted of OIER collected as a sludge sample from the KE Basin.

Key Findings

The key results and test matrix are tabulated in Table S.1 and are summarized below.

General Findings

The hydrothermal treatment of sludge at 185°C, from 7 to 72 hours, significantly changed the chemical and physical properties of the sludge. In each test, a number of uranium compound phase changes were identified, resulting from dehydration and chemical oxidation and reduction reactions. Physical properties of the sludge were significantly altered from their initial, as-settled, sludge values including shear strength, settled density, weight percent water, and gas retention.

The presence of organic ion exchange resin and flocculent in the Container sludge composite did not appear to have a significant impact on the physical behavior of the post-treated sludge. In both the testing with non-radioactive simulant and with actual K Basin sludge, the OIER beads did not physically interact appreciably with sludge or with other OIER beads.

Under test conditions (time, temperature, and U metal coupon dimensions), ~80% of fuel fragment mass in Test 2 was expected to react based on the updated rate equation of the KBC Project Sludge Databook (Schmidt 2006), and the expected remaining metal should have been recoverable on a 2000-µm sieve. However, no residual uranium metal was found on either 2000- or 1000-µm sieves. One of the pieces of bare cladding was recovered. These findings increase the confidence that uranium metal will react in accordance with the rate laws at STP process corrosion conditions.

Specific Findings

- The sludge set up to form a very stiff solid that exhibited very high shear strength (120,000 to 170,000 Pa) after hydrothermal treatment at 185°C for 7 to 10 hours in the static tests designed to mimic Settler sludge (Test 1 and 2). The treated sludge was difficult to remove from the test vessels, with some sludge firmly adhering to the Teflon vessel surfaces. Also, the water content in the settled sludge decreased by about 20%. Significant uranium phase changes were identified. Similar physical changes in the Settler sludge (resulting from the chemistry changes) can be expected in the STP corrosion process in quiescent locations where sludge can settle, or if agitation is lost.
- The strength of the agglomerates (small sludge concretions) from Tests 1 and 2 also were evaluated by mixing. In a 600-ml beaker, with 400 ml water (at ~30°C), the diameters (1 – 2 cm) of agglomerates were reduced by about 40 to 50% after 1 hour of agitation with a 2-in. diameter impeller rotated at a tip speed of 80 cm/s.
- Products from static tests with an actual Container sludge composite (Tests 3, 4, and 5) produced soft solids of increased shear strengths (9,000 to 16,000 Pa) after hydrothermal treatment at 185°C for 72 hours. The Container sludge sample was a composite of KE sludge samples that had previously measured shear strengths ranging from 270 to 8,100 Pa. While some sludge adhered to the Teflon liner, it was not tenaciously bound. The water content in the settled sludge was not significantly affected by the hydrothermal treatment.
- The agglomerates from Tests 3 through 5 were relatively weak, and in some cases, were disintegrated with a gentle stream of water.
- In Test 1, 2, and 4, the sludge volumetrically expanded due to gas retention (gas voids accounted for ~25% of the expanded sludge volume). Tests 1 and 2 contained uranium metal, and the gas was most likely hydrogen. In Test 4, which did not contain added uranium metal, the gas was most likely carbon dioxide, based on gas analyses performed after prior hydrothermal treatment of the constituent sludges at lower temperatures (Delegard et al. 2000).

Summary of Underlying Chemistry

Information on the chemical reactions occurring during STP processing was determined by XRD analyses of the initial and product sludges and analyses obtained in 1999 from the same or related sludge materials. The non-uranium phase changes occurring by STP processing in simulated sludge also were studied by

XRD. The following chemistry findings, derived from the XRD data, from inferences from prior hydrothermal testing of K Basin sludges, and from other test observations, allow better understanding of the physical changes occurring during sludge processing by the STP process.

- The uranium metal from N Reactor fuel particles corrodes to form uraninite ($UO_{2.x}$) phases by 7 to 72 hours of 185°C STP processing.
- Simulated sludges containing aluminum hydroxide [$Al(OH)_3$, gibbsite] and ferric oxyhydroxide [$Fe_5O_7(OH)\cdot 4H_2O$, ferrihydrite] dehydrate to form boehmite, AlOOH, and hematite, Fe_2O_3, respectively, plus free water after 72-hour hydrothermal treatment at 185°C.

  $$Al(OH)_3 \rightarrow AlOOH + H_2O$$

  $$2\ Fe_5O_7(OH)\cdot 4H_2O \rightarrow 5\ Fe_2O_3 + 9\ H_2O$$

  The boehmite product was observed to agglomerate with itself but not with the hematite product. The hematite product remained as disperse as the starting ferrihydrite and did not agglomerate.
- Metaschoepite, $UO_3\cdot 2H_2O$, the dominant uranium phase found in the starting K Basin sludge, dehydrates to form “dehydrated schoepite” phases including $UO_3\cdot 0.8H_2O$ and $UO_3\cdot H_2O$ after 7-10 hours at 185°C STP process conditions. This reaction, which is irreversible (i.e., the dehydrated schoepite will not re-hydrate to form metaschoepite), has the potential to account for much of the change in the sludge free water content observed in Tests 1 and 2.
- Metaschoepite reacted with silica (from infiltrated soils or concrete) to form the uranium silicate soddyite [$(UO_2)_2SiO_4\cdot 2H_2O$] in Tests 1 and 2. This is also a dehydration reaction.

  $$2\ UO_3\cdot 2H_2O + SiO_2 \rightarrow (UO_2)_2SiO_4\cdot 2H_2O + 2\ H_2O$$
- Metaschoepite, becquerelite [$Ca(UO_2)_6O_4(OH)_6(H_2O)_8$], and a calcium uranium oxide hydrate ($CaU_3O_{10}\cdot 4H_2O$) are the only crystalline uranium phases found in the KE Container sludge prepared for the present testing and all are U(VI) compounds. In Tests 4 and 5, conducted without added uranium metal, chemical reduction of the U(VI) compounds occurred to form uraninite ($UO_{2.x}$), ianthinite ($[U_2(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$), and uranium octoxide (U_3O_8) – all three with uranium oxidation states lower than (VI). The chemical reductants responsible for the U(VI) reduction likely were the flocculating agent and OIER, respectively. For OIER, the active reductant may have been sulfite.
- The observed chemical reactions to form dehydrated schoepite (dehydration), soddyite (mineralization and dehydration) in Tests 1 and 2, and uraninite, ianthinite, and U_3O_8 (all chemical reductions) in Tests 3, 4, and 5 are observed in the formation of uranium minerals in other laboratory tests and in nature under STP-relevant heat and pressure conditions.
- Because most of the described chemical reactions involve significant structural change, they must occur by dissolution and reprecipitation and not merely by solid phase rearrangement. Solid phase rearrangement reactions are not excluded, however.
- Because the precipitation reactions are more likely to occur on existing sludge solid particle surfaces, the precipitating solids can act to bind the particles by cementation. Cementation reactions also are observed in nature in the formation of sedimentary minerals such as sandstone. Cementation is postulated to be the phenomenon explaining the observed higher strength of the STP process sludge products compared with the starting sludges, particularly for Tests 1 and 2.

- Gaseous products in STP processing include hydrogen from the reaction of uranium metal with water and carbon dioxide (CO_2) from the reactions of carbonate minerals (e.g., calcite, $CaCO_3$) present in the sludge. These reactions likely are responsible for generating the gas voids observed in the product sludge.
- Scanning electron microscopy (SEM) and limited energy dispersive spectrometry (EDS) of the initial sludge and the sludge following the STP processing support the succession of phases observed by XRD. Furthermore, moderate to high uranium concentrations were observed by EDS on the surfaces of nearly all interrogated particles. Iron was also found to be broadly distributed on particle surfaces. EDS also provided evidence for the partial decomposition of OIER to release sulfur species (likely sulfite).

Comparison of Sludge Treatment Project Process Conditions and Laboratory Testing Conditions

It is useful to compare the conditions proposed for operation of the STP corrosion vessel with those used in the present bench-scale tests. The tests were designed to evaluate and understand the chemical changes that may be occurring under the hydrothermal conditions of the STP corrosion process and the effects that any changes would have on sludge rheological properties. Efforts were made to simulate in the tests, to the extent practical, the full-scale plant conditions. However, certain conditions could not be matched. Comparisons between the process and the test conditions, including a discussion on how differences may impact the use and interpretation of the test results, are provided in Table S.2.

Table S.1. Summary of Bench Scale Matrix and Test Results

Test ID	**Test Matrix**			**Changes with Hydrothermal Treatment**				**Post-Test Properties**	
	Sludge Type Simulated(a)	**Test Material Description**	**Time at 185°C, h**	**Observations**	**Weight % H_2O, settled sludge(b)**		**Key Phase Changes(c) [crystalline phases identified by X-ray Diffraction (XRD) Analyses]**	**Shear(d) Strength, Pa**	**Gas(e) Retention, Vol% in Product**
					Start	**End**			
Cold Tests (Non-Radioactive Surrogates)									
C-1	Container	Blow Sand + Organic Ion Exchange Resin	72	No agglomeration Sludge readily poured	NM	NM	NM	low	NM
C-2	Container	Blow Sand + $Al(OH)_3$ + $Fe_5O_7(OH)\cdot 4H_2O$ + Flocculent	72	Stiff solid Evidence of layering No wall adhesion	NM	NM	Gibbsite, $Al(OH)_3$ → boehmite, AlOOH $Fe_5O_7(OH)\cdot 4H_2O$ → hematite, Fe_2O_3	36,000 ± 5,000	NM
T-1	Component	$Al(OH)_3$	72	Agglomeration	NM	NM	Gibbsite → boehmite	NM	NM
T-2	Component	$Fe_5O_7(OH)\cdot 4H_2O$	72	No agglomeration	NM	NM	$Fe_5O_7(OH)\cdot 4H_2O$ → hematite	NM	NM
T-3	Component	$Al(OH)_3$ + $Fe_5O_7(OH)\cdot 4H_2O$	72	White agglomerates [$Al(OH)_3$]	NM	NM	Gibbsite → boehmite Ferrihydrite, $Fe_5O_7(OH)\cdot 4H_2O$ → hematite (Fe_2O_3)	NM	NM
Tests with Actual K Basin Sludge and Irradiated N Reactor Fuel									
1	Settler	Fine KE Canister Sludge Composite + U Metal Fuel Particles	7	Very stiff solid Material adhered to vessel (Teflon) wall	24	19 (16)	U metal → uraninite $UO_{2.x}$ Metaschoepite, $UO_3\cdot 2H_2O$ → uranium oxide hydrate [$UO_3\cdot 0.8H_2O$ + $UO_3\cdot H_2O$] and soddyite [$(UO_2)_2SiO_4\cdot 2H_2O$]	170,000	28
2	Settler	Fine KE Canister Sludge Composite + U Metal Fuel Coupons	10	Very stiff solid Material adhered to vessel (Teflon) wall	24	21		120,000	25
3	Container	KE Floor, Pit, & Can Composite + Flocculent + U Metal Fuel Particles	72	Soft solid Mild agglomeration	48	45 (51)	U metal → uraninite (Test 3) Metaschoepite → uranium oxide hydrate (Test 3); uraninite, uranium octoxide, U_3O_8, and ianthinite, $[U_2(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$ (Test 4 and 5)	16,000	0
4	Container	KE Floor, Pit, & Can Composite + Flocculent	72	Very soft solid Mild agglomeration	52	50 (53)		9,000	23
5	Container	KE Floor, Pit, & Can Composite + Organic Ion Exchange Resin Sludge	72	Soft solid Mild agglomeration	45	50 (49)		13,000	5

(a) Container = Floor and Pit sludges containerized at the KE Basin; Settler = less than 600-μm sludge captured in Settler tanks during fuel washing at the KW Basin.
(b) Weight percent water in product sludge at end of test was determined by either bulk material balance or by drying a subsample at 105°C (value shown in parenthesis).
(c) Iron and aluminum compounds, known to be in the sludge at high concentrations, were not detectible by XRD and are assumed to be amorphous.
(d) Values determine via unconfined compressive strengths measurements using a soil penetrometer (literature reported measurement variability is 28%). Shear strength of untreated sludges range from 270 to 8100 Pa (measure by shear vane rheometer).
(e) Gas retention = volume of retained gas/volume of expanded sludge. NM = not measured.

Table S.2. Comparison of STP Corrosion Process and Bench-Scale Tests

Parameter	STP Corrosion Vessel	Bench-Scale Test	Discussion of Comparison and Impact on Data Use
Agitation	Continuous	None	Agitation should affect physical agglomeration in agitated zones, but will not affect chemistry that results in formation of different compounds. Also, the corrosion vessel may contain un-agitated zones, such as pipes that will contain sludge at the process conditions, and may include a semi-quiescent zone at the bottom of the vessel below the impeller and nitrogen sparge ring. During a loss of agitator event, the entire vessel contents will be un-agitated or only moderately mixed, depending upon the status of the nitrogen sparge system.
Material Balance	N_2-sparged and continuously vented with significant water vapor removal.	Closed System. [Before sealing, test vessel head space was purged with nitrogen.]	Nitrogen gas would not be expected to affect the chemistry. By being conducted as closed system tests, detailed material balances were possible, which provides data on changes in settled density, water content, and potential gas holdup in the solids.
Vessel Wall Temperature	Above 185°C. Sufficient to evaporate water and maintain contents at 185°C.	Outside the test pressure vessels, temps were controlled to 185°C; temp inside the test vessel liners ≤185°C.	Heating of the corrosion vessel will be via heaters on the outside vessel wall, at temperatures in excess of the slurry temperature. This likely will increase the potential for scale formation on the heated surfaces of the STP corrosion vessel.
Vessel Wall Material	Stainless steel	Teflon	In the bench tests, the sludge was in direct contact with Teflon liners. Sludge may adhere more strongly to the actual corrosion vessel stainless steel walls than to the Teflon used in the tests.
Pressure	225 psig	Not measured; theoretically, up to 560 psig (assuming 100% U metal fuel reacted, all H_2 released to headspace and no diffusion from vessel).	Two of the tests did not contain additional uranium metal and therefore pressure was close to that of STP process. At the conclusion of all five tests, the Teflon liners were found to be under vacuum. If the H_2 had remained in the vessels, the contents should have been under pressure. Based on these post-test observations and data on H_2 permeability through Teflon, it appears likely that much of the generated H_2 diffused from the Teflon vessels or reacted with sludge constituents, resulting in test pressures near STP process conditions (i.e., test pressures always high enough to avoid boiling).
Gas Composition	162 psig H_2O, <63 psig N_2, >0 psig H_2	162 psig H_2O, 22 psig N_2, up to 376 psig H_2	

Table S.2. Comparison of STP Corrosion Process and Bench-Scale Tests (cont'd)

Parameter	STP Corrosion Vessel	Bench-Scale Test	Discussion of Comparison and Impact on Data Use
K Basins Settler Tank Sludge (Tests 1 and 2)			
Material Processed	Actual K Basin Settler Tank Sludge	KE Canister Sludge + irradiated metallic uranium fuel typical of that stored in K Basins	For the Settler sludge tests, the test material was a KE Canister sludge composite from 11 locations in KE Basin. Approximately 75% of sludge in Settler tanks is expected to have been derived from washing KE Fuel in KE Canisters. U metal concentrations in tests were ~4 wt% (settled sludge basis). In comparison, the U metal content in Design and Safety Settler sludge are: 2.1 and 5 wt% respectively.
Solids Volume (including all water and sludge in vessel)	Initial: 5.9% End of Batch: 9.0%	Constant: 27-28% [Note: Solids content for as-settled Design Basis KE Canister sludge and Settler sludge are 25% and 35%, respectively.]	Solids concentration in test was higher than STP process target to increase the test sample size. However, both the STP corrosion process and the tests include free water above the settled sludge at the start and end of the testing. Tests represent the expected chemical and physical behavior of sludge that is allowed to settle (quiescent zones in corrosion vessel/piping). With the higher water content, in well agitated zones in the corrosion vessel, physical agglomeration and cementation are expected to be minimized.
Temperature Profile	28 h ramp to 185°C 6.8 h hold at 185°C	**Test 1:** ~34 h ramp to 185°C, 7 h hold at 185°C **Test 2:** ~4 h ramp to 185°C 10 h hold at 185°C	Temperature profile in Test 1 was a reasonable match with STP process. Ramp time in Test 2 was decreased and hold time increased by several hours to meet specific test objectives for uranium corrosion rate confirmation.
K Basins Container Sludge (Test 3, 4, and 5)			
Material Processed	Batches of actual K Basin Container Sludge	Volume-weighted nominal composite of KE sludge samples representative of KE Container sludge	For the Container sludge tests, a volume-weighted composite was prepared from KE Weasel pit, main basin floor, and fuel storage canister sludge samples. The material in this composite came from a total of 20 sample locations in KE Basin.
Solids Volume, (including all water and sludge in vessel)	Initial, 10.1% End of Batch: 20%	Constant: 23-28% [Note: Solids content for as-settled Design Basis KE Floor and Canister sludge is 25%.]	While tests were targeted to maintain solids content at 20%, higher values (23 to 28%) were used based on the slightly higher than expected solids contents found in the starting sludge samples. With the exception of the end-state in Test 4, the tests included free water above the settled sludge at the start and end of the testing, and represent the expected physical and chemical behavior of sludge that is allowed to settle (quiescent zones in corrosion vessel/piping). For Test 4, no free water was visible above the sludge at the end of the test and Test 4 exhibited the lowest shear strength (i.e., could be biased low). In well agitated zones in the corrosion vessel, with their higher water content, physical agglomeration and cementation are expected to be minimized.
Temperature Profile	28 h ramp to 185°C 72 h hold at 185°C	**Test 3, 4 and 5:** ~26 h ramp to 185°C, 72 h hold at 185°C	Temperature profiles in tests aligned with STP process targets.

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>
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Terms and Acronyms

Terms and acronyms used within this report are described below.

Term	Explanation
CERCLA	Comprehensive Environmental Release Compensation and Liability Act
CVD	Cold Vacuum Drying building
DI water	distilled and deionized water
DQO	Data Quality Objectives
DSC/TGA	differential scanning calorimeter / thermogravimetric analysis
EDS	Energy Dispersive Spectroscopy
FH	Fluor Hanford
ID	Identification
IXM	Ion Exchange Module
KBC	K Basin Closure
KE Basin	K East Basin
KW Basin	K West Basin
OIER	organic ion exchange resin
PCM	Primary Clean Machine
PDF #	powder diffraction file number
PNNL	Pacific Northwest National Laboratory
RPM	revolutions per minute
RTP	room temperature and pressure
SAL	Shielded Analytical Laboratory
SEM	Scanning Electron Microscopy
STP	Sludge Treatment Project
TOC	total organic carbon
UCS	unconfined compressive strength
U.S. DOE	United States Department of Energy
WIPP	Waste Isolation Pilot Plant
XRD	X-ray diffraction or diffractometry

1.0 Introduction

Radioactive sludges from the storage and degradation (e.g., corrosion) of irradiated fuel from the N Reactor are present in the K East (KE) and K West (KW) Reactor fuel storage basins (K Basins). Sludge is a mix of fuel element corrosion products (including metallic uranium and fission products), iron and aluminum oxides, concrete grit, sand, dirt, and operational and biological debris. Because of its high plutonium and americium concentrations and presence of high activity fission products, the K Basin sludge is destined for disposal as remote-handled transuranic waste at the Waste Isolation Pilot Plant (WIPP). The K Basin sludge also is known to contain particles of irradiated uranium metal. The particulate uranium metal arose from fracturing of metallic fuel during discharge from the reactor and corrosion during subsequent underwater storage. Per the KBC Project, the definition of K Basin "sludge" is any material or particles that can pass through screens with openings of 0.25 in. (6350 μm).

The K Basins sludge is being managed as three distinct sludge streams: Container sludge, Settler Tank (Settler) sludge, and Knock-out Pot (KOP) sludge. The majority of the sludge, Container sludge (~41 m^3) is being consolidated in the basins into large rectangular and box-shaped containers, typically holding 8 to 25 m^3 of sludge. Container sludge consists of sludge from the KE and KW Basin floors and pits, along with smaller volumes of sludge from the KE fuel storage canisters and sludge from fuel washing. All KE and KW fuel (and fuel storage canisters) were washed in the Primary Clean Machine (PCM) located in the KW Basin. In addition to fuel washing, canister cleaning and scrap sorting operations occurred in the KW Basin. Sludge generated from these operations was vacuumed into the Integrated Water Treatment System (IWTS). In the IWTS, pieces of material larger than 0.25 in. are removed in strainers (i.e., because of its particle size, strainer material is not considered sludge). Next, larger sludge particles (~500 to 600 μm up to 6350 μm) are retained in Knock-out pots (KOPs), which include internal or external filters (total KOP sludge volume, ~ 0.26 m^3). After passing through the KOPs, the IWTS sludge stream enters the settler tanks (ten 20-in. diameter, 16-ft long tanks, operated in parallel), where the finer particulate sludge (<500/600 μm) is allowed to settle (total Settler sludge volume, ~5.4 m^3).

Before the sludge can be disposed to the WIPP, the uranium metal, which reacts with water to form uranium dioxide and hydrogen gas, first must be processed such that essentially no uranium metal remains in the sludge. This processing thus assures that hydrogen generation from chemical reaction will be eliminated (or below relevant criteria) in the waste package. One of the objectives of the Sludge Treatment Project (STP) is to design and operate a process to eliminate uranium metal by using high temperature liquid water to accelerate the reaction and produce uranium dioxide and hydrogen. Under nominal STP process conditions, the Container and KOP sludge streams will be heated in water at 185°C for as long as 72 hours to assure the complete reaction of up to 0.25-inch diameter uranium metal pieces. Settler sludge, which only includes uranium metal particles less than or equal to 600 μm, will be heated for about 7 hours at 185°C. Prior tests with uranium metal-bearing K Basin sludge materials have been conducted at less than 100°C; however, no data are available on the behavior of the K Basin sludge under the proposed 185°C process conditions.

Within the STP process equipment, sludge will be treated in a stainless steel vessel (corrosion vessel), about 13 ft high and 7.5 ft in diameter, with a total volume of 3670 gal (maximum operating capacity 3240 gal). In the current design the vessel is continuously mechanically agitated with multiple agitator blades on a single shaft. The agitator will have at least two speeds: a low speed to suspend sludge and enhance heat transfer during heating and corrosion, and a high speed to provide a more uniform blend when transferring corroded sludge out of the vessel. The vessel will also be continuously sparged with nitrogen gas via a sintered metal sparge ring near the vessel bottom. The nitrogen sparge aids in evaporation and cooling, but is not intended to provide significant agitation (nominal sparge rates are low).[a]

A series of electrical resistance heating elements (pads) are attached to the lower dished head and about half-way up the tank cylinder wall of the corrosion vessel to provide the required heat for reaching process temperatures for sludge corrosion. In the corrosion process, sludge is heated step-wise, and pressure is adjusted, over a 28-h period, to the ultimate target corrosion conditions (185°C, 225 psig). As water is removed (evaporation), the top heating pads will be turned off (or not used for smaller batches) to prevent overheating the vessel wall. As noted above, the duration of the corrosion period at 185°C is based on the sludge type and established uranium metal corrosion rate equation. Additionally, the endpoint is also confirmed by monitoring the hydrogen concentration in the corrosion vessel offgas. At the end of a corrosion cycle, the heaters are de-energized, mechanical agitation is continued, and the nitrogen purge rate is increased to accelerate cooling. After sufficient cooling, the nitrogen sparge rate is reduced, and the mechanical agitator is operated at high speed for a period of time to homogenize the sludge. Next, the vessel will be slightly pressurized, and treated sludge will be discharged in small batches through a 1½ inch line via a transfer pump to the assay vessel (working volume under 40 gal). Each corrosion vessel batch will result in multiple assay vessel batches. After each transfer, the discharge line will be flushed with water to clear the line of solids. Between corrosion vessel batches, a heel of sludge (256 gal, minimum low-level operating volume) will remain within the corrosion vessel.

An independent review panel identified several concerns with the STP corrosion process in areas of retrieval and transfer, sludge corrosion vessel operations, sludge assay and packaging, safety, and instrumentation (Heywood 2006). Within the sludge corrosion vessel topic, the panel noted in the excerpt below that the smaller scale demonstrations normally undertaken to validate new processes had not been performed for the proposed STP process (emphasis added).

"Significant experimental data exist describing the corrosion reaction of uranium metal with water. Therefore, while questions may exist on the degree of conservatism required to ensure sufficient uranium metal has corroded to comply with grout product criteria, it is clear that the uranium corrosion reaction can be relied upon to reduce the sludge uranium metal content. ***A larger concern to the review team was the potential impact of corrosion vessel operating conditions on the sludge physical properties and lack of at least scoping experimental studies to investigate this issue.****"*

The panel recommended that at least small-scale demonstrations at the sludge corrosion vessel operating conditions be performed to test the process chemistry, understand rheological properties of the sludge, identify influences on the process endpoint, determine erosion effects on materials of construction of susceptible equipment (e.g., impeller, vessel walls), determine the propensity to foaming, and detect potential other topics of concern to successful process operations.

To address questions raised by the independent review panel, the present testing was performed according to a Test Plan designed in collaboration between Pacific Northwest National Laboratory (PNNL) and Fluor Hanford (FH) engineers and scientists (Schmidt et al. 2006). The Test Plan governing the laboratory experiments was designed to demonstrate that the end point of the oxidation process could be

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(a) Information on corrosion vessel descriptions taken from: "Sizing of Sludge Corrosion Vessel (TRT-TK-201)," November 2006, BNGA Calc-5477-PR-T-004, Rev. 2; "Sludge Treatment System Description," August 2006, BNGA SD-5477-PR-T-0001, Rev. 0; and "Nitrogen Gas Influences in the Mixing of the Slurry in the Corrosion Tank," July 2006, BNGA RPT-5477-PR-T-0001, Rev. 0.

attained and to identify phenomenological problems with the process. This laboratory campaign is generally consistent with a post-ROD (record of decision) treatability study under CERCLA (Comprehensive Environmental Release Compensation and Liability Act).

Formulation of Data Quality Objectives (DQOs) is the first of eleven steps in performing treatability studies according to the Environmental Protection Agency (EPA 1992). Past characterization campaigns for both fuel and sludge from K Basins have been governed by formal DQOs (e.g., Makenas 1998, 1999, and 2000). Methodology in the K Basin Project DQO Strategy Document (Lawrence 1994), used to select objectives for the present testing, is based on EPA guidance (EPA 1994) but modified for a project, such as K Basin Closure (KBC), seeking to determine bounding conditions to pick design, transportation, and mitigation alternatives. Therefore, the issues were limited to those raised by the independent review panel (Heywood 2006) pertaining to the oxidation process. Broader issues with respect to acceptance of the grouted sludge at WIPP are addressed in a separate DQO document (Westcott 2006). Though a formal DQO was not prepared for this study, individual steps in the DQO process were used to first identify the overall problems and state the decisions, then define the specific objectives of the current tests. The evolution of the problem definitions and decisions are discussed in Sections 1.1 and 1.2.

1.1 Identification of the Problems to be Addressed

The problems addressed by the DQO process are focused on the physical behavior of the product, the reaction rates, and foaming within the STP reactor vessel.

1.1.1 Physical Behavior

Sludge contains many uranium compounds and non-uranium constituents which largely are in solid phases but may have enhanced solubilities at the process temperature. New chemical phases may form at process temperature and, since the envisioned process includes a nitrogen gas purge, evaporation and condensation also will occur. The high reaction temperatures, water evaporation, and the subsequent cooling of the process product to ambient temperature thus could precipitate species to cement particles together. Sludge also contains a variable quantity of organic ion exchange resin (OIER) within the IXM (Ion Exchange Module) material (about 1.05 m^3 compared to a total KE sludge volume of about 36 m^3). The OIER has been shown previously to be relatively stable at temperatures <100°C, but its performance and physical behavior at sustained higher temperatures is unknown. In particular, the OIER may melt or soften at process temperatures and harden to congeal with itself or with other sludge solids upon cooling. Flocculating agents have been added to the sludge during K Basin operations and their performance and physical behavior in sludge at high temperatures also are unknown. Some laboratory samples of wet sludge have hardened in storage at ~33°C hot cell temperature (Figure 1.1) and sludge hardpans have been observed in the K Basins.

Two recent laboratory tests at nominal STP process conditions (72 hours at 185°C) with simulated (non-radioactive) sludge also were performed using methods similar to those proposed for the present testing. One sludge simulant contained inorganic components (ferric oxide hydroxide, aluminum hydroxide, and blow sand) with flocculating agent and the second sludge contained OIER and blow sand. Though the OIER test showed little alteration in texture by processing, the inorganic mixture simulant formed a self-cemented monolith of considerable strength (Figure 1.2). Because it is imperative that the product of the current proposed full-scale process be easily transportable out of the corrosion vessel via one or two transfer lines for the follow-on grout emplacement activities, the cementing of sludges in the reaction vessel would introduce a significant process impediment.

Figure 1.1. Image of KE Canister Sludge Agglomerate
Agglomerate (~1.4 in. diameter) formed by self-cementation during a long-term compaction/settling study. The glass test vessel had to be destroyed to recover the agglomerated sludge.

Figure 1.2. Flocculated Simulant Sludge After Testing
Left – with spatula
Right – cracked in original horizontal axis by spatula

The problem thus becomes determining whether hydrothermal reactions among the sludge constituents during processing, perhaps enhanced by precipitation of solid phases from solution, yield self-cemented products that cannot be readily pumped from the reaction vessel and be blended with grout.

1.1.2 Uranium Metal Reaction Rates

Oxidation of uranium metal present in the sludge is the primary goal of the sludge treatment process. Much of the literature data available on uranium oxidation rates in water are at temperatures lower than the anticipated process temperatures and were conducted using distilled or deionized water and bare uranium metal coupons or clad subsections with one or more exposed surfaces. Data on actual K Basin sludge behavior (albeit at <100°C) are available in recent studies of hydrogen and retained fission gas release during uranium oxidation (Delegard et al. 2000, Bryan et al. 2004, Schmidt et al. 2003). In these latter studies, uranium reaction rates with water were found to be lower in the presence of sludge than in water alone. The studies also showed that, at low uranium metal concentrations, some of the hydrogen product did not appear in the gas phase and thus was consumed by sludge constituents. This is of concern because monitoring of the progress of the uranium metal fuel reaction in the actual STP equipment will be done by measuring hydrogen in the released gas phase.

Therefore, two problems arise related to the reactions of uranium metal with water and to the subsequent behavior of the evolved hydrogen. First, it must be demonstrated that the proposed oxidation reaction process will go to completion to eliminate any significant amounts of metallic uranium fuel particles in a reasonable and predictable time (e.g., a few days to a week, depending upon the reaction temperature). Second, it must be determined that reaction progress can be potentially monitored by hydrogen evolution given that the sludge has a multitude of components that may alter the uranium metal oxidation rate or affect the appearance of hydrogen in the gas phase.

1.1.3 Foaming

The entrainment and release of the nitrogen purge gas, the escape of hydrogen, and the evaporation of water during uranium oxidation could potentially foam the sludge during the actual STP processing. This could have adverse consequences in that the sludge level will be hard to monitor, sludge particulates could be transported by the foam to locations not equipped to handle solids (e.g., vent lines, rupture disks, instrumentation). If foaming does occur to a significant extent, then the process design will have to make allowances for it that are greater than currently anticipated.

The problem then is to determine the extent to which foaming is occurring during the oxidation and cool down steps in the sludge treatment process.

1.2 State the Decisions and Define Specific Test Objectives

The decisions which must be made by the KBC project with respect to sludge processing and which are partially addressed in the testing described in this document are listed below. Complete closure of these decisions will require evaluation of the acquired data in comparison with the details of the proposed design. Decisions may be pursued independently or in parallel.

1. Do chemical reactions between various sludge constituents during the oxidation step and precipitation reactions resulting from evaporation, condensation at high temperatures, and cooling affect the rheology of sludge in a way that is adverse to subsequent sludge retrieval, processing, and transport steps?

2. Does the oxidation reaction of irradiated metallic uranium fuel at process temperatures in the presence of non-uranium constituents go to completion in the time predicted by existing equations, and can the process endpoint be monitored using hydrogen evolution?

3. Do the use of nitrogen purge gas and the evolution of hydrogen gas (in concert with new and existing chemical species formed at high temperature) produce foam in quantities detrimental to the overall sludge process?

Only Question 1 is addressed in detail by the current laboratory testing. Confirmatory testing on uranium metal reaction rate (Question 2) also was performed. Recent investigations have provided information to address uranium reaction concerns regarding rate and fragmentation and present a revised Rate Equation applicable to STP conditions.(a) Questions of hydrogen evolution, particularly for low rates in which hydrogen may be consumed by side reactions, were not addressed by the present testing. Foaming issues (Question 3) are addressed by design and process control and are outside of the present testing. To help address foaming, the corrosion vessel will be sufficiently large and the process solution volumes kept adequately low (half-full) to preclude foaming from being an operational issue, if it were to occur.

Section 2.0 of this report describes the experimental materials and methods used for the five tests, and Section 3.0 presents the results and observations from the testing. Considerations for future testing to support the STP process are outlined in Section 4.0. Section 5.0 lists the references cited in this report. Appendix A provides the bases for uranium metal quantities in Tests 1, 2, and 3, flocculent loading for Tests 3 and 4, and OIER concentration in Test 5. Appendix B presents the vessel loading and post-heating vessel contents data. Appendix C provides information on the design, performances, and outcomes of the cold (non-radioactive) testing performed in preparation for the tests with radioactive K Basin sludges.

(a) $\log_{10}$ rate, μm/h = 9.694 – 3565/T where T is in K; Plys and Schmidt (2006).

2.0 Experimental Materials and Methods

Five tests were conducted in sealed reaction vessels using existing samples of N Reactor fuel and samples and mixtures of KE Canister sludge and KE Floor sludge collected from the KE Basin. The tests materials also included OIER taken from the KE Basin and the polymer flocculent being used in K Basin sludge consolidation operations. Because of the high radioactivity arising from the irradiated N Reactor fuel and K Basins sludge, the laboratory testing was performed in a shielded hot cell within the 325 Building. The testing was conducted according to Test Instructions performed under an existing laboratory procedure.(a) Existing operation-specific procedures (such as for hot cell operations) and analytical procedures also were used in performing this work. A limited series of tests were conducted with non-radioactive sludge simulants (cold testing) to validate the procedures and test apparatus prior to the testing with radioactive materials in the shielded hot cells.

The apparatus used in the testing is described in Section 2.1. Descriptions of the preparation and compositions of the sludge materials used in the testing are given in Section 2.2. The experimental design is outlined in Section 2.3 and Section 2.4 describes the post-test examinations. Section 2.5 summarizes the testing conducted with non-radioactive sludge surrogates.

2.1 Apparatus

The bench-scale testing was conducted in ~125-ml capacity Teflon-lined 304 stainless steel vessels (Parr Model 4748) at temperatures up to ~185°C. The Parr Model 4748 test apparatus (Figure 2.1) is designed as an isolated, closed reaction system, equipped with an overpressure rupture disk and can operate up to 1900 psig (pounds per square inch, gauge) at 250°C. This apparatus normally is heated externally by placement in an oven and is designed to perform acid digestions of minerals for their chemical analysis but also is used in hydrothermal synthesis and testing.

The water vapor pressure at 185°C is about 11 atmospheres, or 162 psig, which, with the contained nitrogen cover gas, brought the initial total pressure to about 184 psig. Three of the tests contained ~5 grams of irradiated uranium metal fuel from the N Reactor. Reaction of 5 g of uranium metal to extinction in the half-filled, sealed test vessels should have produced H_2 sufficient to increase the final total pressure to about 560 psig, well below the 1900 psig test vessel limit at 250°C. In comparison, the pressure in the STP Process corrosion vessel will be controlled at 225 psig and the H_2 product gas will be bled off with the nitrogen purge gas and water vapor.

(a) Lumetta, GJ. 2006. PNNL Operating Procedure, *Routine Research Operations,* RPL-OP-001, Rev. 4.

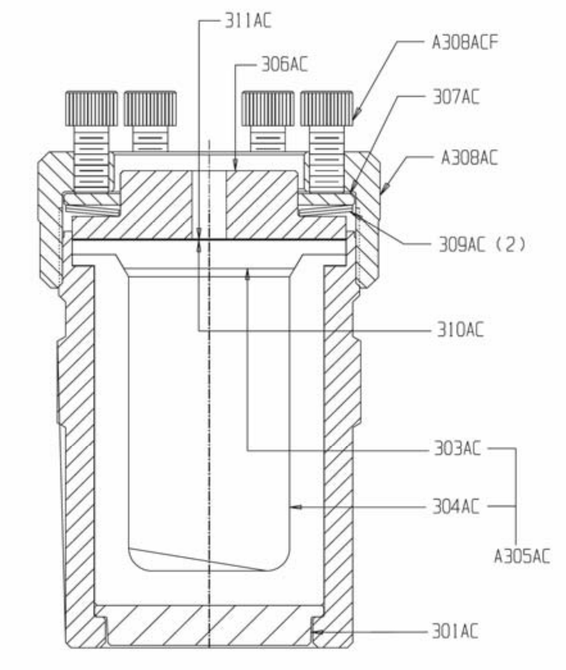

Figure 2.1. Parr Model 4748 Vessel
Steel vessel parts in hatched lines; Teflon parts (303AC, lid, and 304AC, vessel cap) not hatched.

2.2 Experimental Materials

The tests were performed using sludge samples taken from the KE Basin during two prior sludge sampling and characterization campaigns in FY 1999 (Pitner 1999). The origins and initial preparations of the parent sludges used in the testing are summarized in Table 2.1.

The four types of sludge used in the present testing were taken from samples listed in Table 2.1 and prepared according to approved test instructions.(a) The first type used in testing was the uranium-rich sludge KC-2/3 M250. The second sludge type was a composite, identified as KE Container Composite sludge, prepared to emulate KE Container sludge. It included constituents from the KC-2/3, KC-4, KC-5 P250, and FE-5 sludge samples. Because flocculating agent is used in containerization activities at the K Basins, a portion of the KE Container Composite sludge was blended with flocculating agent to prepare the third sludge type, KE Container Composite Floc. The fourth sludge used was sample KC-6 which is rich in OIER. Preparations of the various sludges are described in the following paragraphs.

(a) Delegard, CH. 2006. *Preparation of KE Basin Container Sludge Composite for Sludge Treatment Project (STP) Testing and N Reactor Fuel Coupon Measurement*, Test Instruction 51623-TI03, Rev. 0 and Addendum 1, Pacific Northwest National Laboratory, Richland, WA.

Table 2.1. Sources and Preparations of Parent Sludges Used in Testing

Sample ID	Source	KE Basin Sampling Locations	Barrel Type and Material[(a)]	Sampling Date	Preparation
KC-2	Consolidated sample from fuel storage canister barrels with highly damaged fuel from all three bays	668E & W 2229E 4571E 6071W	Mark 0 Mark 0 Modified Co-Product Mark 0	4-13 March 1999	Composite KC-2/3 created in 325 Laboratory
KC-3	Consolidated sample from canister barrels with moderately damaged fuel from all three bays	4850W 4869E 3125W 2905E 450E 455W	Mark 0 Mark 0 Mark 0 Mark 0 Mark 0 Mark 0	1-8 April 1999	
KC-2/3 M250	KC-2 and KC-3 samples	–	–	4 March - 8 April 1999	Portion of KC-2/3 wet-sieved through 250-µm screen
KC-4	Consolidated sample from floor between barrels of open bottom canisters with highly damaged fuel from all three bays	0550 4573 5465	Modified Co-Product Modified Co-Product Modified Co-Product	30-31 March 1999	–
KC-5 P250	Consolidated sample from deep sludge areas on the main basin floor in all three bays	4648 3133 0548	Mark II Mark 0 Modified Co-Product	29-30 March 1999	Portion of KC-5 wet-sieved on a 250-µm screen and not passing
KC-6	Consolidated sample from floor area in west bay known to be very high in ion exchange material beads	6758	Mark 0	13 and 26 March 1999	–
FE-5	Weasel pit including South Loadout Pit sludge Composites of Two Weasel Pit core samples, (one near South Wall 8 ft from East End and other near Center, 11 feet from West End)		–	26 April & 13 January 1999	Composite created in 222-S Laboratory from KE-9 and KE-10 single-pull samples

(a) All barrel materials were aluminum except that of the Mark II from location 4648 for KC-5.

Somewhat similar to the KE canister sludge sample shown in Figure 1.1 (though not as extreme), canister sludge sample KC-2/3 M250, was found to have self-cemented in the storage jar, even though the sludge had been kept immersed in water in capped containers at hot cell (~25-35°C) temperatures. The self-cemented sludge exhibited significant strength and could not be retrieved using conventional techniques (i.e., mixing with a stainless steel spatula and sluicing). Therefore, to recover the sample, free liquid was removed, and the sample jar was broken. The sludge was removed in its intact cemented shape and was cut into fragments and transferred to a receiver jar where it was mixed and homogenized with water using an overhead electric mixer (3.6-cm diameter blade turning at ~720 RPM, giving ~140 cm/sec tip speed). After mixing for 5 to 8 minutes, all large agglomerates disintegrated and the resulting homogenized sludge slurry exhibited a consistency and physical behavior similar to typical settled K Basin sludges. To better understand the makeup of the resulting homogenized sludge, a subsample (~6 g) of the as-settled sludge was sieved using 1000-µm and 500-µm sieves. A number of weak agglomerates, 1000 to 3000 µm in size, were retained on the 1000-µm sieve. Most of these were readily broken up with mild pressure using a flexible plastic pipet. Material collected on the sieves was dried and weighed. On a dry weight basis, approximately 25 wt% of the solids were retained on the 1000-µm sieve and ~14 wt% retained on the 500-µm sieve with the balance of particles passing through the 500-µm sieve. Figure 2.2 shows the appearance of the as-found sludge (after removing it from the sample bottle), the homogenized sludge slurry, and the sludge during sieving.

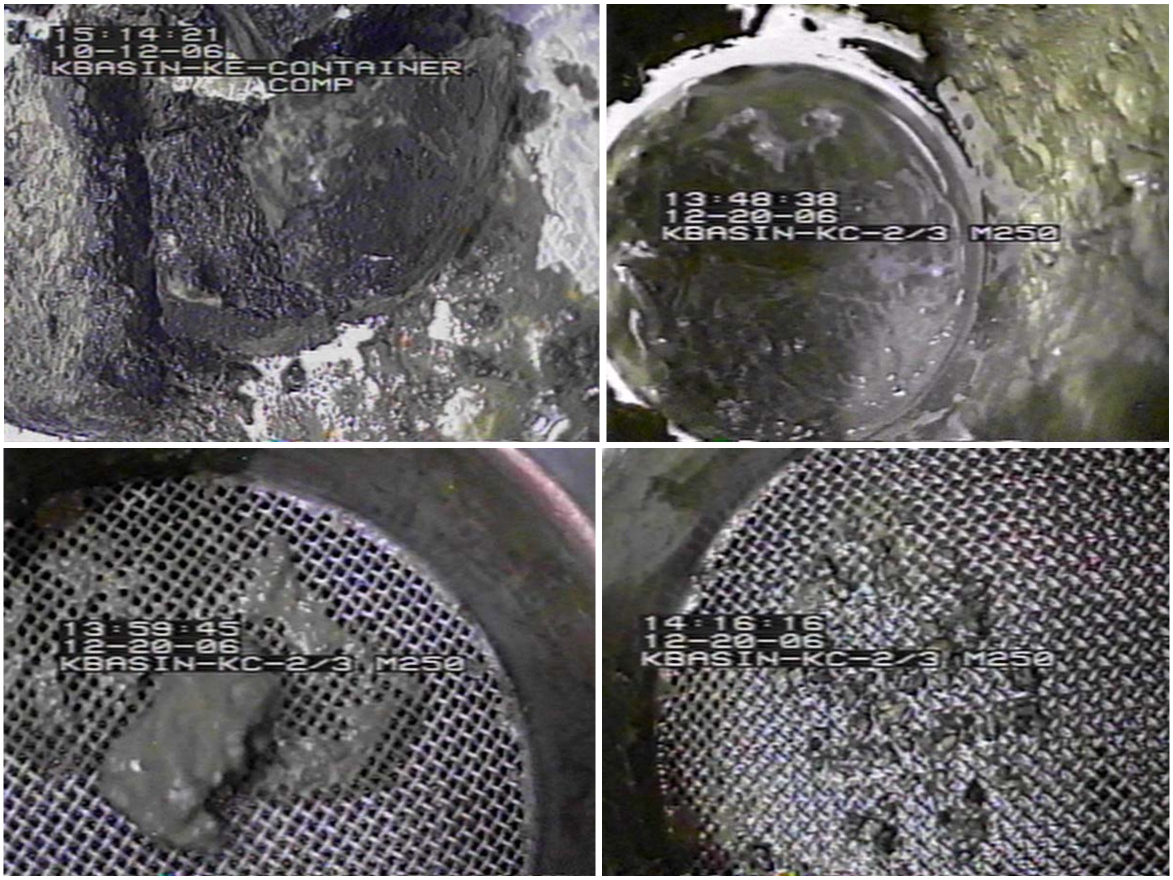

Figure 2.2. KE Canister Sludge Sample KC-2/3 M250 – Untreated

Top left – As-recovered from sludge storage container. Larger pieces are about 5-cm in the longest dimension. Original sludge assumed the inside shape of the jar (~13-cm diameter, 4-cm thick). To prepare for STP testing, the sludge was homogenized with a high speed (720 rpm) electric mixer.

Top right – KC-2/3 M250 after homogenization. Picture shows the sludge remaining after removing most of the sludge for testing. At this point, the material behaved like a typical settled sludge.

Bottom left – Approximately 6 grams of the homogenized sludge on a 1000-µm sieve.

Bottom right – After washing the 6 grams of as-settled sludge with a gentle stream of water (squirt bottle), 1 to 3-mm concretions remained on the 1000-µm sieve. These concretions were readily broken up and passed through the sieve with moderate pressure from the tip of a polyethylene pipet.

In summary, it is likely that the uranium oxyhydroxides (and iron/aluminum oxyhydroxides) within the KC-2/3 M250 sludge sample continued to oxidize and consolidate during storage and active maintenance (periodic water replenishment) at hot cell conditions   The settled density of the homogenized KC-2/3 M250 sludge was measured as 2.68 g/cm^3 (in 2007) compared to a density of 2.13 g/cm^3 measured in 1999 (Bredt et al. 1999). However, based on XRD analyses (discussed later), the uranium oxyhydroxides in the KC-2/3 M250 sludge did not undergo irreversible dehydration during storage. Sludges aged in the hot cells at ~30°C thus have progressed further in reaching chemical equilibrium, including hardening, than sludges freshly taken from the K Basin storage at 15°C. However, it is expected that both fresh and aged sludge (from hot cell storage) would be taken to equilibrium (or complete reaction) by the acceleration of oxidation/dehydration reactions that will be achieved with hydrothermal treatment at 185°C. In conclusion, the homogenized KC-2/3 M250 material represents the best available sample material to represent K Basin Settler sludge (i.e., 75% of Settler tank sludge is derived from processing KE fuel/canisters) and results obtained from hydrothermal testing with this sludge, plus the metallic uranium fuel addition, are judged to be representative of the anticipated behavior of Settler sludge in the STP corrosion process.

The KE Container Composite sludge, representative of the material being collected into containers in the KE Basin, was prepared within the hot cell according to the outline shown in Table 2.2. To prepare the composite, the individual sludge sample weights and volumes were measured. Target weights and volumes were measured to assure that representative (and not gravity-segregated) samples of the entire material were taken. The portions were transferred from the measuring vessel into a jar with water. When all portions were added, they were mixed thoroughly for about 2 minutes with a high-speed overhead mixer (~720 RPM, giving ~140 cm/sec tip speed). The blended sludge then was settled for 5 days and the supernatant water removed.

Table 2.2. Make-up of KE Container Composite Test Sludge

Stream	**KE Container Composite Sludge**							
	Composition		**Sample**	**Target**		**Make-up**		
	Volume, m^3	**Vol%**		**Vol%**	**Vol., ml**	**Vol%**	**Vol., ml**	**Weight, g**
KE Can Full	2.5	7	KC-2/3 Whole	7	21	8.5	21	45.83
Main Floor	21.5	60	KC-4	30	90	28.9	71	92.56
			KC-5 P250	30	90	34.1	84	117.57
Weasel Pit	10	28	FE-5	33	99	28.5	70	109.63
Other Pits	1.8	5						
Total	35.8	100	Total	100	300	100	246	365.59

To prepare the flocculated KE Container Composite (KE Container Composite Floc), a well-stirred 120-ml portion of the KE Container Composite was taken and mixed with 67.2 ml of a 1-wt% water dispersion of Nalco "Optimer 7194 Plus" flocculating agent. This is the same agent as has been used in K Basin operations. The 1% water dispersion of flocculating agent served to invert (unfold) the long chain flocculent molecules as is the practice in using these agents in the K Basins and elsewhere. The inverted 1% dispersion was injected slowly into the KE Container Composite sludge using syringes and gentle stirring to aid in uniform mixing. Water then was added to the mixture to obtain ~320-ml total volume. The sludge components and water were blended continuously with the overhead high speed mixer (140 cm/sec tip speed) for 30 seconds. A second mixing episode for about 60 seconds occurred five minutes later with alternate mixing periods of 3-seconds on followed by 3-seconds off. A third mixing episode occurred for 75 seconds with 3-second on and off pulses. No clear liquid layer existed immediately after the last mixing episode. But, within minutes, the sludge began settling, showing obvious flocs and clear supernatant liquid. The sludge was settled for 14 days before all but 5 ml of the supernatant liquid was removed. The settled sludge volume at that time was 160 ml (not including the 5 ml of supernatant liquid). The settled sludge containing the flocculating agent was left in the settling jar for later use.

The chemical and radiochemical compositions of the sludges used in the present testing have been determined by prior characterization testing and the water concentrations measured by drying sludge samples to constant weight at 105°C during the present experimentation. The sludge compositions shown in Table 2.3 also provide a material balance assuming plausible phases or material stoichiometries for the principal elements found in the sludge (aluminum, calcium, iron, magnesium, sodium, silicon, and uranium). The material balances sum to near 100% for most sludges. Note, however, that sludge KC-6 itself was not analyzed. The composition provided for sludge KC-6 is that of sludge sample KES-H-08 (Makenas et al. 1996). Sample KES-H-08 was taken from the same OIER-rich vicinity on the KE Basin floor as was the KC-6 sample. The marked shortfall seen in the material balance for KES-H-08 is due to the fact that the sample analysis used only acid digestion rather than the fusion digestion used for the other sample analyses. The acid digestion did not dissolve either the OIER or the inorganic ion exchanger [mordenite; nominally $(Ca,Na_2,K_2)Al_2Si_{10}O_{24}\cdot 7H_2O$] also present in the KES-H-08 sludge sample. Because the KC-6 sample used in the present testing appeared to be largely OIER beads, the KES-H-08 analysis given as representative of sample KC-6 in Table 2.3 must be used with reservation when drawing detailed conclusions.

Table 2.3. Chemical and Radiochemical Compositions of Sludges Used in Testing

Sludge	**KC-2/3 M250**	**KC-2/3 Whole**	**KC-4**	**KC-5 P250**	**FE-5**	**KE Comp[(a)]**	**KE Comp Floc[(a)]**	**KC-6[(b)]**
Dry Basis								
Element	**Concentration, Wt%[(c)]**							
Al	1.92	5.16	6.82	15.3	2.66	7.82	7.82	1.87
Ca	0.0960	0.134	1.04	0.481	1.20	0.770	0.770	1.22
Fe	1.43	1.84	24.3	16.1	30.6	20.3	20.3	1.51
Mg	0.0300	0.0462	0.330	0.177	0.146	0.171	0.171	0.225
Na	0.216	0.240	0.360	0.374	<0.03	0.219	0.219	3.26
Si	0.290	0.752	4.91	5.46	0.330	2.81	2.81	NA
U	68.3	59.0	16.6	6.36	4.10	15.7	15.7	0.314
Sum as oxide & carbonate[(d)]	95.1	94.8	101.6	97.0	75.6	89.9	89.9	16.9[(b,d)]
Radionuclide	**Concentration, µCi/g[(c)]**							
^{60}Co	0.452	0.441	1.080	1.10	0.875	0.912	0.912	0.185
^{137}Cs	414	860	1680	132	170	521	521	144
^{154}Eu	9.10	8.14	2.60	1.11	0.985	2.44	2.44	<0.041
^{238}Pu	17.4	16.2	4.91	1.99	2.06	4.78	4.78	0.0618
$^{239/240}$Pu	123	114	39.2	13.1	13.1	33.7	33.7	0.403
^{241}Am	99.4	90.5	29.2	13.1	10.4	27.3	27.3	0.397

Table 2.3. Chemical and Radiochemical Compositions of Sludges Used in Testing (cont'd)

Sludge	KC-2/3 M250	KC-2/3 Whole	KC-4	KC-5 P250	FE-5	KE Comp(a)	KE Comp Floc(a)	KC-6(b)
Settled Sludge Basis								
Element / H_2O	**Concentration, Wt%(c)**							
Al	1.44	3.24	2.20	7.49	1.58	4.16	3.87	0.706
Ca	0.0720	0.0840	0.334	0.236	0.712	0.409	0.381	0.461
Fe	1.07	1.15	7.82	7.88	18.2	10.8	10.0	0.572
Mg	0.0225	0.0290	0.106	0.0867	0.0867	0.0907	0.0844	0.0851
Na	0.162	0.150	0.116	0.183	Not meas'd.	0.116	0.108	1.23
Si	0.218	0.472	1.58	2.67	0.196	1.49	1.39	N/A
U	51.2	37.0	5.35	3.11	2.43	8.36	7.78	0.119
H_2O	25.0	37.3	67.8	51.0	40.6	46.9	50.5	62.2
Radionuclide	**Concentration, µCi/g(c)**							
^{60}Co	0.339	0.277	0.348	0.539	0.519	0.485	0.451	0.0699
^{137}Cs	311	539	542	64.6	101	277	257	54.5
^{154}Eu	6.83	5.10	0.838	0.544	0.585	1.30	1.21	<0.016
^{238}Pu	13.05	10.2	1.58	0.974	1.22	2.54	2.37	0.0234
$^{239/240}$Pu	92.3	71.5	12.6	6.41	7.78	17.9	16.6	0.152
^{241}Am	74.6	56.7	9.41	6.41	6.17	14.5	13.5	0.150

(a) KC Comp is KE Container Composite; KE Comp Floc is KE Container Composite Floc.

(b) No analytical data are available for KC-6. Data are from the similar sample KES-H-08 (Makenas et al. 1996). See text and footnote (c), below.

(c) Dry basis analyses for KC-2/3 M250 are from Delegard et al. (2000). Dry basis analyses for KC-2/3 Whole, KC-4, and FE-5 are from Baker and Welsh (2001, "Laboratory Data from the Consolidated and Single Pull Core Sludge Sampling Campaigns," Internal FH Memo, 01-SNF/RBB-004, May 10, 2001); dry basis analyses for KC-5 P250 are assumed to be identical to those of KC-5, also from Baker and Welsh (2001). Dry basis analyses of KE Comp (KE Container Composite) and KE Comp Floc (KE Container Composite Floc) are derived from analyses, masses, and water concentrations of the constituent sludges. Settled sludge analyses (except KC-6) are calculated based on the water concentrations of the respective sludges.

(d) 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 are observed by 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 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 comprised 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 digest results.

The bulk physical properties of the constituent and composite sludges used in the testing were measured by weighing well-mixed samples of the settled sludges into volume-calibrated centrifuge cones, adding DI (distilled and deionized) water, allowing re-settling for several days, measuring the settled sludge volume and total volume (with supernatant water), measuring the weights with supernatant water, and then decanting the water and drying the settled sludge to constant weight in an oven set to 105°C. The constituent sludge aliquot densities used to prepare the KE Container Composite sludge, sludge KC-6, and the densities of the KE Container Composite, the KE Container Composite Floc, and the KC-2/3 M250 sludge in the volume-calibrated sludge make-up vessels and jars also were determined. The densities for samples and whole items, Table 2.4, match within ~6% or better. The density of sample KC-6 was 1.19 g/mL.

Table 2.4. Bulk Physical Properties of Sludge

Values	KC-2/3 M250	KC-2/3 Whole	KC-4	KC-5 P250	FE-5	KE Comp	KE Comp Floc
Tare, g	6.47	6.60	6.73	6.71	6.67	6.48	6.60
Gross sludge, g	12.76	10.80	11.02	10.07	9.45	15.78	10.55
Gross sludge & H_2O, g	16.24	13.04	15.00	13.85	13.54	17.44	17.73
Settled sludge vol., cm^3	2.30	1.90	3.00	2.25	1.50	5.50	2.50
Sludge & H_2O vol., cm^3	5.90	4.20	7.30	6.00	6.00	7.40	9.80
Dry wt., g	11.10	9.20	8.01	8.37	8.08	11.29	8.49
Settled sludge, g in H_2O [a]	6.17	4.14	3.97	3.39	2.37	9.06	3.83
Settled sludge, g by difference	6.29	4.20	4.29	3.36	2.78	9.30	3.95
Dry solid wt., g	4.63	2.60	1.28	1.66	1.41	4.81	1.89
Dry solid vol., cm^3	0.76	0.36	0.31	0.52	0.54	1.25	0.56
Total H_2O wt., g	5.14	3.84	6.99	5.48	5.46	6.15	9.24
H_2O in settled sludge, g or cm^3	1.54	1.54	2.69	1.73	0.96	4.25	1.94
Stl. sludge density, sample, g/cm^3[a]	2.68	2.18	1.32	1.51	1.58	1.65	1.53
Stl. sludge density, whole, g/cm^3[b]	2.41	2.18	1.30	1.40	1.51	1.54	1.45
Solids in settled sludge, vol%	33.0	18.7	10.3	23.1	35.8	22.8	22.6
Solids in settled sludge, wt%	75.0	62.7	32.2	49.0	59.4	53.1	49.5
Solids particle density, g/cm^3	6.11	7.29	4.13	3.19	2.62	3.84	3.36
H_2O in settled sludge, vol%	67.0	81.3	89.7	76.9	64.2	77.2	77.4
H_2O in settled sludge, wt%	25.0	37.3	67.8	51.0	40.6	46.9	50.5

(a) These values, derived from measurements summarized above in calibrated 15-mL centrifuge cones, were used in subsequent calculations.
(b) These confirmatory values derived from large sample sludge measurements in transfer vessels or collection jars.

Metallic uranium coupons sectioned from spent fuel elements that had been irradiated in the N Reactor and stored in the K Basins were obtained for the present testing from reserves kept in the Shielded Analytical Facility (SAL) in the RPL.[a] Particles of the fuel coupons also were recovered from the storage jars and were size-fractionated by sieving. The retrieval and size-fractionation work was performed according to approved Test Instructions.[b] Fuel particles were collected in the size range passing a 500-μm screen and retained on a 250-μm screen. Fuel particles also were collected passing a 1000-μm screen and retained on a 500-μm screen. The particles were weighed into ~5-gram aliquots and used in the present testing (the basis for the quantities used is provided in Appendix A). Four fuel element fragments or coupons, originally cut by diamond saw for thermo-analytical testing (but not used for this purpose), were collected. The coupons used in the present testing are sketched in Figure 2.3 and their dimensions, obtained by video observations of the coupons as they lay on a millimeter-scale grid, are shown in Table 2.5. It is noted that the fuel coupons and the fuel particles in the -500+250 μm and -1000+500 μm size ranges contain Zircaloy-2 cladding and thus are not solely irradiated uranium metal. The relative amounts of uranium fuel and cladding for the particles was taken to be those of the starting fuel elements; i.e., 93 wt% uranium fuel and 7 wt% Zircaloy-2 (Plys and Schmidt 2006). The amount of cladding for each coupon was ~0.10 g based on a 25-mil (~0.64-mm) thickness, or about 8% of the total coupon weight.

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[a] The remaining samples in SAL were consolidated for return to the KW Basin for disposition.

[b] Schmidt, AJ. August 2006. *Collection of N Reactor Fuel Subsamples for STP Testing*, Test Instruction 51623-TI02, Rev. 0, Pacific Northwest National Laboratory, Richland, WA.

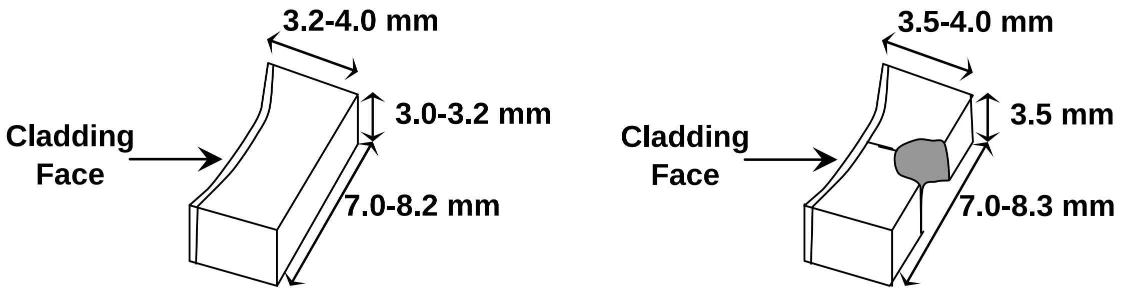

Figure 2.3. Sketch of Irradiated Metallic Fuel Coupons
Left – Coupons A, B, and C
Right – Coupon D with Chip Missing and Crack.

Table 2.5. Dimensions of Irradiated Metallic Fuel Coupons Used in Test 2

Coupon	Total[(a)] Weight, g	Dimensions, mm Length × Width × Thickness
A	1.1448	7.3-8.2 × 4.0 × 3.2
B	1.2856	7.0 × 4.0 × 3.2
C	1.2644	7.0-8.0 × 3.2-4.0 × 3.0
D	1.4115	7.0-8.3 × 3.5-4.0 × 3.5

(a) Fuel + cladding. Mass of cladding on each coupon estimated to be ~8 wt% of total.

2.3 Experimental Design and Methods

This section describes the overall approach and experiments designed to assess the effects of the STP processing on the physical and chemical behavior of K Basin sludge. The laboratory tests were conducted in sealed reaction vessels as described in Section 2.1 using existing samples of irradiated N Reactor fuel, Canister Sludge, and Floor Sludge collected from the KE Basin as described in Section 2.2. The tests also included sludge containing OIER taken from the K Basins and sludge containing the particle flocculent that is being used in sludge consolidation efforts and which was blended with the sludge.

The matrix provided in Table 2.6 summarizes the conditions and materials for each test. The matrix was created based upon the data quality objective needs assessment and on deliberations between FH and PNNL senior staff and stakeholders as summarized in Section 1. The objectives and rationales of each test are described in the following paragraphs.

Table 2.6. Test Matrix for the Sludge Treatment Project Chemistry Testing

Test Number	Target Simulation	Temperature Profile		Sludge Test Material		Water Added above Settled Sludge, cm^3(b)	Uranium Metal (from spent N Reactor fuel from K Basins)	Additional Materials
		Ramp(a) to 185°C, h	Hold Time at 185°C, h	Composition	As-settled Volume, cm^3			
1	Fine Canister Sludge + U Metal Fuel Particles	28	7	KC-2/3 M250 (Canister Sludge <250 µm)	50 (119.35 g)	12.5 (target) 10.73 (actual)	5.05 g (-500, +250 µm) fuel particles	None
2	Fine Canister Sludge + U Metal Fuel Coupons	0	10(c)	KC-2/3 M250 (Canister Sludge <250 µm)	50 (114.48 g)	12.50 (target) 10.24 (actual)	5.09 g (-6350, +4000 µm) in 4 fuel coupons	None
3	Container Sludge + Flocculent + U Metal Fuel Particles	28	72(d)	KE Container Composite(e)	62.5(f) (90.99 g)	0 (target) -0.72 (actual)	5.15 g (500 to 1000 µm) fuel particles	0.28 g of neat flocculent
4	Container Sludge + Flocculent	28	72(d)	KE Container Composite(e)	62.5(f) (90.57 g)	0 (target) -0.14 (actual)	none	0.28 g of neat flocculent
5	Container Sludge + OIER Sludge	28	72(d)	KE Container Composite(e) and KC-6	42.5 (66.70 g)	12.5 (target) 11.86 (actual)	none	7.5 cm^3 (8.50 g) of OIER sludge(g)

(a) Heat-up temperature ramp targeted to simulate the STP profile, and included a 12- to 14-hr intermediate hold at 140°C for Tests 1, 3, 4, and 5.

(b) Values show amount of water added; these values must be adjusted downward, as shown in subsequent discussions, to reflect evaporative loss.

(c) Hold time for Test 2 was calculated based on the actual metallic fuel coupon thicknesses and current Databook uranium metal rate equation ($\log_{10}$ rate, µm/h = 9.694 – 3565/T); at 185°C (T = 185 + 273.15 K), the rate is 82 µm/h (Plys and Schmidt 2006). Total time at temperature is calculated to achieve 80% reduction in fuel coupon mass. For a 3.0-mm thick coupon, an 80% reduction in thickness (attack from both sides) to 0.60-mm thickness would be achieved in 14.6 hours, decrease to 80% of its original mass would require 9.66 hours (10 hours was used in Test 2), and complete extinction of the coupon would occur in ~18.3 hours.

(d) The current Sludge Databook Rate Equation (Rev. 13A, Schmidt 2006) predicts a 39-h extinction time for a ¼ in. diameter particle of U metal. However, the STP corrosion process is based on the rate equation given in Rev. 12 of the Databook. To be consistent with the STP, a 72-h reaction time is being used.

(e) KE Container Sludge Composite: Composite of KE sludge samples formulated to be representative of KE Container Sludge.

(f) Because flocculation expanded the KE sludge volume significantly, no supplementary water was added. Sludge volume is adjusted to 62.5 ml from 50 ml as indicated in Table 1 of the Test Plan (see footnote 1 on page 1).

(g) OIER sludge, collected from KE Basin Floor sample KC-6, is composed primarily of OIER beads.

- KC-2/3 M250 is a composite (from 11 sampling locations) of KE Canister sludge; M250 is the sieved fraction of whole sample containing particles <250 µm.
- Each test vessel was purged with 99.997% nitrogen, as in the STP Process, to remove the oxygen from air which can poison uranium metal corrosion.

2.3.1 Test 1: Fine KE Canister Sludge and Fine Uranium Metal Fuel Particles

Test 1 examined the behavior of an estimated Settler tank sludge composition. The corresponding primary focus of Test 1 was to understand the product rheology after heating finely particulate sludge having high uranium oxide content with fine particles of irradiated metallic uranium fuel. For this test, a composite of fine (<250 µm) KE Canister Sludge was mixed with fine (<500 µm but >250 µm) uranium fuel particles arising from crumbled irradiated N Reactor fuel. Since the Settler tanks contain only fine particulate (less than ~500-600 µm), the baseline STP process hold time of 6.8 h at 185°C for this sludge type is lower than the 72 h required for the larger uranium metal particles (up to 6350 µm) potentially present in Container or KOP (Knock-out Pot) sludge. Consequently, the correspondingly shorter hold time used for Test 1 (~7 h) is consistent with the expected STP processing of Settler tank sludge.

The KE Canister sludge used in this test (sample KC-2/3 M250) emulates the expected properties of the Settler tank sludge. Sample KC-2/3 sludge is a composite of sludge collected from 11 locations in the KE Basin. The KC-2/3 whole sludge sample (all particulate material less than ¼-inch, 6350 µm) was sieved in 1999 at 250 µm to provide a "plus (P250)" and "minus (M250)" fraction and the M250 fraction used in Test 1. Approximately 75% of the whole sample (in 1999) was made up of the particles less than 250 µm. On a dry weight basis, KC-2/3 M250 is 68.3 wt% uranium compared with 59.0 wt% uranium in the KC-2/3 whole sludge sample (Table 2.3).

2.3.2 Test 2: Fine KE Canister Sludge Composite and Uranium Metal Coupons

Test 2 was designed to provide rheological information on high uranium content sludge held at the STP process temperature for a longer period of time (compared to Test 1) and to provide confirmatory information on the reaction rate of uranium metal immersed in the sludge at 185°C. For this test, four uranium metal coupons (-6350, +4000 µm) from irradiated N Reactor fuel from K Basins were immersed in finely particulate KE Canister sludge (KC-2/3 M250). Before the test, the axial dimensions (height, length, width) and weights of the coupons were measured (see Table 2.5). Based on the coupon dimensions and the Databook rate equation, the time at temperature (185°C) to corrode ~80% of the coupons was calculated and used to establish the target test run time (see Table 2.6). By using <250 µm sludge material, recovery of the remaining portion of the fuel coupons was to be accomplished by sieving, provided that significant sludge cementation did not occur and that residual unreacted metal still was present.

For this test, the reactor vessel was placed in the oven after the oven had first been heated to 185°C to provide a simple time/temperature profile for the uranium metal rate evaluation. Thus, the test was not subjected to a STP prototypical 28-h heat-up ramp. Nevertheless, some heat-up lag occurred. After ten hours at 185°C, the vessel was removed from the oven and set on the hot cell deck to accelerate cooling. After the test, the reaction vessel contents were sieved to recover the residual fuel coupons. It was planned that the uranium reaction rate could be estimated based on the test vessel temperature and the remaining coupon material mass and dimensional measurements and the rate compared with the design basis reaction rate.

2.3.3 Test 3: KE Container Sludge + Flocculent + Fuel Particles

This test was designed to examine the effects of flocculent and uranium metal fuel particles on the physical behavior and rheology of K Basin Container sludge in the STP corrosion process. During sludge retrieval and containerization in the KE Basin and the subsequent transfer and containerization of sludge in the KW Basin containers, it is anticipated that flocculent (Optimer 7194 Plus, Nalco) will be added to all Container sludge. The use of flocculent will add approximately 1,300 µg (0.0013 g) of total organic carbon (TOC) per cm^3 of settled sludge, or ~5.5 ml of neat flocculent per liter of sludge. The basis of the floc loading is given in Appendix A. The flocculent addition will almost double the TOC concentration of KE Floor and Weasel Pit sludge, whose average TOC concentration is ~1,400 µg/cm^3 before flocculent addition.

The behavior of the flocculent during hydrothermal processing is not known. As described in Section 2.2, flocculent (Optimer 7194 Plus, Nalco; the same material as used in the K Basin operations) was added to the Container Sludge Composite in a manner by which neat flocculent was inverted (i.e., diluted with water to allow the flocculent polymer to unfold) and prepared as a 1 wt% solution prior to being mixed with sludge.

This test also examined the effects of uranium metal corrosion on Container sludge rheology. In prior testing at 60°C for 1100 hours followed by ~70 h at 80°C and ~48 h at 95°C, a similar mixture of KE Floor sludge and uranium metal particles but lacking flocculent (Test SNF + Can 60L) was found to be difficult to remove from its stainless steel reaction vessel and found to adhere to the vessel bottom and walls (Schmidt et al. 2003).

As described in Section 2.2, the KE Container sludge composite was formulated from archived K Basin sludge samples to resemble a 93/7 volume percent mixture of (93 vol%) KE Floor and (7 vol%) KE Canister sludge (Table 2.2). The composite contained the moderate concentrations of iron, aluminum, and uranium (Table 2.3) that are representative of the K Basin sludge. The ratio of 93/7 is based on the nominal volumetric ratio of KE floor/pit sludge (36 m^3) to KE canister sludge (2.5 m^3) expected in KE Basin containers; see Table 2.2. The uranium metal particle sizes ranged from 500 to 1000 µm. This range is consistent with the size range of fuel particles previously determined to be present in typical KE Canister sludge during gas generation testing (Delegard et al. 2000).

2.3.4 Test 4: KE Container Sludge + Flocculent

The primary objective of Test 4 was to examine the effects of the STP process conditions and flocculent on the sludge product rheology. This test is similar to Test 3, with the exception that it did not include added uranium metal particles but included representative concentrations of flocculent. It is likely that a significant fraction of the Container sludge batches processed through the STP corrosion vessel will have very little uranium metal and thus will be similar to the Test 4 composition. However, all Container sludge is expected to contain some flocculent. Therefore, Test 4 serves, in part, as a control test for comparing and interpreting the results of Test 3 and Test 5.

2.3.5 Test 5: KE Container Sludge + Organic Ion Exchange Resin Beads

Test 5 was conducted to examine the propensity for the OIER beads found in the sludge to soften and potentially contribute to sludge agglomeration at STP process conditions. OIER from spilled IXM material is a significant component of the floor sludge from the KE Basin. The OIER in the K Basins, NRW-37 (Purolite), is a mixed bed material consisting of strong acid cation exchange resin and strong base anion exchange resin. Both resin types are composed of polystyrene divinylbenzene polymers; the cation resin has sulfonate and the anion resin has quaternary ammonium functional groups.

It is not known how these aged used resins, in contact with the KE Floor sludge for over 12 years, will behave in the 185°C hydrothermal processing. They may soften to self-cement or cement with other sludge solids. They also may thermally decompose to release sulfur-bearing anions (e.g., sulfite, SO_3^{2-}) and organic amines or organic acids that also may alter the solution pH. It is estimated that the West Bay floor of the KE Basin contained between 1.05 m^3 (nominal) and 2.78 m^3 (bounding) of OIER (Pearce 2001). This OIER was distributed in a fairly limited area across about 12.5 to 25% of the West Bay floor. The OIER also has almost neutral buoyancy and thus is readily suspended. It is likely that concentrations of OIER exceeding 10 vol% will be present in one or more of the individual batches in the STP due to fractionation caused by slurrying and re-settling. The basis for the OIER loading (15 vol%) is discussed in Appendix A.

2.3.6 Test Vessel Preparation

The hydrothermal testing was performed according to approved Test Instructions, beginning with the loading of the test vessels (Teflon liners used in the Parr Model 4748 vessels).(a) The vessels for each of the five tests were loaded by transferring weighed portions of sludge materials (including the OIER sludge), water, and fuel particles and coupons into each respective vessel. Transfers of sludges to the vessels in Tests 1, 2, and 5 were aided by rinsing sludge from loaded and weighed intermediate vessels using aliquots of the added water. Weighing of the intermediate vessels before and after each water rinse aliquot was used to record the total quantity of water added. The differences between the weights of the loaded and unloaded (rinsed) intermediate vessels were taken to be the sludge weights added to the test vessel. No additional water was used for Test 3; the sludge weight added to test vessel 3 was the difference between the weights of the loaded and unloaded intermediate vessel. In Test 4, 2.0 ml of water was added to the sludge to make up for its perceived drying but no rinse water was used. The quantities of metallic uranium fuel added to Tests 1, 2, and 3 were determined as the differences between the weights of the vials holding the fuel before and after emptying into the respective test vessels.

The sealing of the test vessels requires that the sealing surfaces be clean. Test vessels 1, 3, 4, and 5 required wiping to remove particles of sludge present on the sealing surfaces. The contents of vessels from Tests 1 and 3 also were stirred to mix the fuel particles into the sludge. The test vessels were weighed before and after stirring and wiping to determine the quantities of sludge removed by these actions. The differences between the respective empty test vessel weights and their full weights were used to verify the quantities added. In all cases, the filled vessels weighed less than the sums of the empty vessel, the added sludge (corrected for that removed by stirring and wiping), the added water, and the added fuel metal. The shortfalls, ranging from 0.29 to 2.57 g, are ascribed to water evaporating in the hot cell from the sludge and from the added water. The water quantities in each test thus were adjusted based on the evaporative losses. The weight data from the vessel loading are summarized in Appendix B.

The appearances of the five test vessels after filling but before wiping are shown in Figure 2.4.

(a) Delegard, CH. 2006. *Hydrothermal Testing of K Basin Sludge and N Reactor Fuel Coupons for the Sludge Treatment Project (STP)*, Test Instruction 51623-TI-04, and Addenda 1, 2, 3, and 4, Pacific Northwest National Laboratory, Richland, WA.

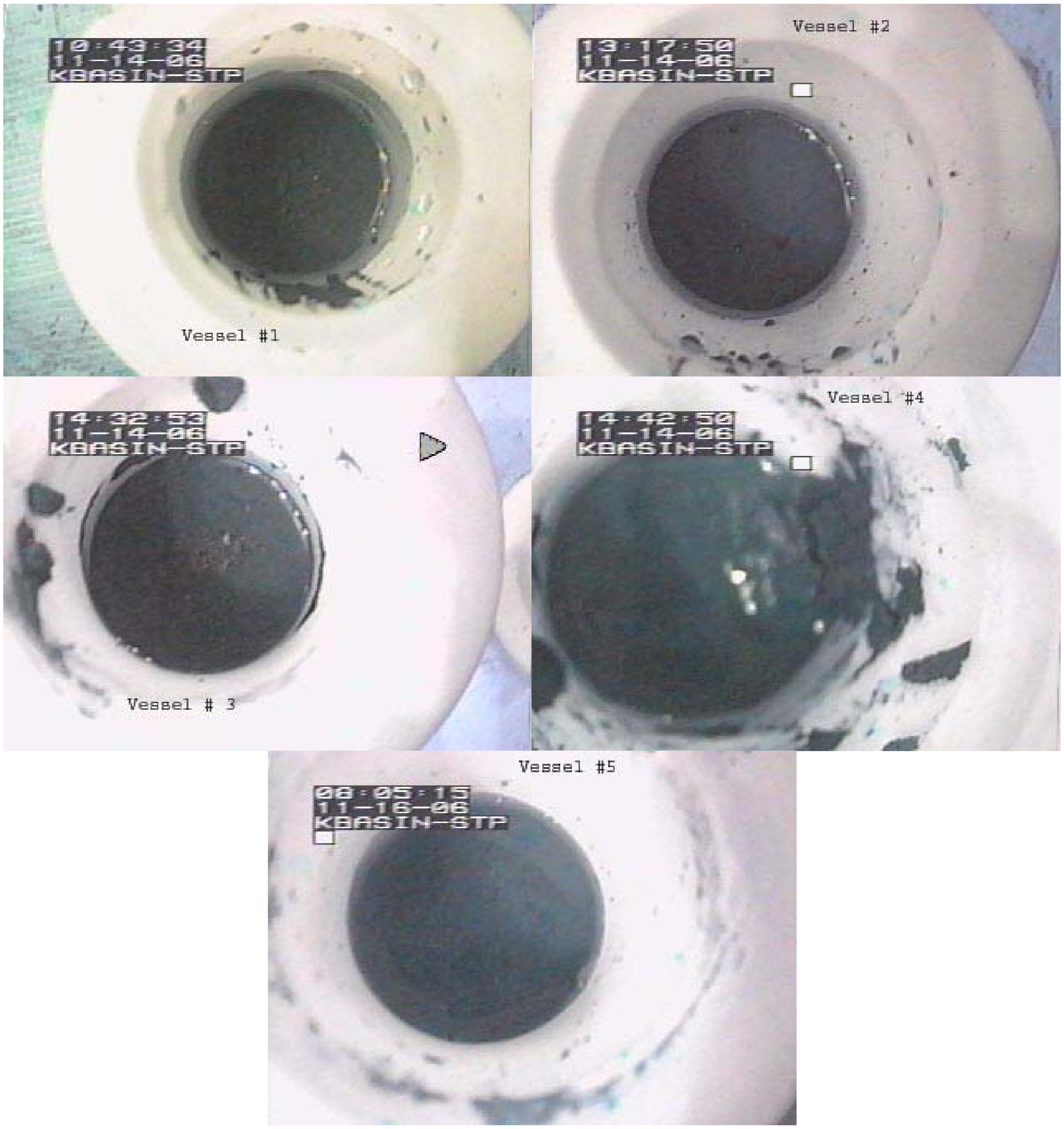

Figure 2.4. Top Views of Filled Test Vessels

The contents of each Teflon liner were blanketed with 99.997% nitrogen gas before closing. This was done by directing a stream of gas from plastic tubing into the gap between the Teflon vessel lid and bottom. After at least two minutes of gas flow, the tubing was withdrawn, allowing the lid to close on the bottom. The lower outer steel liner wall of each test vessel was fitted with a thermocouple to register the vessel temperature. Each thermocouple, located on the outside wall about 2 cm from the bottom, was fixed in placed with an epoxy cement and wrapped with heat-resistant tape. The vessels were loaded into a convection oven and heated at controlled rates and durations according to the parameters defined in Table 2.7. The tests were conducted in two groups with Tests 1 and 2 constituting the first group and Tests 3, 4, and 5 (which had identical temperature profiles) constituting the second group. The idealized temperature profile for Tests 3, 4, and 5 are shown in Figure 2.5.

Table 2.7. Operating Parameters for the STP Corrosion Process

Sludge Type/ Parameter	Corrosion Temp., °C	Heat-up Time, h	Corrosion Hold Time, h	Cooling Time, h
Container Sludge	185	28	72	12.6
Settler Sludge	185	28	6.8	2.1
KOP Sludge	185	28	72	4.7

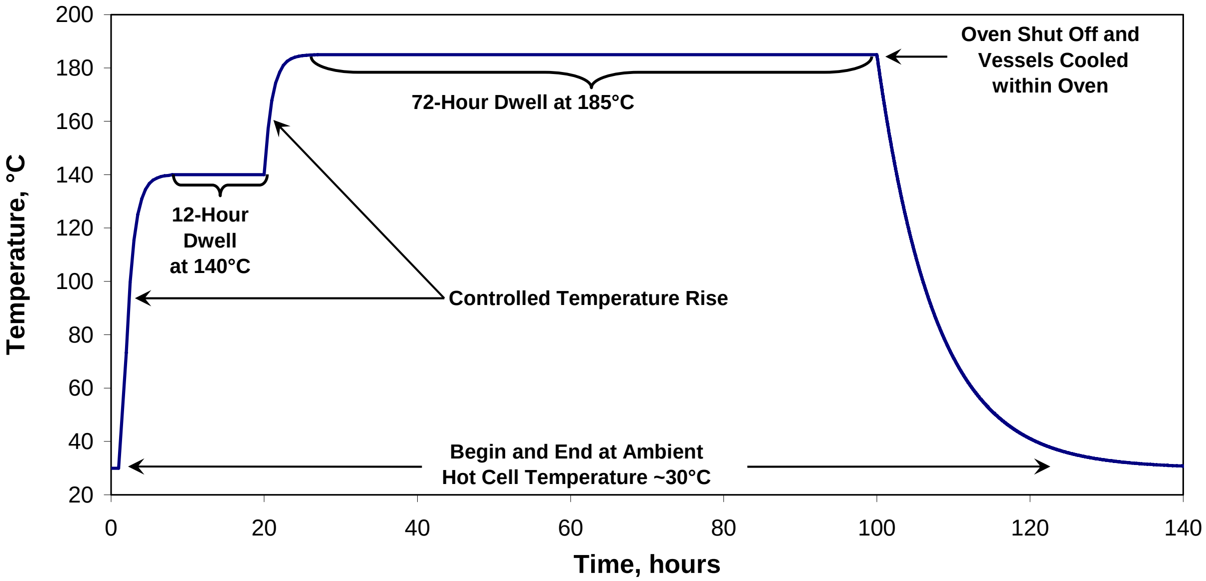

Figure 2.5. Target Vessel Temperature Profile for Tests 3 through 5

Except for Test 2, temperature profiles were designed to match envisioned ramp times and dwells for actual sludge processing (see Table 2.7). Thus, for Test 1, which contained finely particulate sludge and fuel particles simulating Settler sludge, the dwell time at the 185°C processing temperature was ~7 hours while Tests 3, 4, and 5, which used KE Container Composite or KE Container Composite Floc sludge, 72-hours at 185°C was used. For these four tests, the ~28-hour heat-up profile included a 12-14 hour dwell at 140°C. In Test 2, which contained the four larger irradiated fuel coupons, the vessel and contents were placed directly into the oven pre-heated to 185°C. The vessel was kept in the oven for 10 hours after the vessel reached 183°C and then was removed and placed on the hot cell deck to cool rapidly. The contents of the Test 2 vessel were searched for the presence of residual unreacted metal. If the residual pieces could be found, their sizes could be used to estimate the uranium metal reaction rate.

The heating cycle for Test 1 began at 09:05 on November 15 and was at ~125-135°C maximum temperature for about 5½ hours but was terminated by 16:20 of the same day when it was determined that the oven could not heat adequately. The oven settings were re-adjusted and the heating cycle for Test 1 resumed at 10:50 on November 20 according to the intended temperature profile. The profile included a 14-hour dwell at ~140°C followed by a ~7-hour dwell at ~185°C. The vessel for Test 1 was removed from the oven at 17:45 on November 21. The Test 2 vessel began heating at 17:56 on November 21 upon introduction to the oven pre-heated to 185°C and was removed from the 185°C oven at 08:20 on November 22. Tests 3, 4, and 5 began heating at 11:00 on November 27 according to the intended temperature profiles and the heat to the oven was shut off at 11:40 on December 1 with the vessels allowed to cool in the oven. All dates are in the year 2006.

The measured temperature profiles for the two sets of tests are shown, respectively, in Figures 2.6 and 2.7. It is seen that the vessel in Test 2 required about 4½ hours to reach 183°C from room temperature and cooled to 30°C within about 3 hours after removal from the oven. Tests 1, 3, 4, and 5 underwent stepped temperature increases according to the profiles intended to emulate STP process conditions including 12-to 14-hour dwells at ~140°C followed by ramping to ~185°C. Test 1 spent about 7 hours at ~185°C and Tests 3, 4, and 5 spent about 72 hours at ~185°C. Test 1 was cooled quickly (about 2 hours was required to reach 30°C) by removal from the oven while Tests 3, 4, and 5 cooled more slowly (about 14 hours to reach 30°C) by remaining in the closed and switched-off oven.

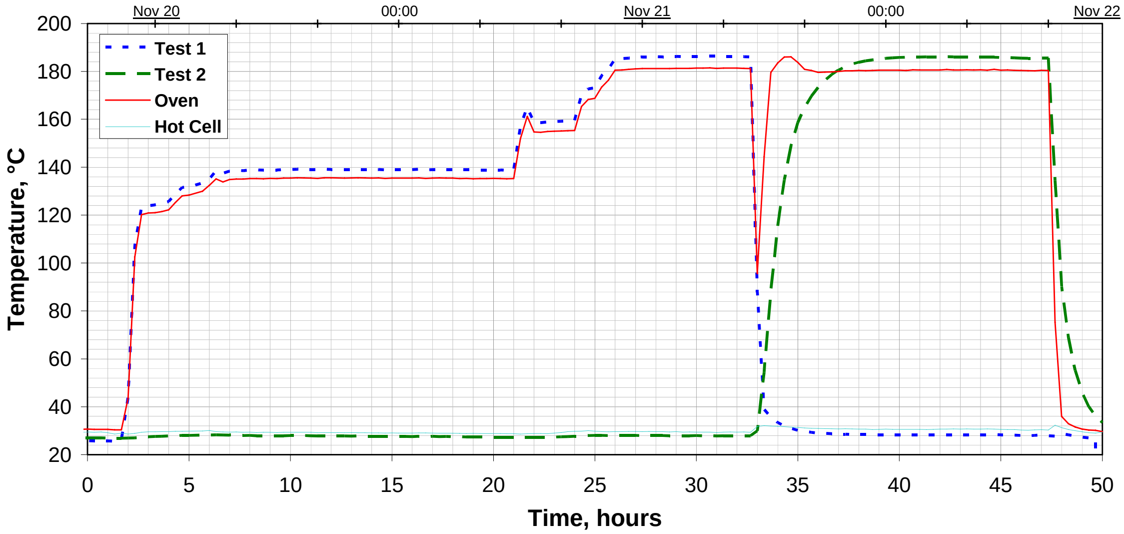

Figure 2.6. Temperature Profiles for Tests 1 and 2

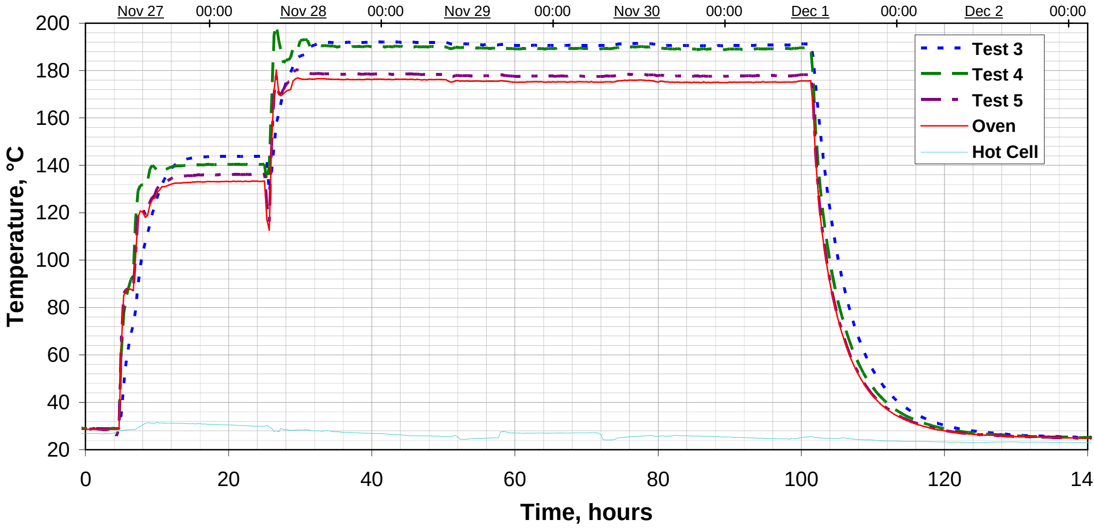

Figure 2.7. Temperature Profiles for Tests 3, 4, and 5

2.3.7 Comparison of Sludge Treatment Project Process Conditions and Laboratory Testing Conditions

It is useful to compare the conditions proposed for operation of the STP process corrosion vessel with those used in the present bench-scale tests. The tests were designed to evaluate and understand the chemical changes that may be occurring under the hydrothermal conditions of the STP process and the effects that any changes would have on sludge rheological properties. Efforts were made to simulate the full-scale plant conditions in the tests to the extent practical; however, certain conditions could not be matched. The comparison between the process and the tests is shown in Table 2.8, including a discussion on how differences may impact the use and interpretation of the findings derived from the tests.

2.4 Post-Test Examinations

Measurements of the products from the five hydrothermal tests were performed to assess their physical and chemical properties consistent with the test plan (Schmidt et al. 2006). The weights of the inner Teflon vessels with their lids and contents also were measured to determine if any weight losses occurred, such as due to loss of water through the vessel-lid closure, during the hydrothermal treatments.

The pH values of the starting and product sludges were measured using a calibrated pH meter.(a) The pH meter was calibrated with commercial buffers(b) at pH 4.01 and 7.00, the measurements made for the supernatant waters from the sludges (or from DI water slurries of sludge if insufficient water was present), and the pH values of the buffers, including also a pH 10.01 buffer, re-checked during and after the sludge measurements. The pH values of the standards matched the listed values within 0.07 pH units in all cases.

The densities of the product sludges were calculated based on the weights of the decanted product sludge and the sludge volume within the vessels determined by measuring the distance from the top of the sludge to the top edge of the vessel and the known vessel inner dimensions.

(a) Stick pH and Temperature Meter, model HI 9214, Hanna Instruments, Woonsocket, RI.

(b) Orion Application Solution.

Table 2.8. Comparison of STP Corrosion Process and Bench-Scale Tests

Parameter	STP Corrosion Vessel	Bench-Scale Test	Discussion of Comparison and Impact on Data Use
Agitation	Continuous	None	Agitation should affect physical agglomeration in agitated zones, but will not affect chemistry that results in formation of different compounds. Also, the corrosion vessel may contain un-agitated zones, such as pipes that will contain sludge at the process conditions, and may include a semi-quiescent zone at the bottom of the vessel below the impeller and nitrogen sparge ring. During a loss of agitator event, the entire vessel contents will be un-agitated or only moderately mixed, depending upon the status of the nitrogen sparge system.
Material Balance	N_2-sparged and continuously vented with significant water vapor removal.	Closed System. [Before sealing, test vessel head space was purged with nitrogen.]	Nitrogen gas would not be expected to affect the chemistry. By being conducted as closed system tests, detailed material balances were possible, which provides data on changes in settled density, water content, and potential gas holdup in the solids.
Vessel Wall Temperature	Above 185°C. Sufficient to evaporate water and maintain contents at 185°C.	Outside the test pressure vessels, temps were controlled to 185°C; temp inside the test vessel liners ≤185°C.	Heating of the corrosion vessel will be via heaters on the outside vessel wall, at temperatures in excess of the slurry temperature. This likely will increase the potential for scale formation on the heated surfaces of the STP corrosion vessel.
Vessel Wall Material	Stainless steel	Teflon	In the bench tests, the sludge was in direct contact with Teflon liners. Sludge may adhere more strongly to the actual corrosion vessel stainless steel walls than to the Teflon used in the tests.
Pressure	225 psig	Not measured; theoretically, up to 560 psig (assuming 100% U metal fuel reacted, all H_2 released to headspace and no diffusion from vessel).	Two of the tests did not contain additional uranium metal and therefore pressure was close to that of STP process. At the conclusion of all five tests, the Teflon liners were found to be under vacuum. If the H_2 had remained in the vessels, the contents should have been under pressure. Based on these post-test observations and data on H_2 permeability through Teflon, it appears likely that much of the generated H_2 diffused from the Teflon vessels or reacted with sludge constituents, resulting in test pressures near STP process conditions (i.e., test pressures always high enough to avoid boiling).
Gas Composition	162 psig H_2O, <63 psig N_2, >0 psig H_2	162 psig H_2O, 22 psig N_2, up to 376 psig H_2	

Table 2.8. Comparison of STP Corrosion Process and Bench-Scale Tests (cont'd)

Parameter	STP Corrosion Vessel	Bench-Scale Test	Discussion of Comparison and Impact on Data Use
K Basins Settler Tank Sludge (Tests 1 and 2)			
Material Processed	Actual K Basin Settler Tank Sludge	KE Canister Sludge + irradiated metallic uranium fuel typical of that stored in K Basins	For the Settler sludge tests, the test material was a KE Canister sludge composite from 11 locations in KE Basin. Approximately 75% of sludge in Settler tanks is expected to have been derived from washing KE Fuel in KE Canisters. U metal concentrations in tests were ~4 wt% (settled sludge basis). In comparison, the U metal content in Design and Safety Settler sludge are: 2.1 and 5 wt% respectively.
Solids Volume (including all water and sludge in vessel)	Initial: 5.9% End of Batch: 9.0%	Constant: 27-28% [Note: Solids content for as-settled Design Basis KE Canister sludge and Settler sludge are 25% and 35%, respectively.]	Solids concentration in test was higher than STP process target to increase the test sample size. However, both the STP corrosion process and the tests include free water above the settled sludge at the start and end of the testing. Tests represent the expected chemical and physical behavior of sludge that is allowed to settle (quiescent zones in corrosion vessel/piping). With the higher water content, in well agitated zones in the corrosion vessel, physical agglomeration and cementation are expected to be minimized.
Temperature Profile	28 h ramp to 185°C 6.8 h hold at 185°C	**Test 1:** ~34 h ramp to 185°C, 7 h hold at 185°C **Test 2:** ~4 h ramp to 185°C 10 h hold at 185°C	Temperature profile in Test 1 was a reasonable match with STP process. Ramp time in Test 2 was decreased and hold time increased by several hours to meet specific test objectives for uranium corrosion rate confirmation.
K Basins Container Sludge (Test 3, 4, and 5)			
Material Processed	Batches of actual K Basin Container Sludge	Volume-weighted nominal composite of KE sludge samples representative of KE Container sludge	For the Container sludge tests, a volume-weighted composite was prepared from KE Weasel pit, main basin floor, and fuel storage canister sludge samples. The material in this composite came from a total of 20 sample locations in KE Basin.
Solids Volume, (including all water and sludge in vessel)	Initial, 10.1% End of Batch: 20%	Constant: 23-28% [Note: Solids content for as-settled Design Basis KE Floor and Canister sludge is 25%.]	While tests were targeted to maintain solids content at 20%, higher values (23 to 28%) were used based on the slightly higher than expected solids contents found in the starting sludge samples. With the exception of the end-state in Test 4, the tests included free water above the settled sludge at the start and end of the testing, and represent the expected physical and chemical behavior of sludge that is allowed to settle (quiescent zones in corrosion vessel/piping). For Test 4, no free water was visible above the sludge at the end of the test and Test 4 exhibited the lowest shear strength (i.e., could be biased low). In well agitated zones in the corrosion vessel, with their higher water content, physical agglomeration and cementation are expected to be minimized.
Temperature Profile	28 h ramp to 185°C 72 h hold at 185°C	**Test 3, 4 and 5:** ~26 h ramp to 185°C, 72 h hold at 185°C	Temperature profiles in tests aligned with STP process targets.

In accordance with the Test Plan, the unconfined compressive strengths (UCS) of the sludge products from the five tests were determined using a pocket soil penetrometer (Figure 2.8).(a) Before use, the penetrometer readings were checked by pressing onto a calibrated analytical balance. The readings were noted at balance loadings ranging from 500 to 7000 grams (force) and compared with the readings that should have been obtained at the same force loadings. The expected and observed penetrometer readings are summarized in Table 2.9 and plotted in Figure 2.9. Based on this calibration, the as-read values obtained from the penetrometer used in the measurements of the materials from Tests 1-5 were multiplied by 1.058 to obtain the true values. This calibration is generally consistent with related vendor literature on penetrometer precision, which is given as ~±5%. The penetrometer measurement consists of pressing the ¼-inch diameter probe ¼-inch into the sludge product. The UCS was read directly from the penetrometer shaft by noting the location of the sliding white ring. The UCS value can be converted to shear strength by calculation.

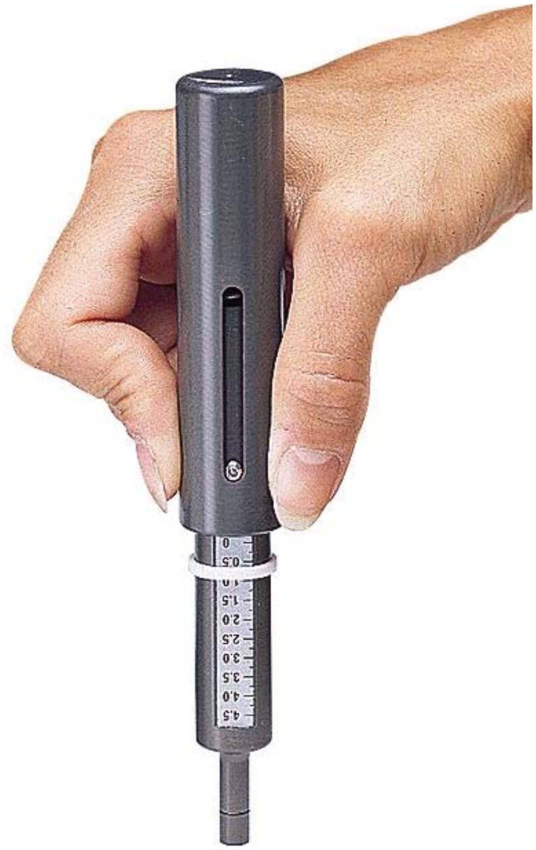

Figure 2.8. Pocket Penetrometer

(a) Marketed by Hogentogler & Co., Inc., Columbia, MD.

Table 2.9. Penetrometer Check with Analytical Balance

Balance Load, kg(f)	**Unconfined Compressive Strength, kg(f)/cm^2**			
	True[(a)]	**As-Read[(b)]**		
0.00	0.00	0.00	0.00	0.00
0.50	0.28	0.25	0.25	0.25
1.00	0.57	0.50	0.50	0.55
2.00	1.14	1.05	1.05	1.10
3.00	1.71	1.60	1.60	1.70
4.00	2.28	2.15	2.15	2.20
5.00	2.85	2.65	2.65	2.80
6.00	3.42	3.20	3.25	3.30
7.00	3.99	3.70	3.65	3.85

(a) Value of UCS for ¼-inch diameter probe taken to ¼-inch penetration is 0.5695 × Load, kg(f) (Soiltest 1984). Note that kg(f) refers to kg of force.

(b) As-read UCS, kg(f)/cm^2 = 0.5384 × Balance load, kg(f); $R^2 = 0.999$. Therefore, the as-read penetrometer value should be adjusted by the factor 0.5695/0.5384 = 1.0577 to obtain the true value. The as-read values are recorded in the Test Instruction, "Hydrothermal Testing of K Basin Sludge and N Reactor Fuel Coupons for the Sludge Treatment Project (STP)," 51623 TI04 Rev. 0, CH Delegard, November 3, 2006.

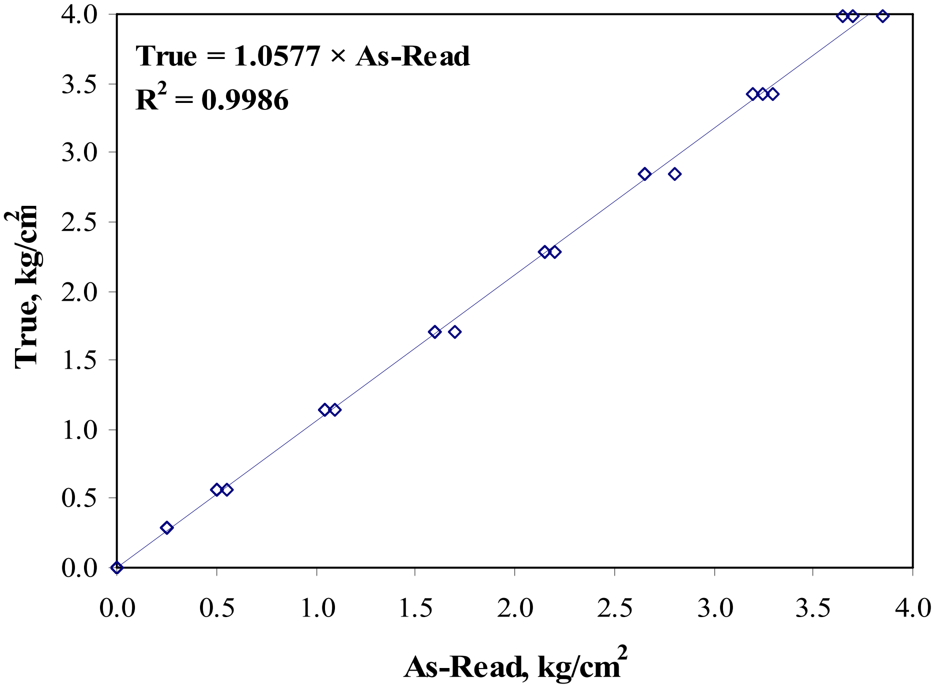

Figure 2.9. Comparison of As-Read and True Values of Compressive Strength for the Penetrometer

Further observations of the durability of the hydrothermally-processed sludges were performed by eroding intact sludge pieces with circulating water. This was done by retrieving sludge pieces from the test vessel and placing one or two intact portions of sludge into a 600-ml beaker (8.5-cm diameter) near the curved bottom edges. Four-hundred ml of distilled water were added carefully to the beaker to avoid unduly disturbing the sludge pieces. The beaker water then was agitated overhead using a 2-inch (5.08-cm) diameter four-bladed stirrer. The stirrer blades, pitched to provide a downward flow, were set to rotate 1.6-cm from the beaker bottom at 40, 100, and 300 RPM (10.6, 26.6, and 79.8 cm/s tip speeds, respectively) in staged periods ranging from 5 to 35 minutes. The sludge/water mixtures were allowed to settle between intervals of stirring and images of the settled sludge were gathered after settling to determine, by visual observation of the sludge piece sizes, the extents of their erosion.

Erosion tests were performed for sludge from Tests 1, 2, 4, and 5. The product sludge from Test 3 was sufficiently fluid that intact agglomerates could not be collected from the test vessel. For Tests 3 and 5, sludge samples were placed on screens and washed with water directed from a squirt bottle. Visual and video observations of the sludge behaviors were noted to assess durability.

The X-ray diffraction (XRD) patterns of the starting and product sludges were gathered to determine what changes in the chemical phases might have occurred by the hydrothermal treatment. The XRD patterns obtained from the sludge samples were compared with the patterns of thousands of solid compounds, winnowed based on the presence of the principal sludge elements (e.g., uranium, iron, aluminum, silicon) contained in a computerized database to identify those crystalline compounds present in the sludge. Note, however, that non-crystalline solids, such as glass, and solids that are finely particulate, such as iron hydroxide, do not produce an XRD pattern. The preparation of samples for XRD analyses and the collection of XRD scans were performed according to existing laboratory procedures.(a)

Images of the same starting materials and the products from the five tests as were examined by XRD were gathered using scanning electron microscopy (SEM). The induced x-ray spectra from the SEM also were examined in some cases by energy dispersive spectroscopy (EDS) to determine the spatial distribution of elements in the SEM image. In SEM, an electron beam is directed at the sample being investigated. The electron beam interacts with the sample to cause it to emit electrons from its surface. The emitted electrons are detected to produce a high resolution image of the sample. The emitted electrons lost from the sample must be replaced by other electrons within the sample. These electrons, in turn, lose energy, in the form of X-rays, when they drop down to replace the emitted electrons. The X-ray energies are characteristic of the chemical element from which the electrons are emitted. The energies are detected and interpreted by EDS to identify the elements present in the area of electron beam impingement to depths of ~1 μm.

The SEM/EDS examinations were performed for air-dried sludge particles placed onto conductive carbon tape that were then carbon-coated. The sample preparation and examination were performed by established procedures.(b)

(a) Scheele, RD and CH Delegard. 2005. *Preparing Sealed Radioactive Samples for XRD and Other Purposes*, RPL-PIP-4, Pacific Northwest National Laboratory, Richland, WA.
Schaef, HT. 2004. *Operation of Scintag Pad-V X-Ray Diffractometer*, RPL-XRD-PIP, Pacific Northwest National Laboratory, Richland, WA.

(b) MacFarlan, PJ. 2006. *Scanning Electron Microscope Examinations*, RPL-611A-SEM, Rev. 1, Pacific Northwest National Laboratory, Richland, WA.

2.5 Simulated Sludge Cold Shake-Down Testing and Results

Before initiating tests with archived K Basin sludge and irradiated N Reactor fuel samples at prototypical STP temperatures and time, two tests with non-radioactive simulated K Basin sludges were conducted using the test apparatus described in Section 2.1. The primary objective of this "cold testing" was to design and evaluate the test apparatus and protocols for hot cell application. A secondary objective was to gain some insight on whether the textures of the two simulant non-radioactive sludge types would be altered by the thermal treatment. Results from the cold testing are briefly summarized here. Detailed results are shown in Appendix C and were previously communicated in a project letter report.[a]

The non-radioactive K Basin sludge simulants, whose compositions are shown in Table 2.10, were prepared to generally mimic properties of genuine Container Sludge at the end of a STP corrosion cycle. One simulated sludge contained OIER and blow sand. The second sludge simulant contained aluminum hydroxide, ferric oxide hydroxide, and blow sand at mass ratios roughly proportional to those expected for nominal KE Container Sludge. The second simulant also contained the flocculent that is being used in the KE Basin.

Table 2.10. Simulated Sludge Compositions

OIER Simulant (Test C-1)		**Flocculated Sludge Simulant (Test C-2)**[a]	
Component	**Value**	**Component**	**Value**
Blow sand, wt%	40.6	Blow Sand, wt%	20.5
NRW-100 (anion), wt%	13.2	$Al(OH)_3$ (gibbsite), wt%	20.5
NRW-400 (cation), wt%	6.9	$Fe_5O_7(OH)\cdot 4H_2O$, wt%	27.4
Water, wt%	39.3	Water, wt%	31.5
		Flocculating agent, wt%	0.0269
Total, wt%	100.0	Total, wt%	100.0
Water, vol%	51.2	Water, vol%	55.2
(a) The flocculated sludge simulant is 10.4 wt% aluminum, 23.3 wt% iron, and 14.0 wt% silicon, dry basis, assuming the blow sand is SiO_2.			

The temperature profile for the cold tests was targeted to simulate the STP corrosion vessel profile for Container sludge. Heating from room temperature to 140°C required about 14 hours and was followed by a dwell at 140°C for 12 hours. Heating from 140°C to 185°C required about 12 hours and was followed by a 72-hour dwell at 185°C. Cooling from 185°C to 40°C required about 33 hours.

The contents of the test vessels were examined after the hydrothermal treatment. Water losses were 0.44 g and 0.16 g for the OIER and flocculated sludge tests, respectively, or 1.4 wt% and 0.5 wt% of the initial water. A layer (~0.5-cm or less) of free water observed upon opening each vessel indicated that the simulants remained saturated during testing. The OIER and flocculated sludge solution pHs (~7.06 and 8.80, respectively) were not affected by the thermal testing.

The OIER simulant showed no signs of agglomeration and poured readily from the Teflon vessel. No evidence of resin bead melting or fusing was observed, and sieving tests confirmed that no agglomeration occurred.

(a) "Results from Sludge Treatment Project Process Chemistry Validation Tests – Cold Shake-Down Testing," 51623-RPT01, CH Delegard, AJ Schmidt, PK Berry, and SA Bryan, September 29, 2006.

The texture of the flocculated sludge simulant that contained the mixed aluminum hydroxide, ferric oxide hydroxide, and sand was greatly affected by the heating. Before heating, the flocculated simulant exhibited a pudding-like consistency. Instead of pouring from the reaction vessel as in its original slurry condition, the flocculated sludge was removed from the vessel as a monolithic block that had significant structural integrity (see Figure 1.2). Consistent with the post-test protocols described in Section 2.4, the resistance of the product sludge solids to a soil penetrometer and erosion by circulating water were measured. The shear strength of the product sludge was found to be 36,000 Pa ± 5000 Pa. Significant erosion of agglomerates cut from the monolith product was observed at mixing tip speeds of 20 to 40 cm/sec.

Phase analysis by XRD of the starting aluminum and iron hydroxide crystalline phases had been done previously. The aluminum hydroxide was found to be pure gibbsite [γ-$Al(OH)_3$; density (ρ) 2.42 g/cm^3] while the iron hydroxide was found to be poorly crystalline "6-line" ferrihydrite [$Fe_5O_7(OH)\cdot 4H_2O$; $\rho \cong 3.9$ g/cm^3] with lesser amounts of goethite [α-$FeO(OH)$] and hematite (α-Fe_2O_3). After heating at 185°C, the gibbsite in the sludge had transformed entirely to boehmite [γ-$AlO(OH)$; ρ=3.01 g/cm^3] while the ferrihydrite had transformed almost entirely to hematite (ρ=5.24 g/cm^3) with only some residual, but better crystallized, ferrihydrite.

After the initial set of cold testing, several smaller-scale tests (Tests T-1, T-2 and T-3) were conducted with aluminum hydroxide, ferrihydrite, and an aluminum hydroxide/ferrihydrite [$Al(OH)_3/Fe_5O_7(OH)\cdot 4H_2O$] mixture to better understand which components formed agglomerates under hydrothermal conditions and to generate samples of known composition to evaluate the use of optical microscopy and scanning electron microscopy for understanding sludge agglomeration. The tests showed that $Al(OH)_3$ agglomerated with itself and that $Fe_5O_7(OH)\cdot 4H_2O$ remained disperse after hydrothermal treatment. The self-agglomeration of the $Al(OH)_3$ occurred even with the $Al(OH)_3/Fe_5O_7(OH)\cdot 4H_2O$ mixture. The interiors of the cemented agglomerations observed when broken after hydrothermal treatment were white, indicating the aluminum boehmite phase.

Some of the results from these cold tests are discussed in Section 3.0 to provide additional insights into the physical and chemical changes observed during testing with the actual sludge materials.

3.0 Results and Discussion

Results and observations of the five tests with K Basin sludge are presented in this section. Section 3.1 describes the physical properties (weight losses, densities, water concentrations) and pH observations of the products of the five tests, and compares those results with those of the starting materials. Section 3.2 describes the chemical phases of the materials in the five tests as determined by XRD. Comparison of the phases found before and after hydrothermal treatment indicates some of the chemical transformations that occurred. Scanning electron microscopy images of the initial and product materials are described in Section 3.3; EDS of selected materials also was done. The SEM showed particle sizes and shapes while EDS identified the chemical elements present in the particles. Analysis and interpretation of the solid phase changes is presented in Section 3.4. The strength properties of the test products are explained in Section 3.5. Strength tests include soil penetrometer measurements and observations of resistance to water erosion.

3.1 Physical and pH Measurement Results

Measurement results of the physical dimensions of the contents of each test vessel and the calculations derived from these measurements are provided in Appendix B.

The test vessels sealed the contents well during the heating and cooling cycles with water losses being less than 1 gram for each test. Supernatant liquids at the completion of each test were withdrawn and the liquid quantities determined by weight difference. The water concentrations in the settled sludges before and after testing, calculated based on the starting sludge compositions and the added and withdrawn or lost water weights, are shown in Table 3.1. The water concentrations in the decanted product sludges from Tests 1, 3, 4, and 5 were measured by drying in an oven set to 105°C; water concentration in the sludge sample from Test 2 was not obtained due to an experimental mishap. The gas void volumes in the product settled sludges were calculated based on the weights of the decanted settled sludges, the total sludge volumes, and their expected volumes based on the volumes of settled sludge added, uranium metal reaction (as applicable), and the amounts of water lost by evaporation and decantation. The product solid particle densities were calculated by deducting the contributions of water weights and volumes and estimated gas void volumes from the weights and volumes of the settled product sludge.

Table 3.1. Supernatant Water and Settled Sludge Properties

Property	Test				
	1[(a)]	2[(a)]	3[(b)]	4[(b)]	5[(c)]
Post-heating weight loss, g	0.35	0.21	0.64	0.82	0.54
Supernatant Liquid					
Initial weight, g[(d)]	10.73	10.24	-0.72	-0.14	11.86
Final weight, g[(e)]	18.26	15.10	3.60	0.00	2.04
Settled Sludge					
Initial water concentration, wt%[(f)]	24.1	23.9	48.2	51.8	44.9
Product water concentration (calculated), wt%	19.0	20.6	45.1	50.0	49.5
Product water concentration (measured), wt%	16.1	ND	50.9	52.8	49.3
Initial water concentration, vol%[(f)]	66.7	66.5	77.0	77.3	70.4
Packed (gas void-free) product water concentration, vol%	59.1	61.5	74.5	77.0	70.9
Initial bulk density, g/cm^3[(f)]	2.76	2.78	1.60	1.53	1.52
As-found (including gas void) product bulk density, g/cm^3	2.23	2.25	1.86	1.19	1.36
Packed (gas void-free) product bulk density, g/cm^3	3.12	2.99	1.65	1.54	1.43
Initial particle density, g/cm^3	6.29	6.31	3.61	3.26	2.83
Product particle density, g/cm^3	6.17	6.18	3.56	3.34	2.49
Gas Void					
Estimated gas void in product, vol%	28.4	24.7	none	22.9	4.8

ND – not determined.
(a) KC-2/3 M250 + U metal.
(b) KE Container Composite Floc (+ U metal in Test 3).
(c) Non-flocculated KE Container Composite plus added KC-6 sludge containing OIER.
(d) Includes water added plus water provided with the OIER in Test 5 and decreased by water occupied in fuel particles in Tests 1 and 3 and water lost through evaporation during vessel loading as determined by weight loss.
(e) Decanted water only. Total water loss also should include evaporative loss that occurred in hydrothermal processing. Evaporative losses as determined by weighing are shown in the first row as Post-heating weight loss.
(f) Includes starting sludge and metal added for Tests 1, 2, and 3 and OIER beads added for Test 5.

The pH of each supernatant liquid sample was measured. For Test 4, which had no free supernatant liquid, a ~2-g portion of the sludge solids was mixed with ~5-ml of DI water and the pH of the mixture measured. The results are compared with those of the starting sludge materials in Table 3.2.

Table 3.2. Supernatant Liquid/Sludge pH

pH	Test				
	1[(a)]	2[(a)]	3[(b)]	4[(b)]	5[(c)]
Initial	4.73. 4.77	4.73, 4.77	4.80	4.80	5.23, 5.39 7.4 (KC-6)[(d)]
Final	4.98	3.85, 4.46	5.88, 5.86	6.84, 6.79	6.66, 6.71

(a) KC-2/3 M250.
(b) KE Container Composite Floc.
(c) KE Container Composite (not flocculated) with KC-6.
(d) From Bryan et al. (2004).

3.1.1 Tests 1 and 2

Tests 1 and 2, containing KC-2/3 M250 sludge (68.3 wt% uranium, dry basis, with ~1.9 wt% aluminum and 1.4 wt% iron) and metallic fuel particles, were meant to simulate the behavior of Settler tank sludge under the proposed STP hydrothermal processing. Because the Test 1 and 2 experimental conditions only differ substantially in the added irradiated fuel fragments' particle sizes and the process heating time and temperature profile, the tests are very similar. As such, the Test 1 and 2 findings should yield comparable experimental results. This expectation is borne out in the results presented in Tables 3.1 and 3.2 and in solid phase and strength analyses to be discussed later in this report.

Water losses from Test 1 and 2 during the 7-10 hour hydrothermal treatments at 185°C were 0.35 and 0.21 g, respectively, and lower than the remaining three longer duration tests. The settled sludges of Tests 1 and 2 released ~7.3 and 4.9 cm^3, respectively, of additional supernatant water during heating. As a result, the water concentrations in the settled sludges decreased from ~24 wt% in the starting sludge to ~20%, on average, for the product sludge. The measured water concentration for Test 1 settled sludge was about 16 wt%, agreeing, within experimental error, with the calculated value (19.0%). Water concentration in Test 2 was not measured due to experimental mishap. As will be shown in the following section describing the XRD results, metaschoepite [$(UO_2)_8O_2(OH)_{12}(H_2O)_{10}$; equivalent to $UO_3{\cdot}2H_2O$] is the most prominent phase found in the starting sludge and $UO_3{\cdot}0.8H_2O$ is the most prominent phase in the product sludge. If all uranium (not including the added fuel particles) was present as metaschoepite in the starting sludge and converted quantitatively to $UO_3{\cdot}0.8H_2O$ during hydrothermal processing,

$$UO_3{\cdot}2H_2O \rightarrow UO_3{\cdot}0.8H_2O + 1.2\ H_2O$$

about 5.5 and 5.3 cm^3 of water would be released, respectively, in Tests 1 and 2. Although the amount of metaschoepite present in the starting sludge is not known, it is plausible that at least some of the additional supernatant water from Tests 1 and 2 arose from metaschoepite dehydration.

Despite loss of water (with its density of 1.00 g/cm^3) from the settled sludge both by evaporation and release to the supernatant layer, the settled densities in both test sludges decreased from about 2.77 g/cm^3 before hydrothermal reaction to about 2.24 g/cm^3 after reaction. The decreased density can be only partially due to the conversion of uranium metal in the fuel particles to the $UO_{2.x}$ found, as will be shown, by XRD. The fuel particles have a density of 16.8 g/cm^3 (which includes both uranium metal and cladding; Plys and Schmidt 2006) whereas the product $UO_{2.x}$ (modeled as $UO_{2.25}$) plus unreacted Zircaloy fines have a combined density of 10.8 g/cm^3 (0.93 g U per g of fuel reacting to $UO_{2.25}$ with density of 11.3 g/cm^3 and 0.07 g Zircaloy per g of fuel with density of 6.55 g/cm^3). The ~5 g of added metallic fuel particles, having 0.30 cm^3 volume, used in Tests 1 and 2 thus would have grown in sludge volume from 0.50 cm^3 (includes interstitial water) and 0.30 cm^3, respectively, to ~1.76 cm^3, an increase of only 1.26 to 1.46 cm^3 in sludge solids volume. However, the observed Test 1 and 2 settled sludge volumes (~45.0 and 43.0 cm^3) increased ~7.5 cm^3, on average, after 7-10 hours of hydrothermal treatment at 185°C (to 52.3 and 50.8 cm^3, respectively). Accordingly, most of the density loss is attributed to the retention of gas in the sludge, primarily as hydrogen from the reaction of irradiated metallic uranium fuel with water.

The gas void volumes in the settled sludges produced in Tests 1 and 2 were estimated by deducting the starting settled sludge and water volumes (adjusted for evaporated water and water removed by decantation) from the observed volume of the settled and drained product sludge. The gas void volumes in Tests 1 and 2, 14.9 and 12.5 cm^3, respectively (Appendix B), comprise 26.6 vol% (on average) of the decanted settled sludge volumes as shown in Table 3.1.

Gas production in Tests 1 and 2 mostly was from the reaction of uranium metal with water to produce hydrogen. However, as shown in prior gas generation testing experiments, significant amounts of carbon dioxide (CO_2) also are released when sludges were heated in water at lower temperatures. The sludge KC-2/3 M250 was found to produce 4.2×10^{-5} moles of CO_2 per gram of settled sludge at temperatures below 100°C (Delegard et al. 2000). In the seven years since this gas generation testing, the KC-2/3 M250 sludge has been stored in a hot cell at ~30°C meaning that CO_2 production should be lower than this calculated value. For Tests 1 and 2, which each contained about 5 grams of fuel particles (generally composed of 93 wt% uranium metal), about 0.039 moles of H_2 (about 940 cm^3 of gas at room temperature and atmospheric pressure, RTP) would be produced by complete uranium corrosion. At the same time, it is judged at most 0.0049 moles of CO_2 (~120 cm^3 at RTP) would be produced – assuming the reaction to product CO_2 occurs at 185°C and went to completion.

The particle densities of the solids present in the products from Tests 1 and 2 were calculated, as shown in Appendix B, by dividing the dry solids mass by the solids volume (adjusted by deducting the volumes of the retained water and the gas void volume from the total sludge volume). The particle densities decreased slightly from 6.29 and 6.31 g/cm^3, respectively, to 6.17 and 6.18 g/cm^3 due to the corrosion of the uranium metal fuel to $UO_{2.x}$. The particle density of KC-2/3 M250 sludge when measured in 1999 was 7.57 g/cm^3 (Bredt et al. 1999). The decrease in particle density is consistent with the oxidation of the uranium materials to less dense phases during hot cell storage. Phase changes will be discussed later in light of the XRD analyses.

The pH of the supernatant solutions removed from Tests 1 and 2 were 4.98 and 4.16, respectively, compared with about 4.75 (on average) for the starting sludge. The starting sludge pH is lower than that expected for equilibration of the sludge waters with atmospheric carbon dioxide, CO_2, to form carbonic acid (pH ~5.65). It is possible that the lower pH was caused by radiolysis of atmospheric nitrogen during sludge storage. Radiolysis of humid air produces nitric acid (HNO_3; Choppin et al. 2002) and radiolytic nitrate was observed in long-term testing of UO_2 corrosion (Wronkiewicz et al. 1996). The observed pH increased slightly (~0.2 pH units) after hydrothermal reactions for Test 1 and decreased about 0.6 pH units for Test 2. As shown in Table 3.2, the reproducibility of the duplicate pH measurements was ~0.05 pH units except for those of Test 2. Given the higher uncertainty of the Test 2 measurement, the observed pH changes are near the measurement precision.

3.1.2 Tests 3 and 4

Tests 3 and 4 were performed to investigate the behavior of flocculated KE Containerized Sludge in the STP process. The tests differed in that Test 3 contained irradiated fuel particles while Test 4 did not. Both tests used the KC Container Composite sludge, prepared from floor, pit, and canister sludge samples, that was blended with flocculating agent to produce a flocculent concentration in the settled sludge equivalent to that anticipated for containerized sludge. The composite sludge contained ~20 wt% iron, ~16 wt% uranium, ~7.8 wt% aluminum, and ~2.8 wt% silicon (dry basis). Because the flocculent increased the volume of the parent settled sludge, supernatant liquid was not added to either test. Both tests underwent prototypic heating and cooling cycles with 72 hours dwell time at 185°C. The results of Test 3, which contained irradiated fuel particles, may be compared directly with those of Test 4, which did not, to determine the effects of fuel addition on the processed sludge properties.

Tests 3 and 4 lost 0.64 g and 0.82 g of water, respectively, by evaporation from the Teflon test vessels during the hydrothermal step (Table 3.1). Though begun with no supernatant liquid, Test 3 produced

3.6 cm^3 of removable supernatant water after heating whereas Test 4 released no supernatant liquid and the top surface appeared to be dry upon opening the test vessel. The water concentration in the Test 3 settled sludge decreased from 48.2 wt% before processing to 45.1 wt% following the evaporative water loss and supernatant water decantation. The water concentration in Test 4 decreased only slightly (from 51.8 initially to 50.0 wt%). Experimentally measured water concentrations in Test 3 and 4 settled sludge samples, 50.9 and 52.8%, respectively, agree within experimental error with the calculated water concentrations but the measurement uncertainties are too great to make statements about the relatively small differences between the two tests.

Although the sludge in Test 3 contained added irradiated metallic uranium fuel particles, the sludge evidently was sufficiently fluid that, unlike Tests 1 and 2, the product hydrogen gas was not retained. The Test 3 product sludge density (1.86 g/cm^3) was greater than that of the starting sludge (1.60 g/cm^3).

The Test 4 settled sludge density decreased from 1.53 g/cm^3 to 1.19 g/cm^3, strongly suggesting that gases were created and retained in the product sludge. The estimated gas void volume in the Test 4 product (~17 cm^3) comprised about 23% of the product volume. The top of the Test 4 sludge product also appeared to be vesicular, as shown in photographs later in this report, supporting the contention that the product sludge contained gas voids despite the absence of uranium metal.

The gas produced in Test 4 likely was CO_2 based on the observation of significant CO_2 generation during closed-vessel heating of various K Basin sludge materials during the three gas generation test series at ~33-95°C. The flocculated KE Container Composite sludge used in the present testing contains portions from KC-2/3 (whole), KC-4, KC-5 P250, and FE-5 sludge samples. The CO_2 yield for these constituent sludges were 5.8×10^{-5}, 2.5×10^{-5}, 1.3×10^{-4}, and 7.9×10^{-6} moles per gram of settled sludge, respectively, based on gas generation tests run up to 95°C (Delegard et al. 2000 for KC-2/3, KC-4, and KC-5; Bryan et al. 2004 for FE-5). The weight-averaged CO_2 production rate for the KE Container Composite sludge is 5.7×10^{-5} moles/g based on the constituent values and 4.6×10^{-5} moles/g for the flocculated and settled KE Container Composite sludge used in Tests 3 and 4. Though CO_2 still was being produced slowly at the ends of the prior 95°C tests (run as long as ~3600 hours), the component sludges have been stored for about seven years since that time at warm hot cell conditions. This means that the CO_2 production likely is lower than the projected values. The ~91 grams of flocculated KE Container Composite sludge used for each of the Tests 3 and 4 would produce about 0.0042 moles of CO_2 (~100 cm^3 at RTP) at the projected 4.6×10^{-5} moles/g yield (assuming gas generation behavior at 185°C is similar to behavior observed at temperatures less than 100°C). In comparison, the amount of H_2 produced in Test 3 would be 0.039 moles (~940 cm^3 at RTP); Test 4 has no added fuel and thus no expected H_2 production.

The calculated density of the particles found in Test 3 (3.61 g/cm^3 initially and 3.56 g/cm^3 in the product) was higher than that of Test 4 (3.26 g/cm^3 initially and 3.34 g/cm^3 in the product) as would be expected by the presence of fuel metal in the Test 3 starting sludge.

The pH of the supernatant solutions removed from Tests 3 and 4 were 5.87 and 6.82 (on average, respectively) compared with about 4.80 for the starting sludge (Table 3.2). Again, the starting sludge pH is lower than the pH ~5.65 expected for water absorption of atmospheric CO_2 to form carbonic acid but radiolytic HNO_3 may be a factor. The pH increased about 1 pH unit for Test 3 and about 2 pH units for Test 4 during hydrothermal treatment.

3.1.3 Test 5

Test 5 was conducted with flocculent-free KE Container Composite sludge and OIER beads from sludge sample KC-6. The objective of Test 5 was to determine the effects of OIER on sludge texture or consistency. In particular, Test 5 was conducted to determine if OIER beads would soften during hydrothermal treatment and congeal and agglomerate either with themselves or with other sludge solids. Because of the presence of OIER beads, the KE Container Composite sludge is diluted to ~17 wt% iron, ~13 wt% uranium, ~6.7 wt% aluminum, and ~2.4 wt% silicon (dry basis) in the Test 5 sludge mixture. Test 5 also contained nearly 12 cm^3 of supernatant liquid, provided partially by the KC-6 component (Table 3.1). Test 5 underwent hydrothermal treatment concurrently with Tests 3 and 4 and thus experienced heating and cooling cycles prototypic of STP processing with 72 hours dwell time at 185°C.

Water loss from Test 5 was 0.54 g, slightly less than that observed for the parallel Tests 3 and 4 (Table 3.1). Unlike Tests 1, 2, and 3, the quantity of supernatant water in Test 5 decreased by hydrothermal treatment (the amount of water loss/gain from Test 4 was inconclusive). Accordingly, the water concentration in the starting settled sludge, 44.9 wt%, increased to 49.5 wt% in the product settled sludge as determined by mass balance, essentially matching the measured water concentration of 49.3 wt%.

The redistribution of water from the supernatant to the settled sludge decreased the settled sludge density from 1.52 g/cm^3 to 1.43 g/cm^3 in the packed product. Loss of density in the unpacked settled sludge to 1.36 g/cm^3 occurred because of the apparent retention of gas. The estimated gas void volume, 2.9 cm^3 (Appendix B), comprised ~5% of the settled sludge volume. In the absence of uranium metal in this test, the gas most likely was CO_2. About 0.0038 moles of CO_2 (90 ml at RTP) would be produced at the projected 5.7×10^{-5} moles CO_2/g yield of the KE Container Composite settled sludge assuming the reaction occurred at STP conditions and went to completion.

The calculated particle density of the Test 5 sludge, which used non-flocculated KE Container Composite sludge and included OIER, initially was 2.83 g/cm^3 and decreased to 2.49 g/cm^3 after hydrothermal treatment. As might be expected, Test 5 product particle density is lower than that of Test 4 conducted with flocculated KE Container Composite Sludge but without OIER.

The pH of the starting non-flocculated KE Container Composite sludge used in Test 5 was 5.31 (Table 3.2); the added KC-6 OIER sludge pH was 7.4. With the OIER likely acting as a pH buffer, the product sludge pH after hydrothermal treatment was 6.68 (average of two measurements).

3.2 XRD Analyses

The crystalline phases present in the starting and product sludges were determined by XRD. Note that XRD cannot identify non-crystalline (amorphous) phases. Therefore, the presence of very fine (nanometer-scale) particles or non-crystalline materials (e.g., glass) is not registered by XRD. Three samples were taken from Test 1 materials. One sample (Test 1) was representative of the entire Test 1 product. Samples Test 1 Black and Test 1 Green were taken, respectively, from portions that contained black and green solids. Similar areas of black and green solids also were observed in the Test 2 products. The XRD results are summarized in Table 3.3 and presented for Tests 1 and 2 in Figure 3.1 and for Tests 3, 4, and 5 in Figure 3.2. The scans were displaced in 1000-CPS increments in the vertical scale in Figure 3.1 and in 500-CPS increments in Figure 3.2.

Table 3.3. XRD Analysis Results

Tests 1 and 2		**Prominence in Sludge(a)**				
		Initial	**Product**			
Phase	**PDF #(b)**	**KC-2/3 M250**	**Test 1**	**Test 1 Black(c)**	**Test 1 Green(c)**	**Test 2**
Metaschoepite, $UO_3\cdot 2H_2O$	43-364	H	N	N	N	N
Uraninite, UO_2	41-1422	N	N	M	N	N
U_4O_9	75-944	N	L	M	L	L
$UO_{2.34}$	75-456	N	N	M	L	L
Uranium oxide hydrate, $UO_3\cdot 0.8H_2O$	53-877	N	H	H	H	H
$UO_3\cdot H_2O$	13-242	N	H	H	H	H
Soddyite, $(UO_2)_2SiO_4\cdot 2H_2O$	79-1323	N	L	L	L	L
Quartz, SiO_2	65-466	L	?	?	?	?

Tests 3, 4, and 5		**Prominence in Sludge(a)**				
		Initial	**Product**		**Initial**	**Product**
Phase	**PDF #**	**KE Cont Comp Floc(c)**	**Test 3**	**Test 4**	**KE Cont Comp(c)**	**Test 5**
Metaschoepite, $UO_3\cdot 2H_2O$	43-364	H	N	N	H	N
Becquerelite, $Ca(UO_2)_6O_4(OH)_6(H_2O)_8$	84-1505	H	N	N	H	L
Calcium uranium oxide hydrate, $CaU_3O_{10}\cdot 4H_2O$	30-283	L	N	N	?	N
Ianthinite, $[U_2(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$	12-272	N	N	H	N	?
Uranium octoxide, U_3O_8	76-1850	N	N	H	N	M
UO_2	41-1422	N	H	N	N	?
Uraninite, U_4O_9	75-944	N	N	L	N	?
$UO_{2.34}$	75-456	N	H	L	N	L
Uranium oxide hydrate, $UO_3\cdot H_2O$	13-242	N	M	N	N	N
Eskolaite, Cr_2O_3(d)	72-4555	L	L	L	L	L

(a) H – high; M – medium; L – low; ? – possible; N – not observed.
(b) PDF # is the powder diffraction file numer.
(c) Test 1 Black and Test 1 Green are black- and green-colored samples taken from the Test product. KE Cont Comp is flocculated KE Container composite sludge. KE Cont Comp is non-flocculated KE container composite sludge.
(d) Existence as Cr_2O_3 is unlikely; another phase of similar structure was found.

Uranium phases were conspicuous for both sets of tests whereas non-uranium phases were limited to the corundum internal standard (Al_2O_3), talc (an impurity introduced to some samples by the powder used with radiological gloves), and quartz (SiO_2, present in K Basin sludges from infiltrated soils, sand filters, or concrete sloughing). A phase isostructural with Cr_2O_3, eskolaite, also was found in the KE Container Composite sludges and its products (the flocculated sludge and the Test 3, 4, and 5 products). The actual presence of Cr_2O_3 at concentration sufficient to find by XRD is unlikely. Although the flocculated and non-flocculated KE Container Composite sludges used in Tests 3, 4, and 5 contained 20.3 wt% iron (dry basis), no iron phases were found in either the starting sludges or in the test products.

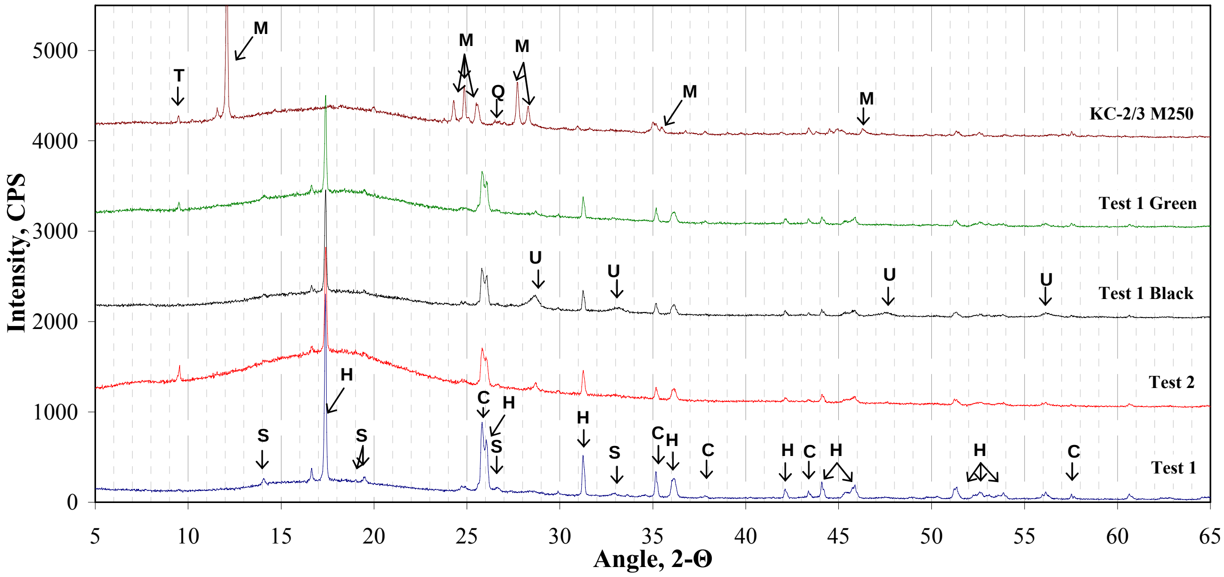

Figure 3.1. XRD of Sludge Before (KC-2/3 M250) and After (Test 1 and 2) Hydrothermal Treatment

C = corundum, Al_2O_3, internal standard
T = talc, glove powder contaminant
Q = quartz, SiO_2
M = metaschoepite, $UO_3{\cdot}2H_2O$
U = uraninite, $UO_{2.x}$ (UO_2, U_4O_9, $UO_{2.34}$)
H = uranium oxide hydrate, $UO_3{\cdot}0.8H_2O$, $UO_3{\cdot}H_2O$
S = soddyite, $(UO_2)_2SiO_4{\cdot}2H_2O$

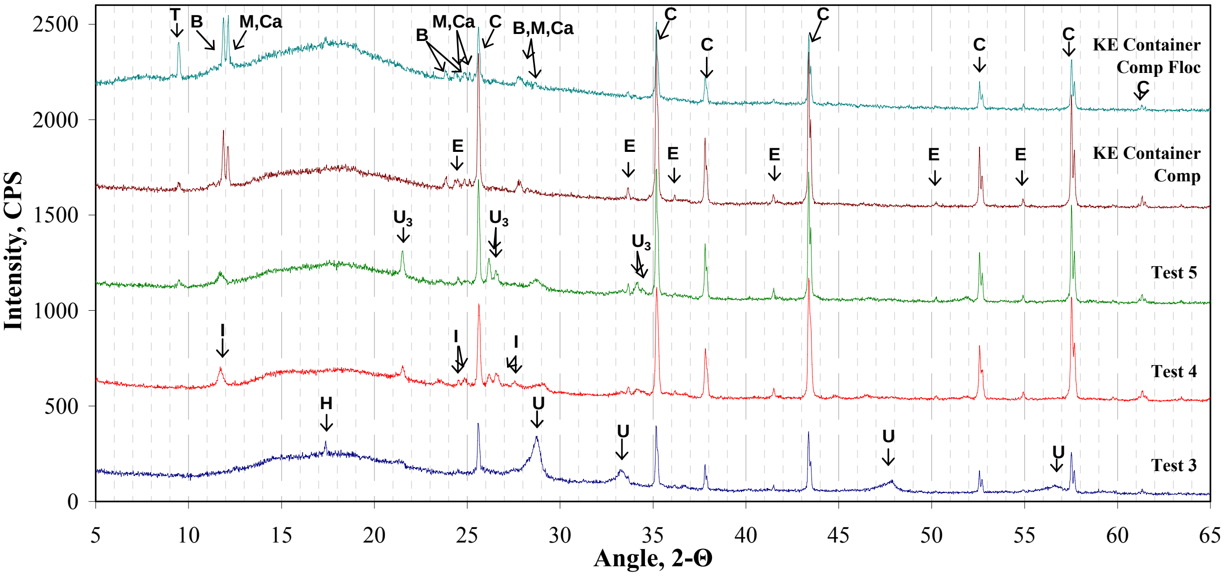

Figure 3.2. XRD of Sludge Before (KE Container Comp Floc and KE Container Comp) and After (Tests 3, 4, and 5) Hydrothermal Treatment

C = corundum, Al_2O_3, internal standard
T = talc, glove powder contaminant
E = eskolaite, Cr_2O_3, unknown isostructural phase
B = becquerelite, $Ca(UO_2)_6O_4(OH)_6(H_2O)_8$
M = metaschoepite, $UO_3{\cdot}2H_2O$
Ca = calcium uranium oxide hydrate, $CaU_3O_{10}{\cdot}4H_2O$
I = ianthinite, $U_2(UO_2)_4O_6(OH)_4(H_2O)_4{\cdot}5H_2O$
U = uraninite, $UO_{2.x}$ (UO_2, $UO_{2.25}$, $UO_{2.34}$)
U_3 = uranium octoxide, U_3O_8
H = uranium oxide hydrate, $UO_3{\cdot}H_2O$

3.2.1 Tests 1 and 2

The starting sludge used in Tests 1 and 2, KC-2/3 M250, had not previously been analyzed by XRD. Its companion material, the KC-2/3 fraction with particles greater than 250 µm (i.e., KC-2/3 P250), was analyzed (Delegard et al. 2000) and found to contain high intensity signals for uraninite ($UO_{2.25}$), medium signals for (meta)schoepite ($UO_3{\cdot}2H_2O$) and gibbsite and bayerite [both $Al(OH)_3$], low signals for nordstrandite [another $Al(OH)_3$ phase], and a potential becquerelite [$Ca(UO_2)_6O_4(OH)_6(H_2O)_8$] signal. The KC-2/3 M250 sludge likely contained many of these same phases in 1999-2000 when the P250 fraction was analyzed. However, because the M250 fraction contained ~0.05 wt% uranium metal (settled sludge basis) versus 7.4 ± 0.9 wt% uranium metal for the P250 fraction, the M250 fraction probably was more oxidized than the P250 fraction and would have contained relatively more schoepite and less uraninite. The uranium phases in KC-2/3 M250 would be expected to have continued to air-oxidize in the seven intervening years of water-immersed ~30°C hot cell storage.

Thus, it is not surprising that the XRD analysis of KC-2/3 M250 in the present tests gave high signals for metaschoepite ($UO_3{\cdot}2H_2O$), and low signals for quartz, but no indication of uraninite ($UO_{2.x}$) despite the dark gray color of the sludge (uraninite is black).[a] Both metaschoepite and schoepite are pure U(VI) phases whereas $UO_{2.x}$ is primarily U(IV).

The Test 1 and 2 products, created in hydrothermal reaction of KC-2/3 M250 and the irradiated metallic uranium fuel, contained poorly crystallized or finely particulate uraninite (as shown by its broad diffraction peaks), evidently from uranium metal fuel corrosion. The reaction products from Tests 1 and 2 showed strongly colored black and green regions. Samples of the individual regions (Test 1 Black and Test 1 Green) were taken to discern differences, if any, in the XRD. As might be expected, the Test 1 Black region produced higher uraninite signals than either Test 1 Green or Test 1.

The metaschoepite phase present in KC-2/3 M250 dehydrated and was replaced by the uranium oxide hydrates $UO_3{\cdot}0.8H_2O$ and $UO_3{\cdot}H_2O$, both U(VI) phases and known as "dehydrated schoepite."

$$UO_3{\cdot}2H_2O \rightarrow UO_3{\cdot}0.8H_2O\ /\ UO_3{\cdot}H_2O + (1.0\text{-}1.2)\ H_2O$$

A small amount of the U(VI) mineral soddyite [$(UO_2)_2SiO_4{\cdot}2H_2O$] also was found in the product. Soddyite likely formed from the following reaction of metaschoepite with quartz (or amorphous silica), both present in the starting KC-2/3 M250 sludge. Like the dehydration reactions of metaschoepite to produce the dehydrated schoepites, the reaction to produce soddyite also releases water.

$$2\ UO_3{\cdot}2H_2O + SiO_2 \rightarrow (UO_2)_2SiO_4{\cdot}2H_2O + 2\ H_2O$$

(a) The absence of discernible phases in uranium-rich sludges has been noted in prior XRD characterization (XRD only detects crystalline phases). K Basin sludge samples 96-04-L-8 and 96-04-L-16B, 93.6 and 93.7 wt% uranium, respectively, had no XRD-identifiable uranium phase. ["Results from Supplementary Analysis: ICP and XRD Results from Analysis of Discrete Fractions of Material from KE Canister Sludge (96-04) and KE Weasel Pit Sludge (KES-S-19)," AJ Schmidt, PR Bredt, BM Thornton, and KL Silvers, PNNL, May 21, 1998].

Aside from the oxidation of uranium metal fuel to produce uraninite, no evidence of oxidation state change could be observed for Test 1 or 2. For example, there was no evidence that the hydrogen from the reaction of uranium metal and water:

$$U + 2.x\ H_2O \rightarrow UO_{2.x} + (2.x)\ H_2$$

reduced schoepite to $UO_{2.x}$ because $UO_{2.x}$ already was present from the uranium metal oxidation.

The dehydration of metaschoepite to yield dehydrated schoepite phases is observed in geologic systems. Like many hexavalent [U(VI)] uranium compounds, metaschoepite has a layered structure with water present between the layers. With heat or mechanical pressure, the metaschoepite will transform to dehydrated schoepite, generic formula $(UO_2)O_{0.25-x}(OH)_{1.5+2x}$. The value of x varies between 0 and 0.15. The dehydration reaction is irreversible such that re-introduction of water to the dehydrated schoepite does not produce schoepite or metaschoepite (Finch and Murakami 1999).

The alteration of many uranium(VI) oxyhydroxides (such as metaschoepite and becquerelite) to soddyite also is observed in geologic systems under conditions similar to those in the present testing. If the chemical activity of silica is sufficient (and silica is present in the starting sludge), UO_2^{2+} from the U(VI) oxyhydroxides can complex with silicic acid, H_4SiO_4, under low pH conditions (the present tests were at pH 4-5) to precipitate soddyite and, as shown above, release water (Finch and Murakami 1999). Further discussion of uranium reactions is provided in Section 3.4.

3.2.2 Tests 3, 4, and 5

The starting sludge in Tests 3 and 4 was flocculated KE Container Composite created from archived KC-2/3, KC-4, KC-5 P250, and FE-5 sludge samples. As noted previously, KC-2/3 P250 contained uraninite (as $UO_{2.25}$), (meta)schoepite ($UO_3{\cdot}2H_2O$), gibbsite, bayerite, and nordstrandite [all $Al(OH)_3$], and potentially becquerelite [$Ca(UO_2)_6O_4(OH)_6(H_2O)_8$] and KC-2/3 M250, the remaining part of KC-2/3, likely contained the same phases though in different proportion when sampled. No XRD analyses were performed for KC-4. Sludge sample KC-5 P250 was found to contain, in descending prominence, quartz, goethite (FeOOH), gibbsite, bayerite, and nordstrandite [all $Al(OH)_3$ phases], schoepite, and becquerelite (Delegard et al. 2000). The FE-5 sludge contained, in order of prominence, quartz (SiO_2) and lepidocrocite and goethite (both FeOOH phases).

The phases found in the flocculated and non-flocculated KE Container Composite were, in order of prominence, metaschoepite, becquerelite, the eskolaite (Cr_2O_3) isomorph, and a calcium uranium oxide hydrate ($CaU_3O_{10}{\cdot}4H_2O$). Despite the appearance of $Al(OH)_3$, FeOOH, and SiO_2 phases in the constituent starting sludges, no aluminum, iron, or silicon phases were found by XRD in the composites used in the present tests. Again, like the KC-2/3 M250 sludge used in Tests 1 and 2, no uraninite ($UO_{2.x}$) was found.

Test 3 contained flocculated KE Container Composite sludge and uranium metal fuel particles. As would be expected, $UO_{2.x}$ from the oxidation of uranium metal was found in the Test 3 product. The Test 3 product also contained a dehydrated schoepite, $UO_3{\cdot}H_2O$. As in Tests 1 and 2, the dehydrated schoepite no doubt came from the dehydration of the metaschoepite starting material. No other phases were found in Test 3.

Products from Tests 4 and 5 were similar and featured, in decreasing prominence, uranium octoxide (U_3O_8), ianthinite [$U_2(UO_2)_4O_6(OH)_4(H_2O)_4 \cdot 5H_2O$], $UO_{2.x}$, and the Cr_2O_3 isomorph. Becquerelite also may have been present in the Test 5 product. It is significant that no chemically reduced uranium compounds (e.g., $UO_{2.x}$, uranium metal) and only hexavalent [U(VI); i.e., the oxidation state is 6] uranium compounds were found in the starting sludges used in Tests 4 and 5 (the flocculated and non-flocculated KE Container Composite, respectively). Despite this, aside from the possible presence of becquerelite in Test 5, only uranium compounds with oxidation state less than 6 (U_3O_8, ianthinite, and $UO_{2.x}$) were found in the products. The oxidation state of uranium in U_3O_8 and in ianthinite is 5.33 and the oxidation state in $UO_{2.x}$ is between 4 and 5. Because there is little or no uranium metal in the starting test materials,(a) the chemical reduction likely occurred by other reactions. The most likely reductants are organic compounds in the sludge flocculent present in Test 4 and organics or sulfur materials in the OIER present in Test 5.

3.3 Scanning Electron Microscopy of Initial and Product Sludges

Scanning electron microscopy of the initial and product sludges were performed. The samples examined by SEM were taken from the same ~0.2-g aliquots as were sub-sampled and examined by XRD. The examinations also included collection of induced X-ray fluorescence spectra by EDS to identify the chemical elements present in selected spots or regions of the samples. The SEM/EDS examinations were performed to identify the particle shapes and element distributions and to discern differences between the initial and product materials. The results of the SEM/EDS analyses of the initial and STP process product sludges are discussed separately for the KC-2/3 M250 materials modeling Settler tube sludge used in Tests 1 and 2 and their products (Section 3.3.1), the flocculated and non-flocculated composite sludge materials used to model the KE Container sludge used in Tests 3, 4, and 5 (Section 3.3.2), the Test 3 and 4 products (Section 3.3.3), and the Test 5 products (Section 3.3.4). An overview of the SEM/EDS examinations is provided in Section 3.3.5.

3.3.1 SEM/EDS Examination of the KC-2/3 M250 Sludge and Test 1 and 2 Products

The KC-2/3 M250 sludge was reacted under STP conditions, including 7 to 10 hours at 185°C, for both Tests 1 and 2. The Test 1 material contained ~5 grams of finely particulate irradiated uranium metal fuel while Test 2 had about 5 grams of irradiated metallic fuel in the form of equal sized coupons. Both the Test 1 and Test 2 products showed regions of intensely black material and other regions of green or yellow-green material. Separate samples rich in black and in green material were taken from the Test 1 product for XRD and SEM/EDS examination. Composite Test 1 and Test 2 product materials also were taken for examination.

Images of the initial KC-2/3 M250 sludge and of the Test 1 products (including the composite material and samples from the black and green areas) are shown in Figure 3.3. The only element found in significant concentrations in the KC-2/3 M250 sludge test materials is uranium (~68 wt%, dry basis). Because uranium dominates the views of the KC-2/3 M250 materials and products, only SEM images are provided for the KC-2/3 M250 and Test 1 and 2 product materials and no EDS spectra were gathered.

(a) It is expected that uranium metal originally present in these sludge samples has corroded to extinction during storage at hot cell temperatures since 1999. At the ~30°C hot cell temperature, the corrosion rate is ~0.0086 µm/h, and uranium metal particles smaller than ~1 mm would have corroded to extinction.

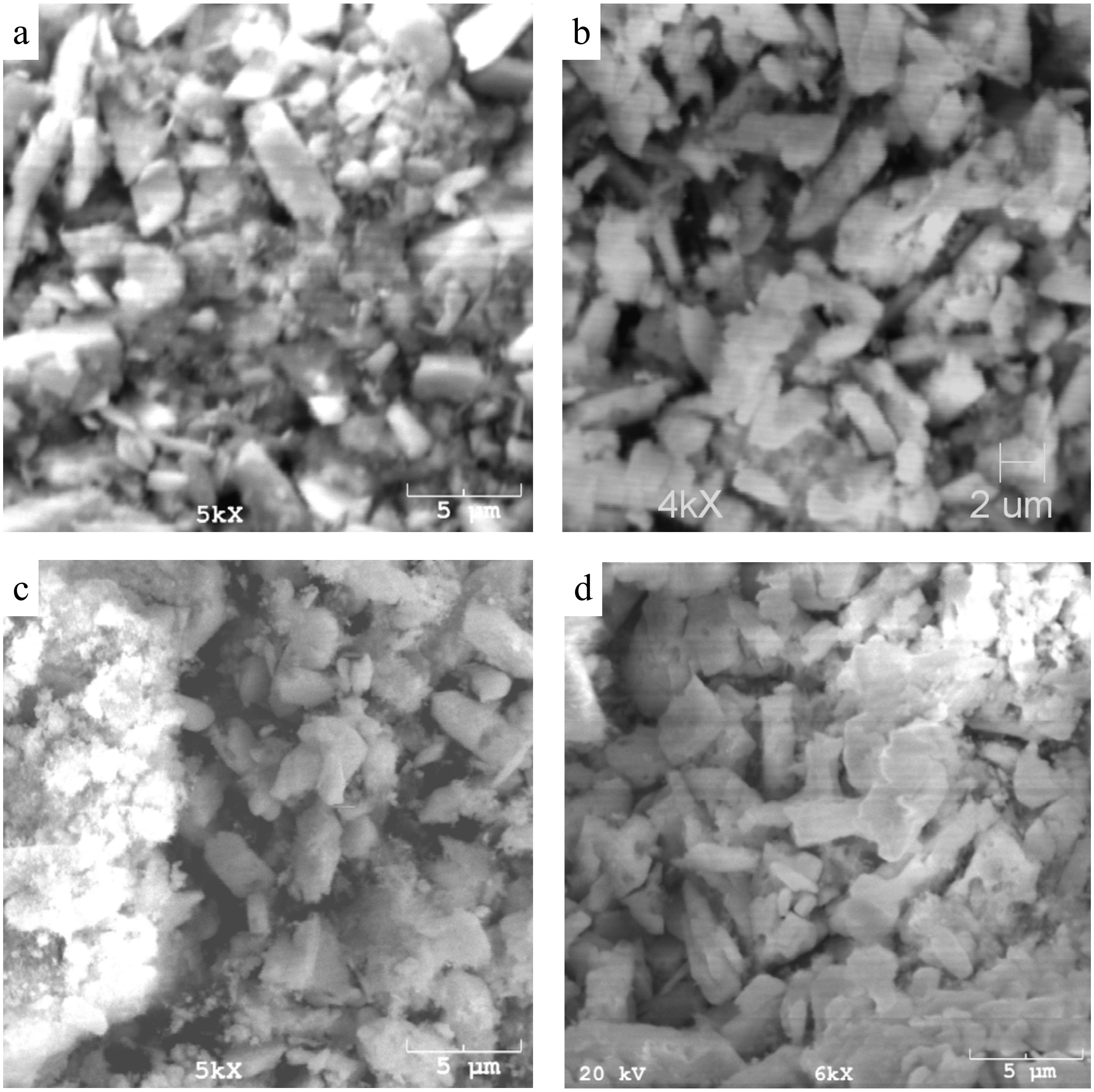

Figure 3.3. SEM Images of Test 1 Starting and Product Materials
a – KC-2/3 M250 starting material
b – Composite Test 1 product
c – Black solids from Test 1
d – Green solids from Test 1
(note that the scale, 1 cm ≅ 2.9 µm, is identical in all images)

KC-2/3 M250 Phases as Found by XRD	**Test 1 Phases as Found by XRD**
Metaschoepite: $UO_3 \cdot 2H_2O$	Uraninite: $UO_{2.x}$ (UO_2, $UO_{2.25}$)
Quartz: SiO_2	Uranium oxide hydrate: $UO_3 \cdot 0.8H_2O$ and $UO_3 \cdot H_2O$
	Soddyite: $(UO_2)_2SiO_4 \cdot 2H_2O$
	Quartz: SiO_2

It is seen in Figure 3.3 that the particle shapes and sizes of the initial and product materials are similar. In both cases, rectangular or near rectangular particles, about 5 µm long and 1-2 µm thick, are found. Some of the particles are boat-shaped (i.e., have a pointed end). Images gathered by SEM of products of 90°C hydrothermal corrosion testing of non-irradiated UO_2 in Yucca Mountain groundwater containing ~28 ppm Si, 46 ppm Na, 5 ppm K, and 13 ppm Ca, show particles of similar rectangular and boat shapes but, at ~10-50 µm long and up to 10 µm thick, having greater dimensions than the particles in the present testing (see Figure 6 of Wronkiewicz et al. 1992). The blocky uranium phases identified in the technical literature include schoepite (or metaschoepite) and, with pointed end, dehydrated schoepite ($UO_3{\cdot}0.8H_2O$ and $UO_3{\cdot}H_2O$). Thin (~1 µm wide) and long (~10 µm) blades of soddyite, $(UO_2)_2SiO_4{\cdot}2H_2O$, also are identified by Wronkiewicz and colleagues (1992). Though soddyite is present in the Test 1 and 2 materials as found by XRD, no similar blade-shaped particles are apparent in the SEM images taken of the Test 1 and 2 products.

Agglomerations of small (sub-micron) particles are shown on the left side of the image (c) of Figure 3.3 for the black solids from Test 1. Similar sub-micron particles, found to be $UO_{2.08\pm0.03}$, were generated during 90°C reaction of irradiated N Reactor fuel in water (Kaminski et al. 2005). The agglomerates of fine particles in Figure 3.3 thus may be the black $UO_{2.x}$ product solids from uranium metal fuel corrosion. Agglomerates of larger particles are shown in the bottom and right sides of image (d) of Figure 3.3 for the green Test 1 solids. These agglomerates appear to be particles in which intergrowth or cementation occurred. The images for the Test 1 product materials also show some particles with rounded holes. In analogy with the prior published findings (Wronkiewicz et al. 1992), some solid phase dissolution may have been underway at the time the STP process reactions were quenched at the end of the 185°C heating. The dissolution of initial or intermediary solid phases followed by precipitation of product solid phases, rather than direct solid-solid conversion, is the apparent mode by which most of the phase transformations occurred in Test 1.

An image from the product of Test 2 is compared in Figure 3.4 with same image of the initial KC-2/3 M250 material as was used in Figure 3.3. The Test 2 product image (b) shows that particle agglomerates also may be present.

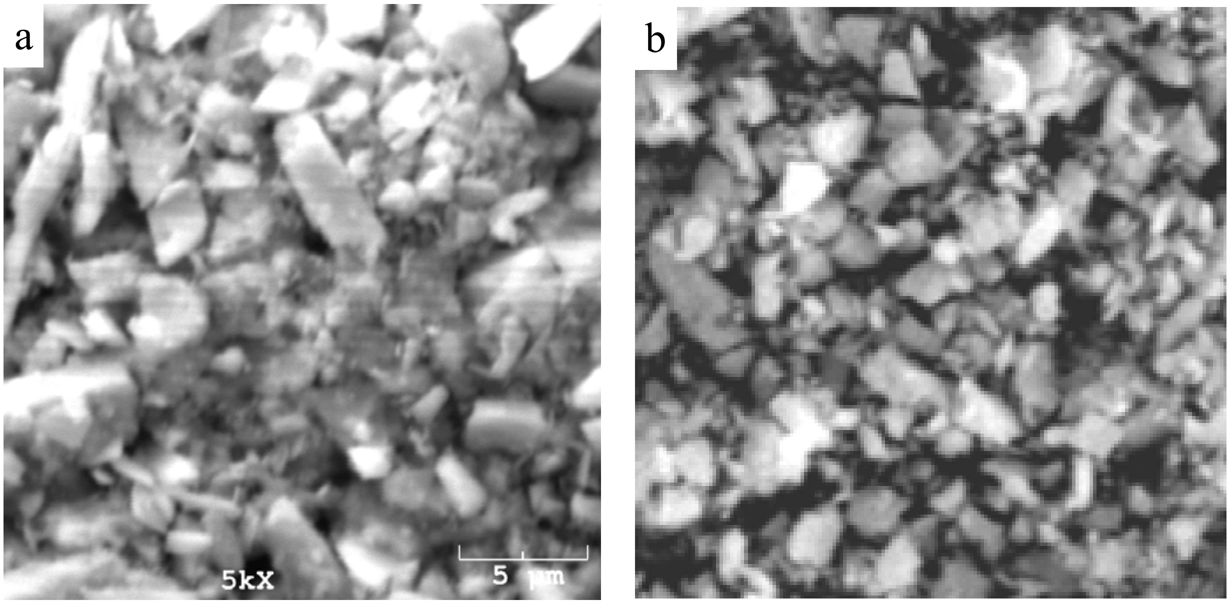

Figure 3.4. SEM Images of Test 2 Starting and Product Materials
a – KC-2/3 M250 starting material
b – Test 2 product
(note that the scale, 1 cm ≅ 2.9 µm, is identical in both images)

KC-2/3 M250 Phases as Found by XRD	**Test 2 Phases as Found by XRD**
Metaschoepite: $UO_3{\cdot}2H_2O$	Uraninite: $UO_{2.x}$ (UO_2, $UO_{2.25}$)
Quartz: SiO_2	Uranium oxide hydrate: $UO_3{\cdot}0.8H_2O$ and $UO_3{\cdot}H_2O$
	Soddyite: $(UO_2)_2SiO_4{\cdot}2H_2O$
	Quartz: SiO_2

3.3.2 SEM/EDS Examination of KE Container Composite Sludge Materials

A composite of KE Basin sludges was collected and treated with flocculating agent to model the composition of the actual KE Container sludge. This sludge, called KE Comp Floc, has the composition shown in Table 2.3 and was used in Tests 3 and 4. The non-flocculated KE Basin composite sludge (KE Comp; composition also shown in Table 2.3) was used in Test 5. The SEM images of the non-flocculated and flocculated KE Container sludges are shown in Figure 3.5. The elements found in selected spots or regions by EDS are identified in the table below Figure 3.5.

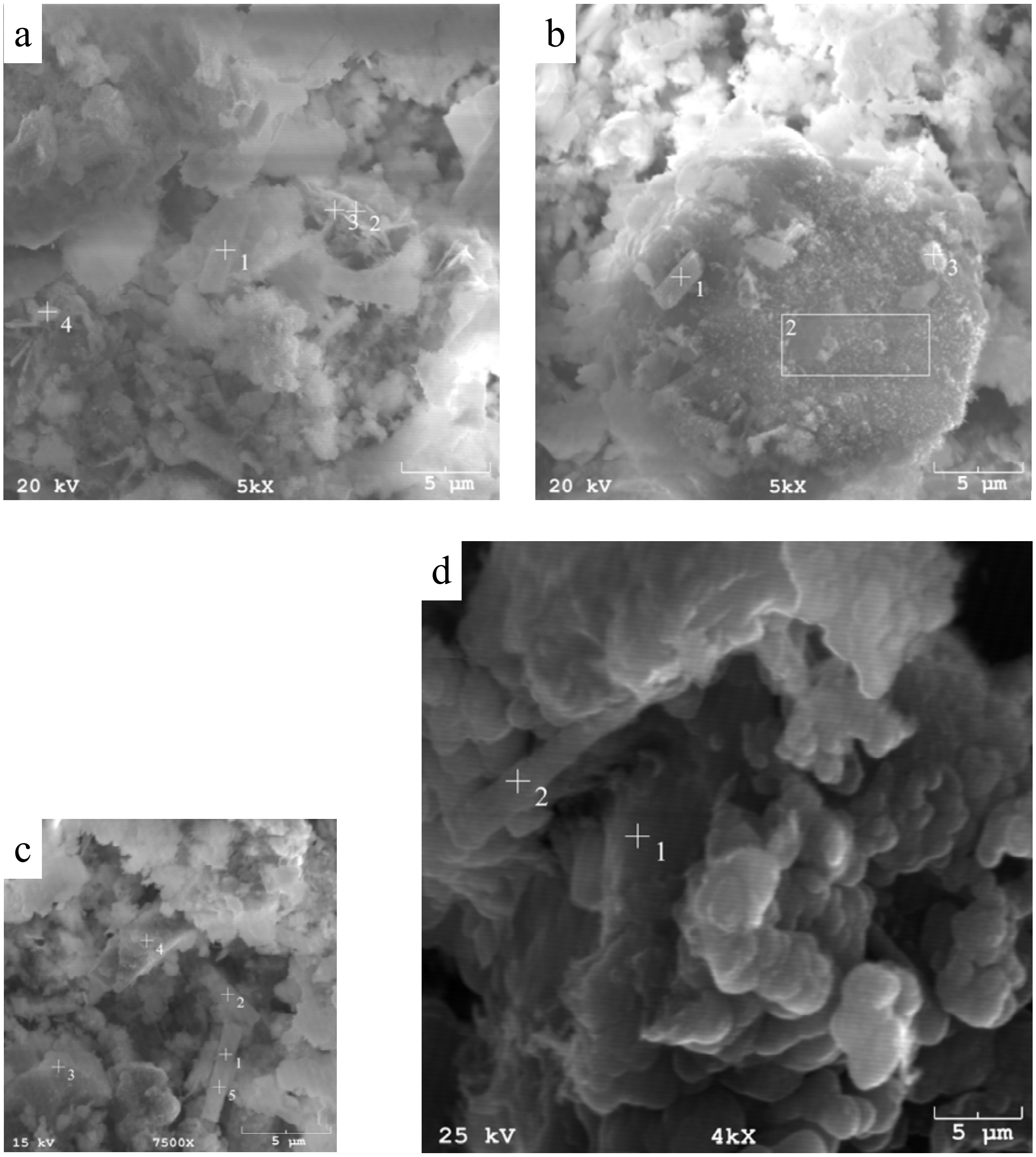

Figure 3.5. SEM/EDS of Non-Flocculated and Flocculated KE Container Composite Sludge (note that the scale, 1 cm ≅ 4.2 µm, is identical in all images)

Element	Relative Element Concentration for Sludge Feed, Image, and Point/Area												
	Non-Flocculated											Floc'd.	
	a				b			c				d	
	1	2	3	4	1	2	3	1	2	3	4	5	1 [(a)]	2 [(a)]
Al	Not run	M	L	L	L	M	M	L	M	L	M	L	H	H
Fe		M	L	H	L	M	M	H	H	H	H	H	H	H
Si		L	L	?	L	H	H	?	?	?	?	?	H	M
U		H	H	M	H	L	M	M	H	M	M	L	H	H

Prominence of element: H – high; M – medium; L – low; ? – possible; N – not observed.
(a) High background.

The four images in Figure 3.5 have been adjusted such that they are all on the same scale. The images a-c are from the non-flocculated KE Comp material; the image d is from the flocculated KE Comp Floc material.

The elemental distributions focused on the four principal elements known to be present in the sludge – aluminum (~8 wt%, dry basis), iron (~20 wt%), silicon (~3%), and uranium (~16 wt%). The prominence of any element in the EDS was assessed in five categories; high, medium, low, possible (?), and not observed; based on the strength of the EDS signal. The responsiveness of EDS to the four elements is Al~Si>Fe>U. The most prominent element was assigned "high" (H). If another element had an EDS signal 70% or greater of the most prominent signal, it, too, was judged to be "high." "Medium" (M) signals were assigned to elements having EDS peaks in the range of approximately 30-70% of the height of the most prominent element peak. "Low" (L) was assigned to peaks having height in the range of ~10-30% of the most prominent peak. The "?", or possible, assignment was made to elements having identifiable peaks that were less than ~10% of the most prominent peak. The "not observed" (N) assignment was accorded elements having no discernable EDS peak.

In general, few points or areas in the non-flocculated or flocculated KE Container sludge were found to have a preponderance of only one element. In most cases, the selected points or areas contained significant ("high" or "medium") contributions from two or more elements. Uranium or iron were found at high or medium levels in all but two of the fourteen points or areas interrogated. Single element dominance was found only for uranium and iron and, when exhibited, was found in particles of distinctive shape. Thus the ~2×5 μm rectangular shape targeted by point 1 of image (b) was rich in uranium while the ~2×5 μm rectangular shapes located by points 1 and 5 and by point 2 of image (c) (both from the non-flocculated sludge) were rich in iron. The bladed shapes marked by points 2 and 3 in image (a) are uranium-rich and are about 1- to 3-μm in length. As will be seen, uranium-rich bladed shapes also were found in the hydrothermal treatment products.

Area 2 shown in image (b) (non-flocculated sludge) showed the lowest relative concentration of uranium of any point or area examined of the initial composite sludges. The EDS shows that the large (~20 μm) round particle in this image is primarily aluminum and silicon with lesser amounts of iron and thus may be a soil mineral. In contrast, the ~2-μm particle identified by point 3, resting on this large round particle, contains appreciable signals from all four elements.

The flocculated sludge shown in image (d) has numerous inter-grown globular shapes. Other images of the same sample, not shown here, have similar appearance. The congealed globular appearance likely arises from the action of the flocculating agent on the sludge particles. Accordingly, the EDS shows the presence of all four elements but with high signal background potentially due to the coating and dilution by the organic flocculating agent.

3.3.3 SEM/EDS Examination of the Test 3 and 4 Products

Tests 3 and 4 each contained about 91 grams of flocculated KE Container sludge and were run according to the STP process heating regime under hydrothermal conditions including ~72 hours at 185°C. Test 3 also contained ~5 grams of irradiated uranium metal fuel particles while Test 4 contained only sludge.

Two images of the product from Test 3 are given in Figure 3.6. The results of the EDS examination follow in the table below the figure.

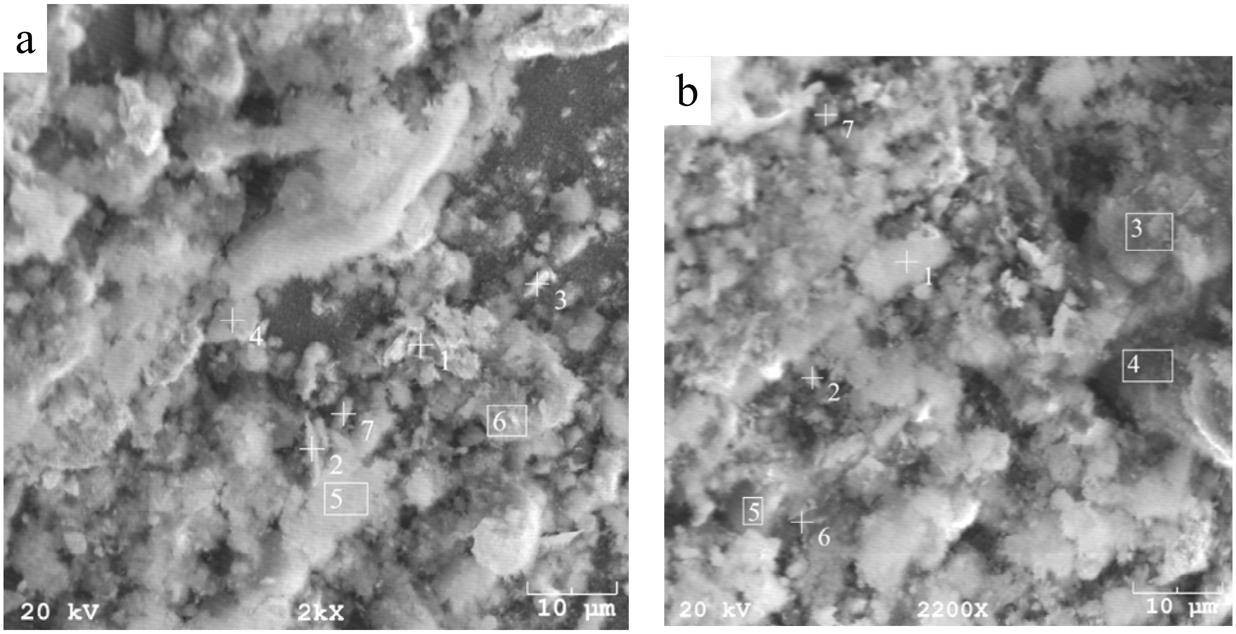

Figure 3.6. SEM/EDS of Test 3 Product of Flocculated KE Container Composite Sludge (note that the scale, 1 cm ≅ 8.7 µm, is identical in both images)

Element	**Relative Element Concentration for Image and Point/Area**													
	a							**b**						
	1	**2**	**3**	**4**	**5**	**6**	**7**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Al	L	L	L	M	H	L	?	M	H	L	L	M	L	M
Fe	L	L	L	M	M	H	L	H	M	H	H	H	L	H
Si	?	?	?	L	L	?	N	L	?	N	?	L	?	L
U	H	H	H	H	H	H	H	H	H	L	L	H	H	H
Prominence of element: H – high; M – medium; L – low; ? – possible; N – not observed.														

It is seen that uranium is prominent in all points and areas in image (a) in Figure 3.6. Points 1, 2, 3, and 7 have low contributions from the other three elements. It is seen that these uranium-rich bladed particles are about 5- to 7-µm long. The particles marked by point 1 appear to have intersecting blades similar to those observed for non-flocculated KE Container sludge in image (a) in Figure 3.5. Point 4 and area 5 are rich in uranium but contain similarly strong signals for aluminum and significant iron as well. The particles associated with point 4 and area 5 both have indistinct shapes with no straight edges or defined corners. The particle or agglomerate associated with area 6 is likewise indistinct and contains prominent EDS signals from uranium and iron.

In contrast with image (a), only one particle (at point 6) is predominantly uranium in image (b) (Test 3 product) of Figure 3.6. It, too, is a ~5-µm blade. Areas 3 and 4 are indistinct and predominantly iron while the remaining points and areas (1, 2, and 7) in image (b) have high concentrations of uranium with either iron or aluminum. Aside from the rough rectangular particle located by point 1 (an iron/uranium-rich particle), the shapes are indistinct.

Two images of the product from Test 4 are shown in Figure 3.7 with results of the EDS examinations of selected points and areas in the associated table.

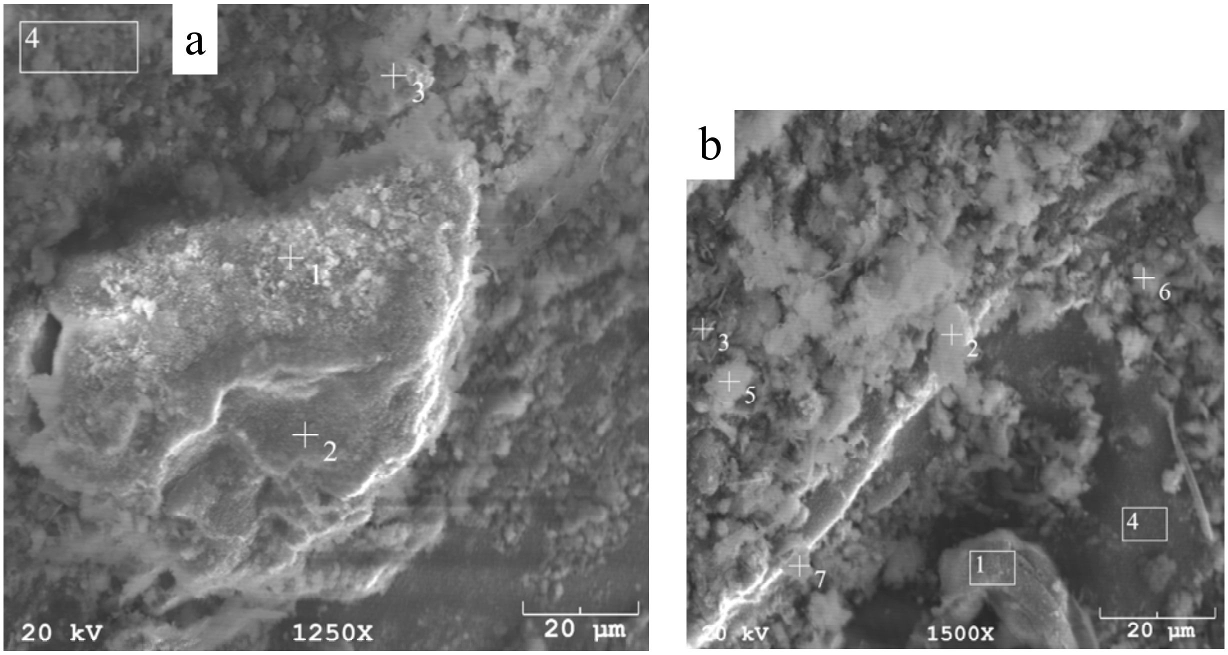

Figure 3.7. SEM/EDS of Test 4 Product of Flocculated KE Container Composite Sludge (note that the scale, 1 cm ≅ 13 µm, is identical in both images)

Element	**Relative Element Concentration for Image and Point/Area**										
	a				**b**						
	1	**2**	**3**	**4**	**1(a)**	**2**	**3**	**4(a)**	**5**	**6**	**7**
Al	L	H	M	M	L	H	M	?	M	M	L
Fe	H	N	H	M	?	M	L	N	H	H	H
Si	?	L	L	L	?	L	L	N	L	L	L
U	M	L	M	H	L	H	H	?	M	H	L

Prominence of element: H – high; M – medium; L – low; ? – possible; N – not observed.
(a) High background.

The two images in Figure 3.7 are at lower magnification than those in Figure 3.6. The large (~80-µm) particle in image (a) is aluminum-rich (see results for point 2), perhaps a corrosion product scale from an aluminum canister, and appears to have iron and uranium deposited over it (see results for point 1). Point 3 and area 4 locate a particle and a region, respectively, containing comparable contributions from aluminum, iron, and uranium. No distinct particle shapes are shown in image (a).

The particle highest in relative uranium concentration in the observed Test 4 product is located at point 3 in image (b). Again, ~5-µm blades are found. Other blades or perhaps needle-like shapes are shown in the same image in the left middle section directly above point 7. However, no EDS data were gathered at these locations. Areas 1 and 4 are practically devoid of aluminum, iron, silicon, and uranium. The unusually shaped particle located under area 1 likely is organic detritus while area 4 appears to be bare of particles (i.e., shows only the carbon tape on which the particle samples were fixed onto the SEM sample stub). Points 5 and 7 locate indistinct iron-rich particles while points 2 and 6 locate particles containing aluminum, iron, and uranium in comparable concentrations. Aside from the blades and needles shown in image (b), no distinctive particle shapes were found in the Test 4 products.

3.3.4 SEM/EDS Examination of the Test 5 Products

The reaction of ~67 grams of non-flocculated KE Container sludge containing ~8 grams of OIER but no added uranium metal fuel was evaluated in Test 5. This test, like those of Tests 3 and 4, included 72 hours of 185°C heating with the associated nominal STP process temperature ramping. Three SEM images with EDS spectra of selected points and areas were taken of the Test 5 product (Figure 3.8).

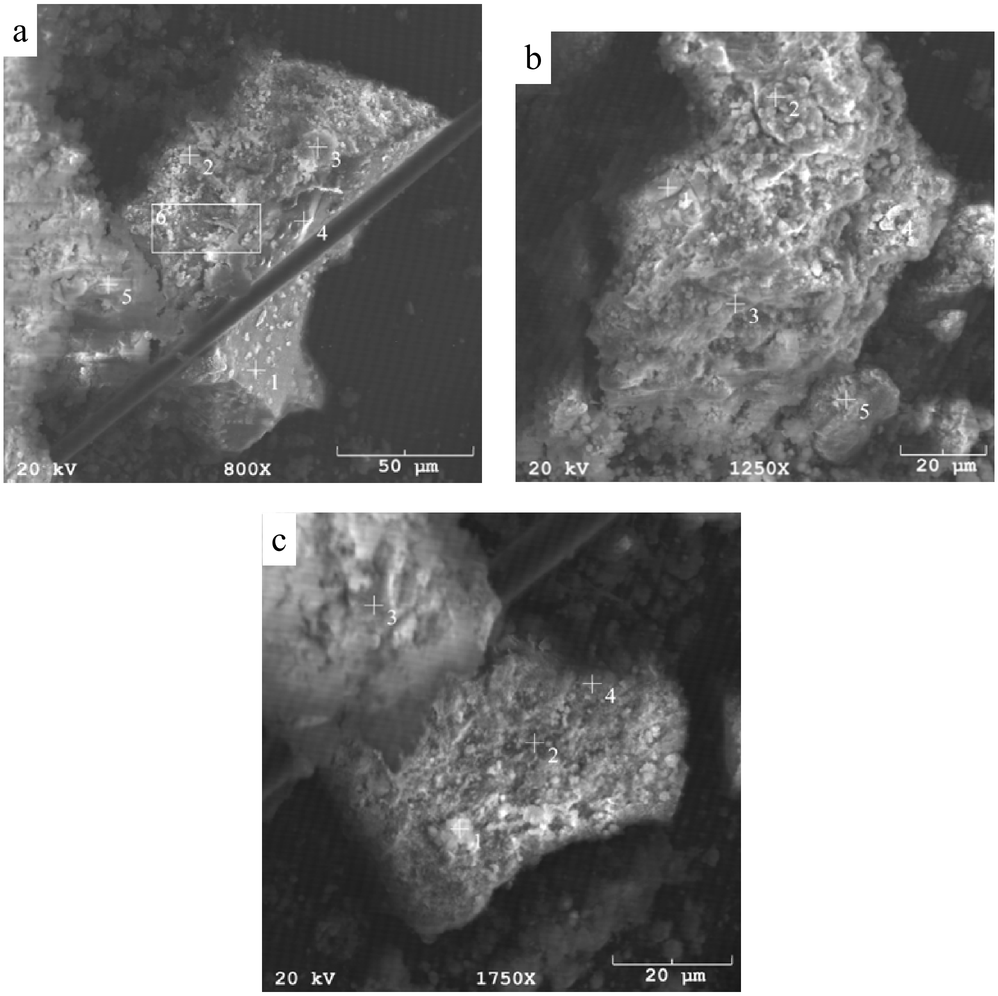

Figure 3.8. SEM/EDS of Test 5 Product of Non-Flocculated KE Container Composite Sludge (note that the image scales vary)

Element	Relative Element Concentration for Image and Point/Area														
	a						b					c			
	1	2	3	4	5	6	1	2	3	4	5	1	2	3	4
Al	?	M	H	L	L	M	L	L	M	M	L	M	M	L	M
Fe	N	H	L	N	L	M	H	H	H	H	H	H	L	H	L
Si	N	L	L	N	L	?	L	L	L	L	L	L	L	L	L
U	H	H	H	L	H	H	M	M	H	M	M	M	H	L	H
Ca	L	N	N	M	N	M	N	N	N	N	N	N	N	N	N
S	L	L	M	H	N	H	N	N	N	N	N	L	M	N	H
Prominence of element: H – high; M – medium; L – low; ? – possible; N – not observed.															

Large (~50-100 μm) irregularly shaped grains are shown in each image and each large grain has significant surface roughness. Based on appearance (see Figure 3.9 and Figure C.6 of Schmidt et al. 1999), some or all of these grains may be the inorganic ion exchange mineral mordenite. Mordenite was used in the K Basins to collect radiocesium from the Basin waters and often is associated with OIER in the K Basin sludge. However, no obvious spherical or hemispherical OIER beads were found in any SEM image of the Test 5 products. A smooth straight fiber, shown by EDS to contain no elemental signal (i.e., likely carbon-based), also is present in the upper left and bottom images of Figure 3.8.

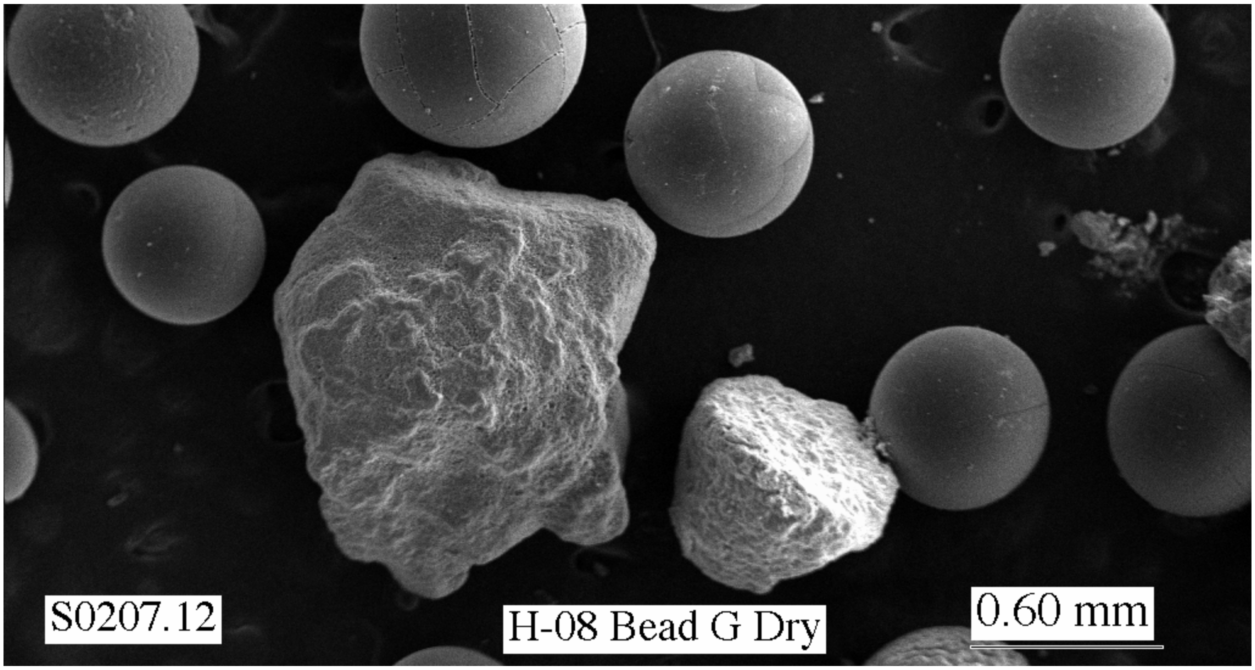

Figure 3.9. Scanning Electron Photomicrograph of OIER (spheres) and Mordenite

Six points and areas were queried by EDS in the image (a) of Figure 3.8. Points 1 and 5 are on particles rich in uranium and practically devoid of other elements. A number of particles similar to the one located by point 1 also are present on the surface of the large (~100 μm) irregular grain. The particle shapes are difficult to discern at this magnification but are not inconsistent with blades. The shape of particle 5 is roughly rectangular. The particle associated with point 2 is rich in uranium, iron, and aluminum and also is located on top of the large grain. Points 3 and 4 and area 6 are rich in the element sulfur. Calcium also is associated with point 4 and area 6, but not with point 3 which has high uranium and aluminum concentrations. Sulfur likely originated from thermal decomposition of sulfonate ($-SO_3^-$) functional groups from the cation exchange resin present in the mixed bed OIER. The loss of the sulfonate exchange sites on the cation exchange resin would release sulfite (SO_3^{2-}) from the resin backbone and simultaneously release the associated cations such as cesium-137 (as $^{137}Cs^+$) and calcium (as Ca^{2+}) from the resin into solution. The released sulfite itself is a chemical reductant that oxidizes to form sulfate (SO_4^{2-}) and could have been responsible for the formation of the reduced uranium compounds found in Test 5 products. The sulfite or product sulfate will readily associate with highly charged metal ions such as the released Ca^{2+} or aluminum (Al^{3+}) and uranyl (UO_2^{2+}).

No sulfur or calcium was found by EDS of the five points selected in image (b) of the Test 5 product. Each point, however, showed high iron concentrations and high or middle levels of uranium. As a result, none of the EDS signals of the selected points was dominated by a single element. The particles associated with the five selected points all had irregular shapes; no evidence of bladed or rectangular shapes is found in this image.

Four points were selected for EDS enquiry in image (c) in Figure 3.8. Points 1, 2, and 4 were from different locations on the same large irregular grain. Each of these points was high in uranium but also contained substantial contributions from aluminum and iron (silica was low in each case). These points also had varying levels of sulfur present but not associated calcium. Point 3 was located on another grain and showed high iron concentration but low or undetectable levels of the other elements. The image of this grain is too blurred to discern the shape of the particle associated with point 3. No blades, rectangles, or other distinctive shapes were found in this image.

3.3.5 Summary of SEM/EDS Examinations

The SEM and EDS examinations of the initial and product sludges from the five hydrothermal tests were performed using the same sample aliquots as were recovered and analyzed by XRD.

The initial sludge and product materials from Tests 1 and 2 were dominated by uranium phases and thus EDS was not performed. The particle shapes and sizes found in these materials were largely rectangular and blocky with some of the rectangles having pointed ends. Other regions in the Test 1 and 2 products showed large agglomerates of small apparently spherical particles. The rectangular particle shapes and sizes were found to be similar to those observed in 90°C hydrothermal testing of non-irradiated and irradiated UO_2 fuel under aerobic conditions. Some of the rectangular particles also had rounded craters suggesting the loss of material by dissolution. The agglomerated small spheres were similar to products found in the corrosion of irradiated uranium metal (N Reactor) fuel.

The initial non-flocculated KE Container sludge material prepared for Test 5 generally consisted of irregularly shaped particles containing, according to EDS, significant contributions from two or more of the elements aluminum, iron, silicon, and uranium. Rectangles and some smaller bladed particles were also found. The rectangles were either largely iron or uranium with little presence of any of the other four elements. The blades contained only uranium and negligible aluminum, iron, or silicon. The flocculated KE Container sludge material prepared for Tests 3 and 4 had fused globular shapes with no distinctly differentiated elemental distribution.

The products of Tests 3 and 4 generally had irregular shapes and the EDS from these shapes indicated the presence in comparable intensity of two or more of the four identified elements (aluminum, iron, silicon, and uranium). In a few instances, bladed shapes were found; these shapes, when analyzed by EDS, again showed that uranium was prominent with little contribution from the other elements.

Test 5 was prepared from non-flocculated KE Container sludge composite and also contained OIER. Likely as a result of the presence of OIER or absence of flocculating agent, the Test 5 product differed appreciably from the products observed in Tests 3 and 4. Large (~50-100 µm) grains were observed in the Test 5 product. These grains have similar shape to mordenite grains often found to accompany OIER. However, no spherical OIER particles were observed in any image of Test 5 product. The influence of OIER is inferred, however, by the presence of sulfur in the EDS of a number of locations in the Test 5 product SEM images. The sulfur, evidently the product of thermal decomposition of sulfonate-bearing cation exchange resin in the mixed bed OIER, sometimes is associated with calcium, an element not otherwise observed in any of the test materials. The particles found in Test 5 were nearly always irregular; blade-shaped particles may be present but are difficult to discern at the magnifications used.

3.4 Comparison of Uranium Phase Formation in the Present Studies with Findings in Related Studies

The chemical products observed in the present testing also are observed in other laboratory tests and in nature under similar or related hydrothermal reaction conditions. The results of relevant studies described in this section help in understanding the observations made in the present reactions of K Basin sludge under hydrothermal STP process conditions. The following discussion examines technical literature test results to understand uranium metal corrosion to form $UO_{2.x}$ and on reactions of the product $UO_{2.x}$ with solution and solid phases to produce the sequence of uranium-bearing mineral products observed in the STP process testing.

3.4.1 Uranium Phase Observations in the Present Testing

As discussed in Section 3.2, XRD analyses of the KC-2/3 M250 sludge used in Tests 1 and 2 showed the presence of metaschoepite [$UO_3 \cdot 2H_2O$ or $(UO_2)_8O_2(OH)_{12} \cdot 12H_2O$] and a small amount of quartz (SiO_2). The KC-2/3 M250 sludge likely also contained uraninite phases ($UO_{2.x}$) when originally sampled in 1999. However, the uraninite oxidized partially to schoepite or metaschoepite[a] in the intervening years of storage under hot cell conditions. The XRD analyses of the flocculated and non-flocculated KE Container Composite sludge used in Tests 3, 4, and 5 also found metaschoepite as well as becquerelite [$Ca(UO_2)_6O_4(OH)_6(H_2O)_8$] and another calcium uranium oxide hydrate, $CaU_3O_{10} \cdot 4H_2O$. The subsequent conversions of metaschoepite to dehydrated schoepite ($UO_3 \cdot 0.8H_2O$ and $UO_3 \cdot H_2O$) observed in Tests 1, 2, and 3, to soddyite [$(UO_2)_2SiO_4 \cdot 2H_2O$] in Tests 1 and 2, and (with a chemical reductant) to ianthinite ($[U_2(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$), uranium octoxide ($U_3O_8$) and possibly $UO_{2.x}$ in Tests 4 and 5 (but not Test 3) likewise were deduced by XRD evidence. The progressive alterations of uranium compounds in the initial and product K Basin sludge in the present hydrothermal tests are shown in Figure 3.10.

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[a] The term schoepite, $UO_3 \cdot 2.25H_2O$ often is used in articles before about 1998 to describe what is, in fact, metaschoepite, $UO_3 \cdot 2H_2O$. The two minerals are practically interchangeable in the present discussions because their inter-conversion can be effected even by mild handling and temperature and humidity changes.

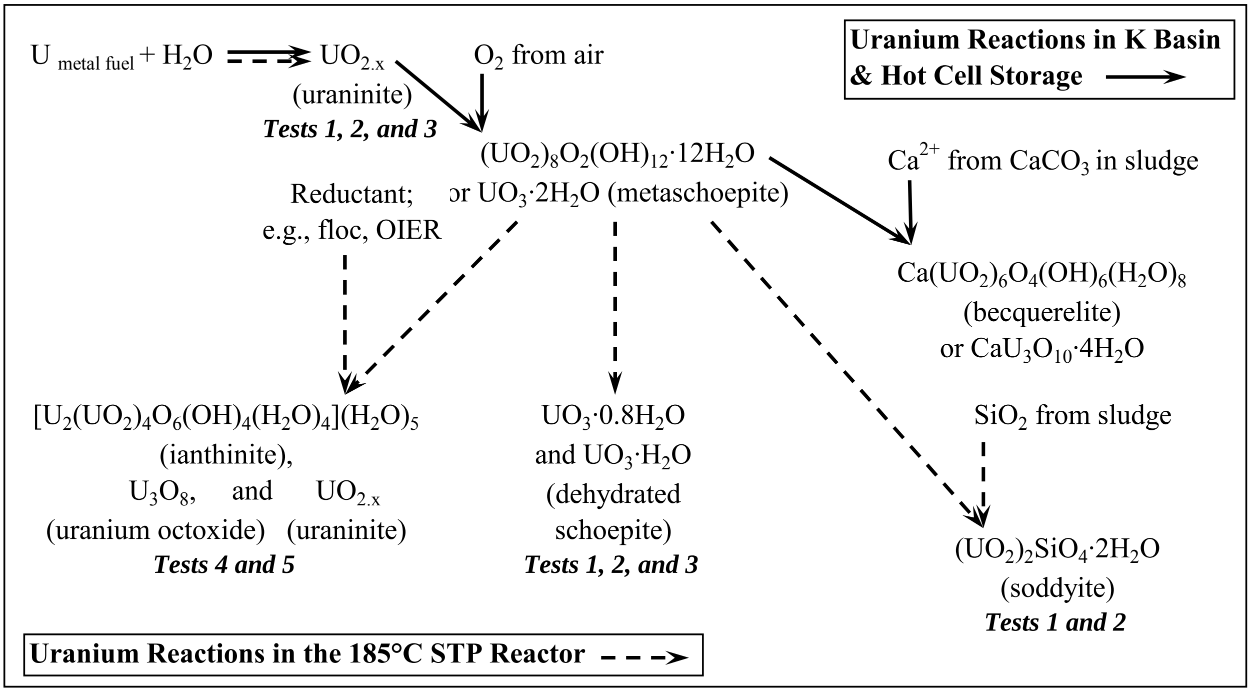

Figure 3.10. Uranium Compound Alterations in the K Basins and Under STP Process Conditions

Properties of the uranium compounds found in the present testing and in related tests and mineral systems are shown in Table 3.4. The material densities decrease steeply and almost linearly from ~19 g/cm^3 to ~5 g/cm^3 as uranium concentrations decrease through oxidation from 100 wt% (uranium metal fuel, oxidation number 0) to ~74 wt% (metaschoepite, oxidation number 6).(a) Further uranium oxidation is not possible and continued mineralization decreases the mineral densities only from ~5 g/cm^3 to about 3.6 g/cm^3 as uranium concentrations further decrease to about 50 wt%. As shown in Table 3.4, aside from the starting uranium metal and initial UO_2 product, the uranium product minerals are relatively soft with hardness on the order of a penny coin or calcite (~3 on the Mohs scale).

As noted in Section 3.2, the reactions of metaschoepite to produce dehydrated schoepite and to produce soddyite in Tests 1 and 2 are both dehydrations but have no associated change in uranium oxidation state. Though the reactions to produce $UO_{2.x}$, ianthinite, and uranium octoxide from metaschoepite observed in Tests 4 and 5 release water, they are most importantly chemical reductions in which the oxidation number of uranium decreases from 6 during the reaction to ~4.5 (for $UO_{2.x}$) and 5.33 (for ianthinite and uranium octoxide). The chemical reductants in Tests 4 and 5 evidently were flocculating agent and sulfite from the thermal decomposition of cation OIER in Test 5. The $UO_{2.x}$ found in Tests 4 and 5 also may have formed from crystallization of previously existing amorphous $UO_{2.x}$ during the hydrothermal treatment.

(a) Another way to view this is that 1000 g of uranium as metal, occupying [1000 g U/(19.05 g/cm^3)] ~52 cm^3, will increase in volume about 5-fold when oxidized to metaschoepite, to occupy [1000 g U/((0.76 g U/g metaschoepite) × (5 g metaschoepite/cm^3))] 268 cm^3.

Table 3.4. Properties of Uranium and Its Mineral Compounds in Sludge and in Nature

Compound	**Formula**	**Oxidation Number**	**Wt% U**	**Density, g/cm$^{3(a)}$**	**Hardness, Mohs$^{(b)}$**
Uranium phases found in present testing					
Uranium metal fuel	U	0	100	19.05	5 (est.)
Uraninite	UO_2	4	88	10.977	6-7
	$UO_{2.25}$	4.5	87	11.353	?
	$UO_{2.34}$	4.68	86	11.555	?
Uranium octoxide	U_3O_8	5.33	85	8.463	?
Ianthinite	$[U_2(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$	5.33	76	5.004	2-3
Metaschoepite	$UO_3{\cdot}2H_2O$	6	74	4.998	2.5
Uranium oxide hydrate or dehydrated schoepite	$UO_3{\cdot}H_2O$	6	78	6.766	?
	$UO_3{\cdot}0.8H_2O$	6	79	6.598	?
Becquerelite	$Ca(UO_2)_6O_4(OH)_6(H_2O)_8$	6	72	5.145	2.5
Calcium uranium oxide hydrate	$CaU_3O_{10}{\cdot}4H_2O$	6	72	5.115	?
Soddyite	$(UO_2)_2SiO_4{\cdot}2H_2O$	6	71	5.088	3.5
Other uranium phases described in the technical literature					
Compreignacite	$K_2(UO_2)_6O_4(OH)_6(H_2O)_8$	6	71	5.13	?
Uranophane	$Ca(UO_2)_2(SiO_3OH)_2{\cdot}5H_2O$	6	56	3.85	2.5
Weeksite	$K_2(UO_2)_2Si_6O_{15}{\cdot}4H_2O$	6	43	4.02	<2
Boltwoodite	$K_2(UO_2)_2(SiO_4)_2(H_3O)_2{\cdot}H_2O$	6	55	3.69	3.5-4
Sklodowskite	$Mg(UO_2)_2(SiO_3OH)_2{\cdot}6H_2O^{(c)}$	6	52	3.64	2-3
Rutherfordine	UO_2CO_3	6	72	5.71	?
Vandendriesscheite	$Pb_{1.57}(UO_2)_{10}O_6(OH)_{11}(H_2O)_{11}{}^{(c)}$	6	68	5.45 (meas'd.)	3

(a) Density data for the phases found in the present testing are from the International Centre for Diffraction Data, Inc., database PDF-2, release 2006. Density data for the other uranium phases described in the technical literature were obtained from Roberts et al. (1990) by calculation from XRD spacings.

(b) Hardness data were obtained from Roberts et al. (1990) except for irradiated uranium metal fuel (Delegard et al. 2004) and UO_2 (Belle 1961).

(c) These formulas are based on more recent structure assessments and differ slightly from the formulas provided in the original reference (Wang and Xu 2000).

Uranium metal fuel corrosion under anoxic and starved oxygen conditions has been studied in the laboratory (Schmidt et al. 2003, Kaminski et al. 2005, and others) and shown to produce $UO_{2.x}$. Aside from the conversion of uranium metal to $UO_{2.x}$, uranium compound alterations similar to those shown in Figure 3.10 also have been observed in the laboratory from the interaction of non-irradiated UO_2 and irradiated UO_2 with Yucca Mountain groundwaters (Wronkiewicz et al. 1992 and 1996 and Finch et al. 1999, respectively), in natural uranium mineral deposits (e.g., Leslie et al. 1993), and in related studies. Results of the published studies are examined in the following sections.

3.4.2 Uranium Metal Corrosion

The corrosion of low alloy uranium metal such as N Reactor fuel under hydrothermal conditions has been the subject of numerous studies, including studies with K Basin sludge. For example, Appendix G of SNF-7765 (Plys and Schmidt 2006) summarizes uranium metal anoxic water corrosion rate data from 32 separate published studies at ~24°C to 350°C while Schmidt and colleagues (2003) describe tests of uranium metal corrosion with and without K Basin sludge at ~33°C to 95°C. In the latter study, sludge materials in test SNF + Can 60L, which contained ~26 grams of 0-6350 μm irradiated uranium metal fuel particles and ~68 grams of uranium-rich (61.2 wt%, dry basis) settled canister sludge, were found to self-cement and adhere to the stainless steel test vessel, making them difficult to remove after testing. In associated tests, the uranium metal fuel particles were found to produce UO_2 plus $UO_{2.25}$.

The corrosion of both non-irradiated and irradiated cladding-free N Reactor fuel pieces was studied under immersed 90°C hydrothermal conditions in both deionized water and J-13 (Yucca Mountain) well water (Kaminski et al. 2005). The corrosion test products were examined by XRD to show that the only direct reaction product from uranium corrosion had the uraninite structure with formula $UO_{2.08\pm0.03}$. The pattern also had pronounced line broadening ascribed to the fine product particle size. These findings are similar to the broadened XRD patterns assigned to $UO_{2.x}$ (various combinations of UO_2, $UO_{2.25}$, and $UO_{2.34}$, all being uraninite structures) observed in the present tests and the UO_2 plus $UO_{2.25}$ observed in prior N Reactor fuel uranium metal corrosion tests (Schmidt et al. 2003).

The corrosion products, when viewed under transmission electron microscopy (TEM), were small spheres primarily <10 nm (i.e., <0.01 µm) in diameter with some 100-150 nm UO_2 particles, i.e., in the colloidal particle size range (Kaminski et al. 2005). Most of these individual particles were agglomerated to sizes ranging from ~0.25 to 1.0 µm. The zeta potential of the UO_2 colloids was zero at about pH 2-3. When exposed to oxygenated conditions in the presence of the J-13 water, the UO_2 began to be converted to the uranium mineral weeksite, a potassium uranyl silicate hydrate [$K_2(UO_2)_2Si_6O_{15}\cdot 4H_2O$]. Weeksite was not observed in the present tests which were conducted without a significant source of potassium.

3.4.3 Uranium Mineral Reactions in the Laboratory

Paragenesis is a geologic term meaning the stepwise sequence of mineral formation from predecessor minerals. Such changes might be instigated during mineral exposure to water, dissolved solutes, or oxygen from the air. Paragenesis of uranium phases was observed in reaction of unirradiated UO_2 pellets in Zircaloy-4 sleeves with aerated J-13 well water at 90°C (Wronkiewicz et al. 1992 and 1996). During this testing, low volumes of the pH 8.2 J-13 well water, which contained ~28 ppm Si, 46 ppm Na, 5 ppm K, and 13 ppm Ca, were periodically injected into the test vessel to drip directly onto the pellets. Intermediate analyses of the solution and altered solid phases were performed over the course of ten years of drip-testing. The solid phases were found to form a mat that changed from a “relatively permeable mesh of crystals” after 3.5 years of exposure to a “dense network of phases” after 8 years of exposure.

The uranium mineral paragenesis observed by Wronkiewicz and colleagues (1992 and 1996) was:

UO_2 →

$UO_{2.25}$ →

uranium oxide hydrates [largely dehydrated schoepite but also with schoepite, becquerelite, and compreignacite, $K_2(UO_2)_6O_4(OH)_6(H_2O)_8$], at ~1-3 years →

soddyite at ~3 years →

uranyl alkaline silica hydrates [uranophane, $Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O$, boltwoodite, $K_2(UO_2)_2(SiO_4)_2(H_3O)_2\cdot H_2O$, and others] at ~4-7 years.

Decreases in pH and depletion of alkali, alkaline earth, and silicon solution concentrations also were observed during these long-term drip tests. Mineral shapes for schoepite, dehydrated schoepite, becquerelite, and soddyite, and signs of dissolution pitting of individual crystals (see Figure 6 of Wronkiewicz et al. 1992) gave evidence for the mineralogical succession.

As shown in Figure 3.10, the present tests produced $UO_{2.x}$ from uranium metal corrosion followed by metaschoepite, becquerelite, dehydrated schoepite, and soddyite in a sequence similar to findings in the tests of Wronkiewicz and colleagues (1992, 1996). However, because their tests were conducted under oxidizing conditions, Wronkiewicz and colleagues did not observe the partially reduced $UO_{2.x}$, ianthinite, and uranium octoxide phases seen in Tests 4 and 5 of the present program. Though confident assignment to particular phases is not possible, crystals shaped similarly to schoepite and dehydrated schoepite were found by SEM examination of the Test 1 products (see Section 3.3). Unlike Wronkiewicz and colleagues (1992 and 1996), however, no XRD or SEM evidence for the further advanced uranophane or other uranyl alkaline silica hydrate paragenesis phases was found in any of the present tests.

Experiments similar to those of Wronkiewicz and colleagues (1992 and 1996) were performed using high burn-up irradiated UO_2 fuel pellets instead of non-irradiated UO_2 pellets (burn-up was ~30,000 and ~45,000 MWD/MTU – megawatt-days per metric ton of uranium). These latter tests used aerated 90°C EJ-13 well water (J-13 well water equilibrated with the host rock) containing ~45 ppm Si, 54 ppm Na, 8 ppm K, and 9 ppm Ca (Finch et al. 1999). After ~5 years' exposure, the pellet surfaces were coated with yellow or white crusts of uranium-rich phases with crust thicknesses ranging from about 5- to 100-µm, depending on solution flow rates (higher flow rates gave thicker crusts). As might be expected, the following phase paragenesis observed by Finch and colleagues (1999) with irradiated UO_2 fuel was similar to that observed in the prior testing with non-irradiated UO_2 (Wronkiewicz et al. 1992 and 1996).

$UO_2 \rightarrow$

uranium oxide hydrates [dehydrated schoepite, metaschoepite, compreignacite] at ~1-4 years →

soddyite at ~4 years →

uranyl alkali(ne) silica hydrates [e.g., uranophane, boltwoodite] at ~4-5 years.

Because the tests of Finch and colleagues (1999) used highly irradiated fuel, however, additional paragenetic uranium phases containing fission and neutron capture products also were observed. These additional uranium phases incorporated cesium, barium, molybdenum, zirconium, and plutonium into their structures. Similar phases were not observed in the present tests because burn-up (~3000 MWD/MTU) and fission and activation product concentrations were much lower.

As in the prior tests with non-irradiated UO_2 (Wronkiewicz et al. 1992 and 1996), the tests with irradiated UO_2 (Finch et al. 1999) showed many of the same paragenetic phases as found in the present testing. The higher concentrations of dissolved alkali and alkaline earth metals (e.g., Na^+ / K^+ and Mg^{2+} / Ca^{2+}, respectively) and dissolved silica (Wronkiewicz et al. 1992 and 1996; Finch et al. 1999) as well as significant fission product concentrations (Finch et al. 1999) led to a greater number and variety of uranium product minerals in the prior published test results than were observed in the present testing.

The alteration of non-irradiated UO_2 fuel in slightly aerated but oxygen-starved water at 200-225°C was studied in autoclave tests run for up to 55 days (Taylor et al. 1991). Yellow crystals formed initially

(3-5 days at 200°C and 18 hours at 225°C). These gave way to fine black powder deposits (after 10-20 days at 200°C and 15 days at 225°C). Dehydrated schoepite (which the authors described as $UO_3{\cdot}xH_2O$ where $x = 0.64$ to 0.9), uranium octoxide (U_3O_8), and, in one case, ianthinite ($[U_2(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$) phases were found. In general, the dehydrated schoepite formed first, then U_3O_8. Recall that the uranium oxidation number is 5.33 for both uranium octoxide and ianthinite as compared with 4 for UO_2 and 6 for metaschoepite, dehydrated schoepite, becquerelite, and soddyite found in the present testing. The report authors speculated that the U_3O_8, which was found deposited on the original UO_2 surface, formed by reduction of dissolved U(VI) based on the product crystal shape and depositional growth on the UO_2 substrate rather than by direct surface oxidation of UO_2. Dehydrated schoepite, the first new phase formed in the reaction of UO_2, served as the source of the dissolved U(VI) which then redeposited with chemical reduction to form U_3O_8 and ianthinite. The reducing agent evidently was UO_2 itself.

3.4.4 Uranium Mineral Reactions in Nature

High concentration uraninite mineral deposits are of interest as natural analogues to studies for the disposal of spent fuel in the Yucca Mountain repository and to the present studies of K Basin sludge behavior in storage and STP processing. Though uranium minerals are widespread in nature, uraninite deposits with high uranium concentrations are not so common. Studies of uranium-rich phases from the Shinkolobwe mine located in the Democratic Republic of the Congo and from the Nopal I deposit in Mexico reveal significant mineralogical parallels to the series of uranium phases found in the present tests.

A partially weathered, $\sim 1.8\times10^9$ year-old, uranium-rich ore deposit is found at the Shinkolobwe mine. The uranium ore is surrounded by dolomitic ($Mg_{0.5}Ca_{0.5}CO_3$) siltstones and infiltrated aerated rainwater is credited with the observed uranium mineral alteration (Wang and Xu 2000). The general sequence of uranium mineralization was uraninite → (possibly uranium hydrates such as schoepite) → uranyl silicate (e.g., soddyite) → calcium uranyl silicates (e.g., uranophane). However, other minerals, not observed in the present testing, are found in the Shinkolobwe ores. They include the lead-bearing mineral vandendriesscheite ($PbU_7O_{22}{\cdot}12H_2O$), which deposits adjacent to the uraninite, and rutherfordine (UO_2CO_3) and sklodowskite [$Mg(UO_2)_2Si_2O_6(OH)_2{\cdot}5H_2O$], which deposit at the ore periphery where the influence of the surrounding dolomite minerals is greatest.

Study of alteration reactions of the mineral uraninite under oxidizing geologic conditions thus must take into account the role on uranium mineral formation of radiogenic lead (Pb) derived from the isotopic decay of uranium (Finch and Ewing 1992). As shown by the Shinkolobwe experience, uranium deposits aged to time scales comparable to tenths of the uranium-238 half-life ($\sim 4.4\times10^9$ years) are influenced by the presence of radiogenic lead. However, uraninite deposits poor in Pb daughter products are developed by more recent uraninite deposition and occur in nature by the oxidation of uraninite to form more soluble U(VI) phases, dissolution and transport of the U(VI) away from its original locale, and redeposition of the uranium as uraninite upon encountering chemically reducing conditions.

Because the K Basin sludges contain little lead, the paragenesis of uraninite in the absence of radiogenic Pb (i.e., “young” deposits) is of more interest to the present study. Such paragenesis is proposed by Finch and Ewing (1992) to occur in nature in zones proceeding outward from the central uraninite deposit or core according to the following scheme:

Zone 1 – uraninite →

Zone 2 – alkaline earth uranyl oxide hydrates (e.g., becquerelite) and schoepite →

Zone 3 – uranyl silicates (e.g., uranophane, soddyite) →

further dissemination, including phosphate minerals for phosphate-rich groundwaters.

These zones appear as sub-millimeter- to centimeter-scale rinds growing outward from central uraninite cores in uranium mineral deposits.

Ianthinite is present in products from Tests 4 and 5 but is rare in natural systems. Explanations for the appearance of ianthinite in natural mineral systems are not conclusive and include oxidation of the surface of uraninite deposits under oxygen-starved conditions and reductive deposition of dissolved U(VI) onto uraninite (Finch and Ewing 1992). As seen previously, reductive deposition can occur under 200-225°C hydrothermal conditions (Taylor et al. 1991). Ianthinite's scarcity in nature thus is due to its delicate dependence on oxygen concentrations and its low thermodynamic stability with respect to other competing uranium minerals (Taylor et al. 1992).

Uranium mineralization reactions will occur over geologic time scales in the proposed Yucca Mountain high-level nuclear spent fuel repository for both the irradiated UO_2 fuel from commercial reactors and for the irradiated metallic uranium fuel largely (~90%) arising from the N Reactor. Aside from the lack of uranium metal, the Nopal I uranium deposit at Peña Blanca, Mexico, is an excellent natural geologic analogue to the Yucca Mountain repository. The Nopal I deposit contains uraninite and associated high uranium concentrations and, like Yucca Mountain and its contained spent fuel, has practically no phosphorus (P) and vanadium (V) to form secondary minerals with U(VI). Nopal I and Yucca Mountain also have similar groundwater and host mineral compositions (Leslie et al. 1993, Pearcy et al. 1994). Finally, the Nopal I uranium mineral deposits are relatively young with respect to radioactive decay of uranium (~44 million years or less) and thus contain little radiogenic lead (Pearcy et al. 1994, Fayek et al. 2006) that would complicate uraninite paragenesis.

The paragenetic sequence observed in the Nopal I deposit presented by Leslie and colleagues (1993) was deduced based on the mineral ordering observed to occur in the following sequence away from the uraninite core materials:

Uraninite (UO_{2+x}) →

ianthinite →

uranium oxide hydrates (schoepite, identified as $UO_3{\cdot}2H_2O$ or metaschoepite, dehydrated schoepite, and becquerelite) →

soddyite →

uranyl alkali(ne) silica hydrates (uranophane, weeksite, boltwoodite).

This sequence encompasses nearly all phases (except uranium metal, U_3O_8, and the potentially redeposited UO_{2-x}) observed in the present testing and continues with further mineralization to form the uranyl alkali(ne) silica hydrates which arise in the silica-rich Nopal I environment and may ultimately form in the STP process-treated sludges.

3.4.5 Summary of Uranium Phase Studies

The technical literature thus supports the uranium mineral paragenesis observed for K Basin sludge both from its storage in the Basins and the hot cells through its continued reactions in the hydrothermal testing under STP process conditions. The chemical reactions observed in the present testing to form dehydrated schoepite and soddyite (dehydration reactions) and uraninite, ianthinite, and U_3O_8 (chemical reductions) also are recorded in the technical literature for STP-relevant conditions in separate laboratory testing and in uranium mineral paragenesis in nature. Both the dehydration and reduction reactions are accelerated by the heat and pressure provided under STP conditions.

Because most of the chemical reactions described in the present testing involve significant structural change, including change in shape, to attain the respective solid product phases, the reactions must occur by dissolution and reprecipitation and not merely by solid phase rearrangement.[a] And because the precipitation reactions are more likely to occur on existing (nucleated) sludge solid particle surfaces, the precipitating solids can act to bridge across the pre-existing particles and cement them together. The formations of mats, dense networks, or crusts of secondary minerals are described in laboratory drip-testing of non-irradiated and irradiated UO_2 and in oxygen-starved hydrothermal reaction of non-irradiated UO_2 (Wronkiewicz et al. 1992 and 1996; Finch et al. 1999; Taylor et al. 1991). Such cementation phenomena, which also are observed naturally in the formation of sandstones and other sedimentary rocks, provide probable explanations for the increased sludge material strengths following STP processing.

3.5 Strength and Erosion Measurements and Observations

The UCS of the sludge products from the five tests were determined using a soil penetrometer. Results of the sludge UCS measurements are presented in Table 3.5. Estimates of the shear strengths of the product sludges are derived from the UCS values using a conversion provided by Holtz and Kovacs (1981). The strength tests show that the KC-2/3 M250 sludge materials, modeled after Settler tube sludge and processed in Tests 1 and 2, are much stronger than the composite KE Basin sludge materials processed in Tests 3, 4, and 5. The strength of the flocculated sludge simulant product (Test C-2) was greater than that of the composite KE Basin sludge product but less than that of the Settler sludge product.

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[a] Solid phase reactions in which one solid converts to another without dissolution and precipitation also may have occurred in some instances. However, such reactions are expected to be rare in immersed conditions and were not observed in the present tests.

Table 3.5. Strengths of Processed Sludges

Test	Unconfined Compressive Strength, kg(f)/cm^2					Shear Strength,[b] kPa	Consistency	
	As-Read			True[a]				
	Rep. 1	Rep. 2	Relative Diff., %	Rep. 1	Rep. 2		Corp of Engineers[c]	British Standard[d]
1	3.15	3.35	6	3.33	3.54	170	Very stiff	Very stiff
2	2.50	2.00	22	2.64	2.12	120	Very stiff	Stiff
3	0.35	0.25	33	0.37	0.26	16	Soft	Very soft
4	0.15	0.20	29	0.16	0.21	9	Very soft	Very soft
5	0.25	0.25	0	0.26	0.26	13	Soft	Very soft

(a) True UCS = 1.0577 × As-Read UCS. See Section 2.4.

(b) Shear strength estimated from UCS according to Holtz and Kovacs (1981):

$$\text{Shear strength, kPa} = \frac{\text{UCS, kg(f)/cm}^2}{2} \times \frac{9.81\text{ m}}{\text{sec}^2} \times \frac{10^4\text{cm}^2}{\text{m}^2} \times \frac{\text{kPa}}{(10^3\text{ kg/m}\cdot\text{sec}^2)}$$

(c) Consistency descriptions obtained from Corps of Engineers (1994) and "Consistency/strength of clay mixtures" (Solum 2005) are based on UCS. These descriptions are used in the present document.

- Fluid mud (UCS <0.02 kg/cm^2).
- Very Soft (UCS 0.02-0.25 kg/cm^2) – Easily penetrated several inches by thumb. Exudes between fingers and thumb when squeezed.
- Soft (UCS 0.25-0.5 kg/cm^2) – Easily penetrated one inch by thumb. Molded by light finger pressure.
- Medium (UCS 0.5-1.0 kg/cm^2) – Can be penetrated ¼" by thumb with moderate effort. Molded by strong finger pressure.
- Stiff (UCS 1.0-2.0 kg/cm^2) – Indented about ¼" by thumb but penetrated only with great effort.
- Very stiff (UCS 2.0-4.0 kg/cm^2) – Readily indented by thumb nail.
- Hard (UCS >4.0 kg/cm^2) – Difficult to indent by thumb nail.

(d) Consistency descriptions by Clayton et al. (1995) and British Standard (1999; *in italics*) are based on shear strengths and are similar to those given for UCS but with ~50% higher strength thresholds. These descriptions are used for comparison and completeness but are not otherwise used in the present document.

- Very soft (shear strength <20 kPa) – Exudes between fingers when squeezed in hand. *Finger easily pushed in up to 25 mm.*
- Soft (shear strength 20-40 kPa) – Molded by light finger pressure. *Finger pushed in up to 10 mm.*
- Firm (shear strength 40-75 kPa) – Can be molded by strong finger pressure. *Thumb makes impression easily.*
- Stiff (shear strength 75-150 kPa) – Cannot be molded by fingers. Can be indented by thumb. *Can be indented slightly by thumb.*
- Very stiff (shear strength 150-300 kPa) – Can be indented by thumb nail. *Can be indented by thumb nail.*
- Hard (shear strength >300 kPa) – Cannot be indented by thumb nail. *Can be scratched by thumb nail.*

Two penetrometer measurements were taken for each test. The agreement between the five paired sets of measurements averaged about 18% (relative). It is seen, by comparison with the calibration data given in Table 2.9, that most of the variability in the sludge measurements was due to the sludge itself and not to the variability in the penetrometer performance. The observed measurement variability is similar to the 28% (relative) variability observed for in-field penetrometer measurements of clay soil shear strength (Zimbone et al. 1996).

The UCS values are compared to qualitative terms used by geotechnical engineers to describe the textures and consistencies of cohesive soils such as clays and clay mixtures. These descriptions are deemed to be valid to aid in the envisioning the states of the STP product sludges because the fine-grained and cohesive KE Basin sludges outwardly have textures similar to clay or other fine-grained soils. It is seen that the products from Tests 1 and 2, which were based on KC-2/3 M250 sludge materials with added irradiated uranium metal particles prepared to model Settler tube sludge, are described as “very stiff” [based on descriptions given by Corps of Engineers (1994)] and would not be penetrated readily by thumb compression but could be indented by a thumbnail. In contrast, the products from the KE Container Composite sludge materials processed in Tests 3, 4, and 5 are described as “soft” to “very soft”, and would exude between the fingers if compressed in a closed fist. The constituent sludges used to prepare the KE Container Composite sludge had previously measured shear strengths ranging from 270 to 8,100 Pa (Plys and Schmidt 2006) and would be described as “fluid mud” to “very soft.”

The unconfined compressive strengths obtained from actual sludge samples bracket those measured for a hydrothermally treated non-radioactive K Basin sludge simulant that contained aluminum hydroxide, ferric oxide hydroxide, blow sand, and flocculent at mass ratios roughly proportional to those expected for nominal KE Container sludge. The simulated sludge product had 36 kPa shear strength (Section 2.5), described as “medium” strength, and would be moldable by strong finger pressure. The UCS of modeling clay, in comparison, was measured to be 0.25 kg(f)/cm^2, equivalent to about 32 kPa shear strength.

The susceptibility of rill formation in soils and the resistance of soils to erosion by raindrop impact (splash) and sheet flow of water have been shown to correlate with soil shear strength (Misra and Rose 1995; Zimbone et al. 1996, and references therein). Therefore, the measurement of the shear strength of the sludge product from STP processing is relevant not only to the resistance offered by the sludge to the mixer in the process reactor but also to the movement of the product sludge from the reactor by water sluicing upon completion of the hydrothermal processing.

The archived KC-2/3 M250 sludge used in Tests 1 and 2 in the storage jar compacted in the storage jar even though the sludge had been stored immersed in water at hot cell (~25-35°C) temperatures. The archived KC-2/3 M250 sludge thus had significant strength before being blended with water for use in the present testing.

Further observations of the durability of the heat-processed sludges were performed by eroding selected intact ~1 – 2-cm diameter sludge pieces with 400 ml of circulating water in a 600-ml beaker. A 2-inch diameter four-bladed stirrer provided agitation 1.6-cm from the beaker bottom at 40, 100, and 300 RPM (10.6, 26.6 and 79.8 cm/s tip speeds, respectively) for periods ranging from 5 to 30 minutes. The sludge/water mixtures settled between intervals of stirring and images of the settled sludge were gathered to determine the extent of erosion for sludge from Tests 1, 2, 4 and 5. No appreciable erosion of agglomerates from Tests 1 and 2 was observed at 40 or 100 rpm. After 65 minutes at 300 rpm, the diameters of the agglomerates from Test 1 were reduced by about 40 to 50%. After 15 minutes at 300 rpm, the diameters of the agglomerates from Test 2 were reduced by about 15%. Consistent with the lower shear strength measurements, agglomerates from Tests 4 and 5 exhibited significant erosion at the lower mixing rates (40 and 100 rpm).

The product sludge from Tests 3 was sufficiently fluid that intact pieces could not be collected. Instead, sludge samples from Tests 3 (and 5) were placed on sieves and washed with water from a squirt bottle. This mild erosion showed the sludges from Tests 3 and 5 had little cohesion or self-cementing. This lack of self-cementation also extended to the OIER present in Test 5. No evidence of OIER agglomeration with other OIER beads or with non-OIER sludge solids was found.

Results of the stirrer testing conducted in the 600-ml beakers are summarized in Table 3.6 and shown in still images obtained from video records collected during the testing (Figures 3.11 through 3.19). The still images are examined individually for each test in the following discussions.

Table 3.6. Effects of Agitation on Agglomerate Erosion

Test	Approximate Initial Sludge Piece Size, cm[(a)]	Agitation Conditions Evaluated[(b)]	Qualitative Observations
Test 1	1.8 cm 1.5 cm 1.0 cm	40 rpm, 7 min	No visible erosion, water clear.
		100 rpm, 5 min	Minimal erosion, trace of particulate in water.
		300 rpm, 5.5 min	10 to 20% reduction in agglomerate diameter.
		300 rpm, 35.5 min	Erosion, but image not interpretable.
		300 rpm, 65.5 min	40 to 50% reduction in agglomerate diameter.
Test 2	1.8 cm 1.4 cm	40 rpm, 5 min	No visible erosion, water clear.
		100 rpm, 5 min	Minimal erosion, trace of particulate in water.
		300 rpm, 5 min	~10% reduction in agglomerate diameter.
		300 rpm, 15 min	~15 % reduction in agglomerate diameter.
Test 3	NA	NA	Sludge did not form large concretions.
Test 4	Cylindrical plug, 1.7 cm dia. 2.9 cm length	40 rpm, 5 min	Disintegrated to particles less than 1 cm.
		100 rpm, 5 min	Little change, largest agglomerates <1.0 cm.
		300 rpm, 5 min	Few larger particles, largest agglomerates <0.7 cm.
Test 5	Cylindrical plug, 1.4 cm dia. 1.3 cm length	0 rpm	After water addition, particles <0.7 cm.
		40 rpm, 5 min	Little change, largest agglomerate <0.7 cm.
		100 rpm, 8 min	Very few, if any, agglomerates remaining.

(a) Sludge piece size estimate from interpretation of images captured from video records and the known beaker diameter of 8.5 cm. The dimensional accuracy is estimated to be ±10%, relative.

(b) Four-bladed, 2 in. (5.08 cm) diameter stirrer. Stirrer rotational speeds of 40, 100, and 300 rpm correspond to tip speeds of 10.6, 26.6 and 79.8 cm/s, respectively.

3.5.1 Test 1 Results and Images

The images collected of Test 1 materials before and after hydrothermal testing (7 hours of initial heating with about 5½ hours at 125-135°C plus another 26 hours ramping to 185°C, with ~14 hours intermediate dwell at 140°C, and 7 hours at 185°C) are discussed. The first image, Figure 3.11, shows the pre- and post-test appearance of the Test 1 sludge. No evidence of solids deposition on the vessel above the sludge (bathtub ring) was observed. The sludge is seen to tightly adhere to the Teflon test vessel surface. As shown in Table 3.5, this was the strongest sludge, and significant effort was required to remove it from the test vessel. It was attempted to remove the sludge from the liner as a single piece; however, removal ultimately required the use of a knife and other instruments.

The appearance of Test 1 sludge during and after erosion testing is shown in Figure 3.12. It is seen that significant erosion of the sludge solids is achieved only after 35 minutes of vigorous mixing at 300 RPM.

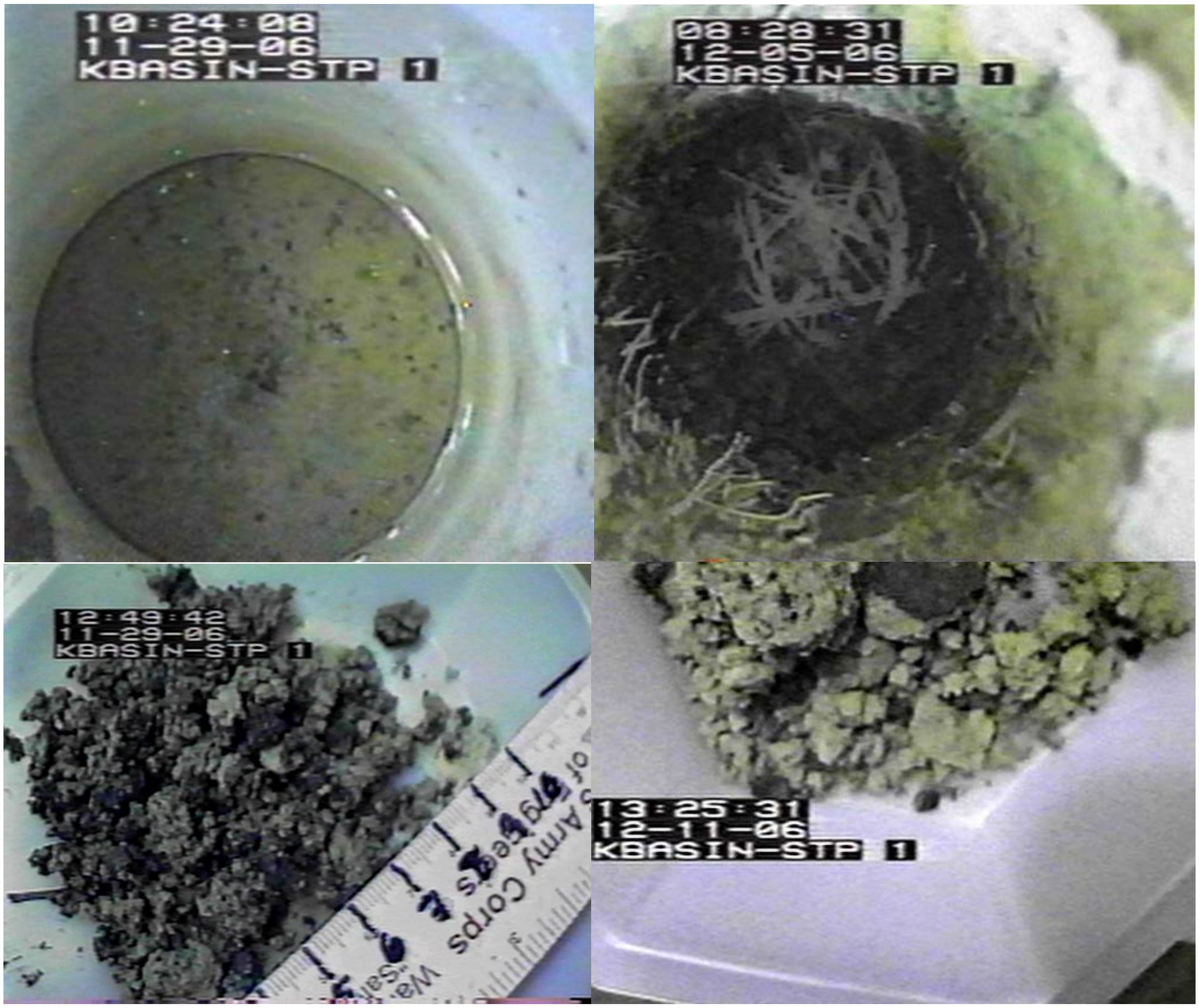

Figure 3.11. KC-2/3 M250 Canister Sludge Containing 5 g of -500 +250 µm Fuel Particles
Upper left – Top view of Test 1 in Teflon liner after hydrothermal testing.
Upper right – Teflon liner from Test 1 after removal of sticky sludge adhered to vessel surfaces.
Bottom left – Sludge concretions/agglomerates from Test 1. Monolithic concretion had to be broken up to remove material from the Teflon liner.
Bottom right – View of concretions ~2 weeks after removal from test vessel.

Figure 3.12. Test 1 Sludge Product Views During Erosion Testing
Top left – Initial apparatus configuration for mixing/erosion evaluation of Test 1 concretions. Apparatus included 600 ml beaker (8.5-cm diameter) and 5.08-cm diameter propeller, raised 1.6 cm above bottom of beaker.
Top right – Mixing/erosion evaluation, Test 1, after 5 minutes at 40 RPM; minimal erosion found.
Middle left – After 5 minutes at 100 RPM; minimal erosion observed.
Middle right – After 5.5 minutes at 300 RPM; significant erosion is observed.
Bottom left – After 35.5 minutes at 300 RPM.
Bottom right – After 65.5 minutes of mixing at 300 RPM.

3.5.2 Test 2 Results and Images

The observations made of the sludge from Test 2 after hydrothermal testing are discussed in this section. Test 2, like Test 1, contained KC-2/3 M250 sludge. Test 2 also initially included four irradiated metallic fuel coupon of size -6350 +4000 µm. Images of the sludge after the hydrothermal testing are shown in Figure 3.13. As in Test 1, the sludge was strong, adhering to the Teflon vessel surface, and required significant effort to remove from the test vessel. In addition to erosion testing in water, the entire sludge product was sieved to attempt to recover any unreacted uranium metal. The sieving was tedious, and to accomplish the sieving, the treated sludge was physically extruded through the mesh screen with various tools. The use of water to wash material through the sieve was not effective. No residue from the original four uranium metal fuel coupons was recovered except the single piece of cladding (of the four initially present) shown in the lower right of Figure 3.13. These findings indicate that the uranium metal reaction rate is not slower than that projected by Appendix G of SNF-7765 (Plys and Schmidt 2006). The bottom left image in Figure 3.13 shows agglomerates with powder black surfaces and green centers.

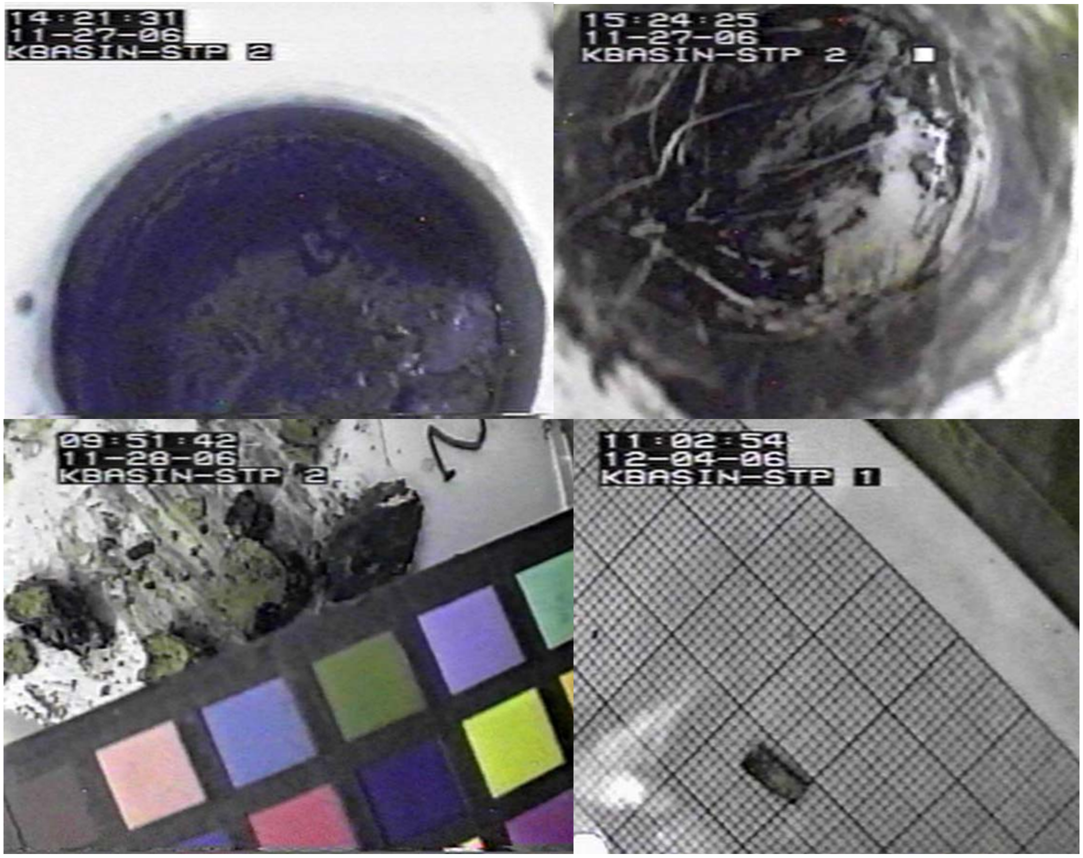

Figure 3.13. Test 2 KC-2/3 M250 Sludge Containing Four (5 g) of -6350 +4000 µm Fuel Particles
Top left – Top view of Test 2 in Teflon liner, after water removal.
Top right – Teflon liner from Test 2, sticky sludge adhered to vessel surfaces.
Bottom left – Clay-like agglomerates from Test 2, with color card. Agglomerate surfaces are black powder while center of agglomerate is avocado green.
Bottom right – Cladding piece recovered from Test 2 on grid. Dark grid lines are 1 cm × 1 cm. Light grid lines are 1 mm × 1 mm. (Note: Caption from image is mislabeled.)

Images taken of the erosion testing of Test 2 are shown in Figure 3.14. Like Test 1, Test 2 solids showed significant resistance to erosion and did not crumble until stirred at the highest, 300 RPM, agitator speed. Even at that, the primary agglomerates were only decreased in linear dimension by about 15%.

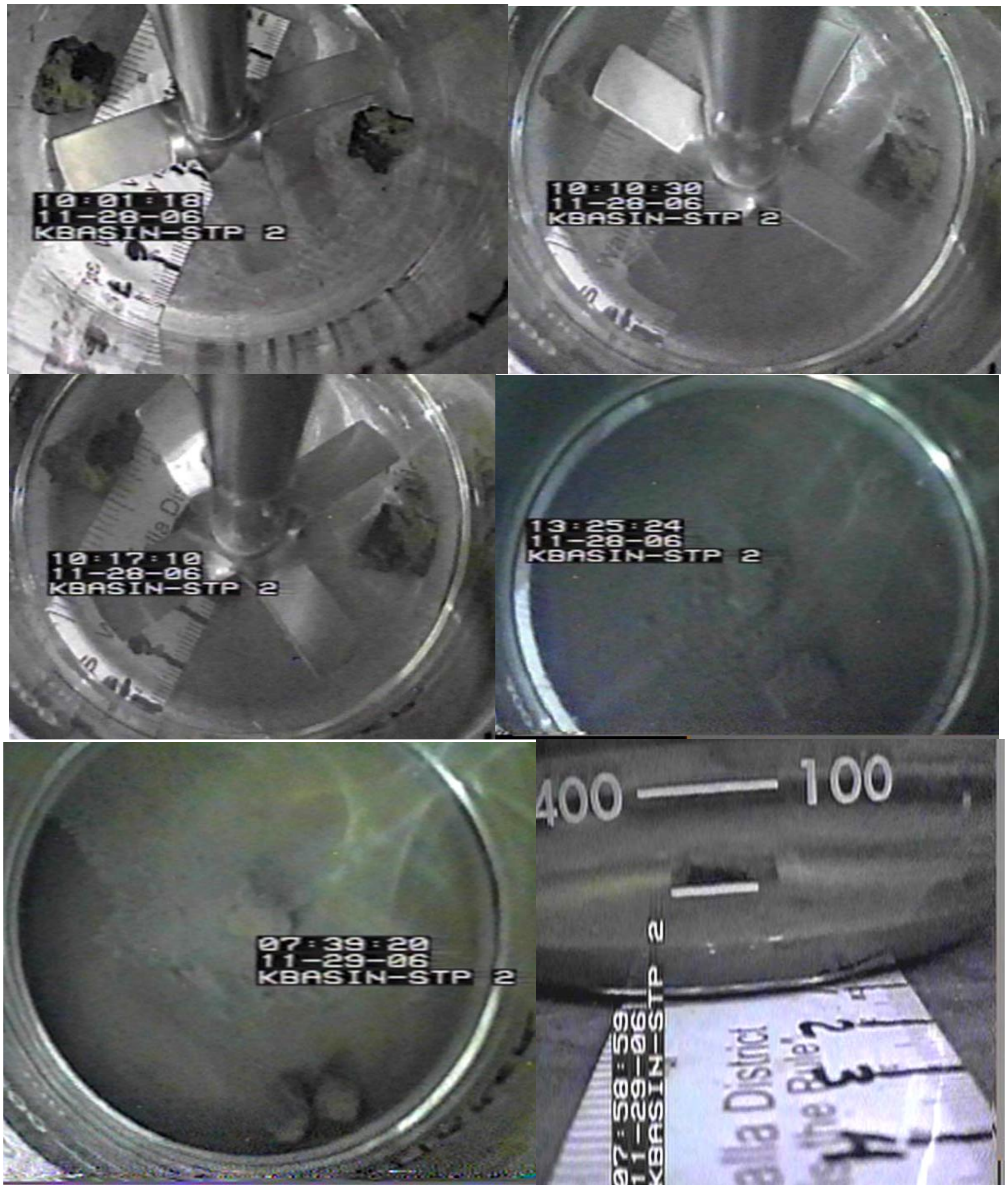

Figure 3.14. Test 2 Sludge Product Views During Erosion Testing
Top left – Initial set-up for mixing/erosion evaluation of concretions from Test 2.
Top right – Mixing/erosion after 5 minutes at 40 RPM showing minimal erosion.
Middle left – After 5 minutes at 100 rpm, minimal erosion.
Middle right –5 minutes at 300 rpm, significant erosion, demonstrated by sludge particle bed.
Bottom left – After 15 minutes at 300 rpm. Significant added erosion demonstrated by the bed of sludge particles and size reduction of primary agglomerates.
Bottom right – Side view of sludge eroded from agglomerates (15 min at 300 rpm).

3.5.3 Test 3 Results and Images

The observations made of the sludge from Test 3, containing flocculated KE Container Composite sludge and 5-grams of -1000 +500 µm uranium metal fuel particles, after 72 hours of 185°C hydrothermal processing are discussed in this section. This sludge had relatively low strength compared with the strengths of the Test 1 and 2 products, as shown in Table 3.5, and was not subjected to erosion testing in water. Observations of the sludge during examination, shown in Figure 3.15, indicate the weakness of the sludge. Views of a floating film or coating on the supernatant water from the post-heated sludge are shown in the upper left image of Figure 3.15. The nature of the film, perhaps arising from the kerosene vehicle present in the flocculating agent, is not known. No evidence of a bathtub ring at the water/air interface was observed.

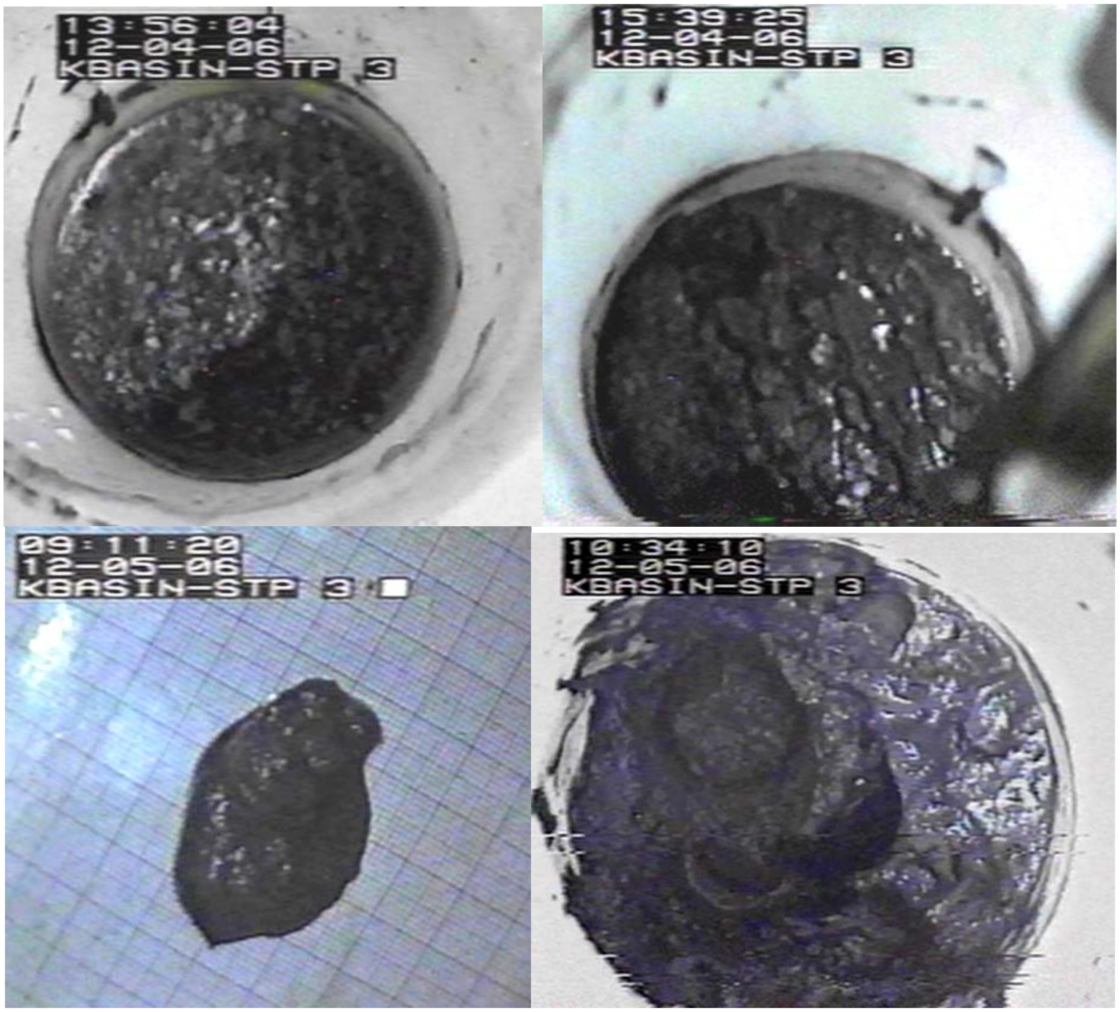

Figure 3.15. Flocculated KE Container Composite Sludge Containing 5 grams of -1000 +500 µm Fuel Particles
Top left – Top view of Test 3 in Teflon liner, with floating flakes/film on water surface.
Top right – Test 3 in Teflon liner, after water is removed and penetrometer testing has been completed. Sludge has very little strength.
Bottom left – Ejected core (from cut-off 10 ml syringe) on grid paper. Material slumps.
Bottom right – Overhead view of Teflon liner after removal of the core sample.

3.5.4 Test 4 Results and Images

Test 4, containing only flocculated KE Container Composite sludge, was processed for 72 hours at 185°C after an initial ~28-hour heating ramp including ~12-hour dwell at 140°C. Observations of the physical properties of Test 4 are discussed in this section. Test 4 had no supernatant liquid above the sludge and had sufficient strength that a core sample could be drawn using a cut-off 10-ml plastic syringe (~1.4-cm diameter). Liquid was observed in the hole (Figure 3.16, bottom left) after the core was removed. The appearance of the sludge and the core is shown in Figure 3.16. Void pockets (postulated to be from retained gas) can be observed in the ejected core.

Figure 3.16. Flocculated KE Container Composite Sludge from Test 4
Top left – Top view of Test 4, in Teflon liner. Upon opening vessel, no free water was observed on top of the sludge.
Top right – Teflon liner from Test 4, after sludge removed.
Bottom left – Sludge in Teflon liner, after core sample removed. Note, free liquid was observed in bottom of hole.
Bottom right – Ejected core from Test 4 on grid paper, with color card.

The appearance of Test 4 during the erosion mixing is shown in Figure 3.17. At 40 rpm, significant turbidity was immediately observed and the core largely disintegrated after 5 min. at 40 rpm. The sludge from Test 4 hydrothermal treatment, the flocculated KE Container Composite, was much less rugged than the sludges produced from the hydrothermal treatment of KC-2/3 M250 used in Tests 1 and 2.

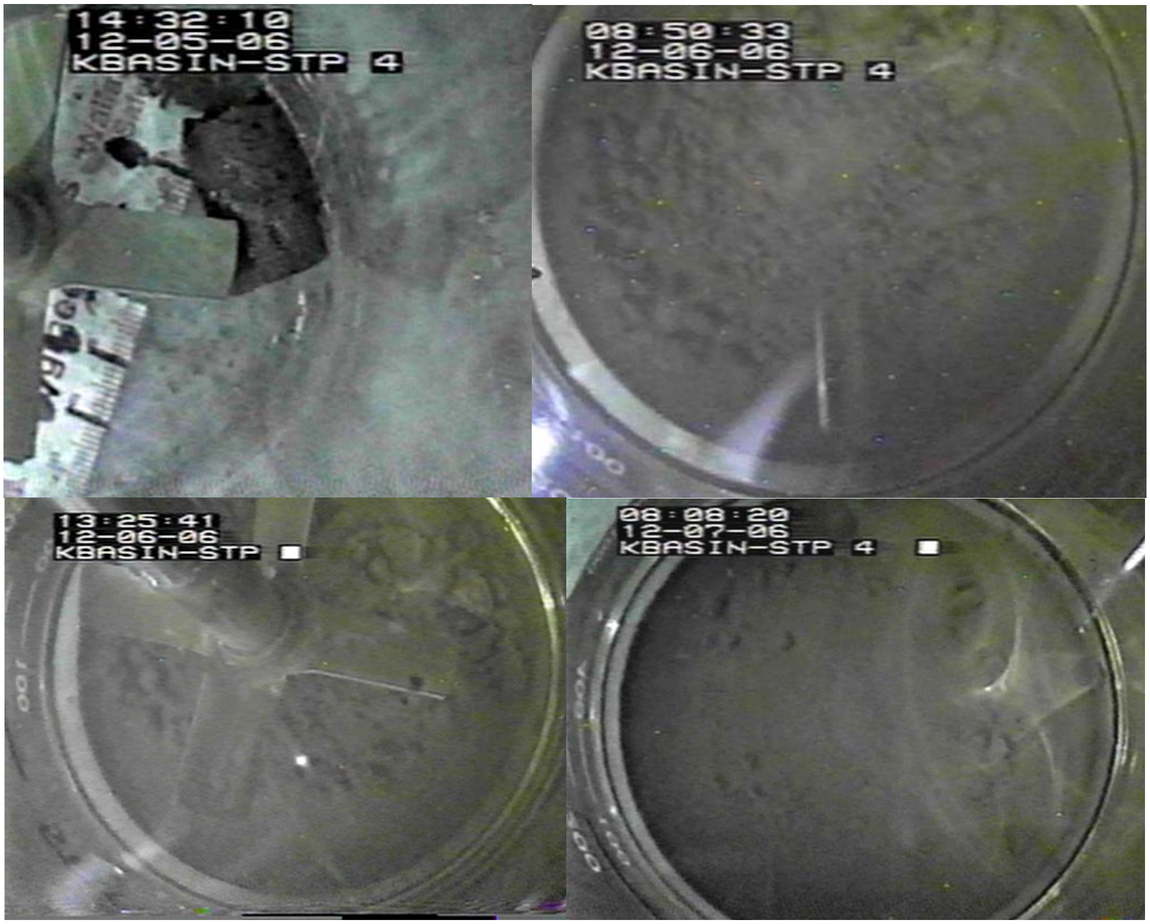

Figure 3.17. Test 4 Flocculated KE Container Composite Sludge During Erosion Testing
Top left – Both pieces of the ejected core were used in mixing/erosion tests.
Top right – Disintegrated core, after mixing for 5 minutes at 40 RPM and settling overnight.
Bottom left – After mixing at 100 RPM for 5 minutes and settling.
Bottom right – After 5 minutes at 300 RPM and settling.

3.5.5 Test 5 Results and Images

The sludge used in Test 5 was non-flocculated KE Container Composite and OIER from sample KC-6. Like Tests 3 and 4, Test 5 was processed for 72 hours at 185°C after an initial ~28-hour heating ramp that included a ~12-hour dwell at 140°C. The physical properties of Test 5 were similar to those of Test 3. The appearance of the Test 5 sludge is shown in Figure 3.18. As noted previously, no evidence of agglomeration of the OIER beads either with itself or with non-OIER sludge particles was observed. A partially intact core collected using a cut-off 10-ml plastic syringe (~1.4-cm diameter) was placed into the beaker for erosion testing (Figure 3.19). Upon addition of water to the beaker, the core partially disintegrated. Mixing at 40 rpm did not appear to result in further erosion; however, after 8 min of mixing at 100 rpm, it appeared that all larger agglomerates had disintegrated.

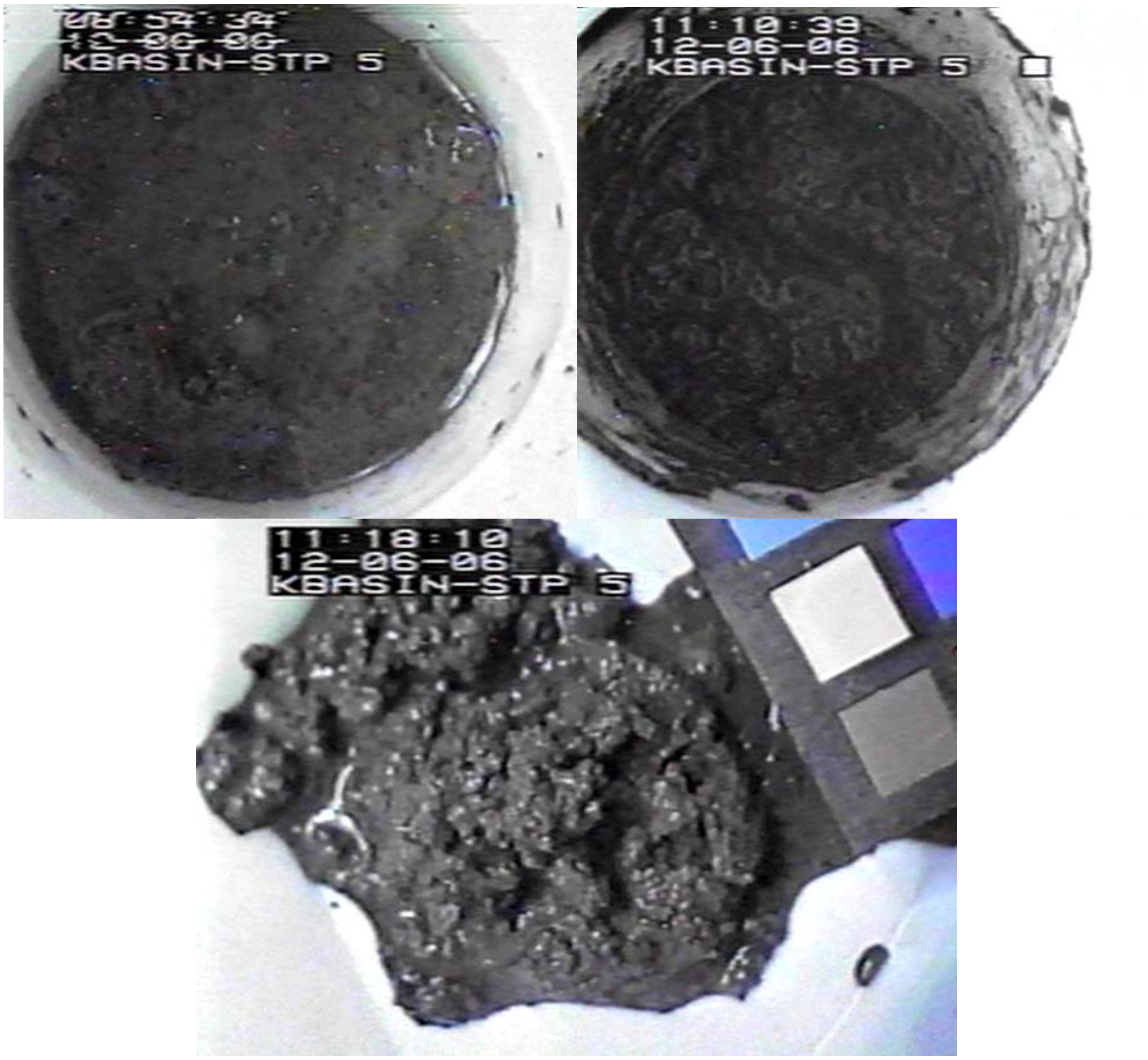

Figure 3.18. KE Container Composite Sludge and OIER from Test 5
Top left – Top view of Test 5 in Teflon liner upon opening vessel.
Top right – Teflon liner after removing sludge.
Bottom center - Sludge in weigh boat with color card.

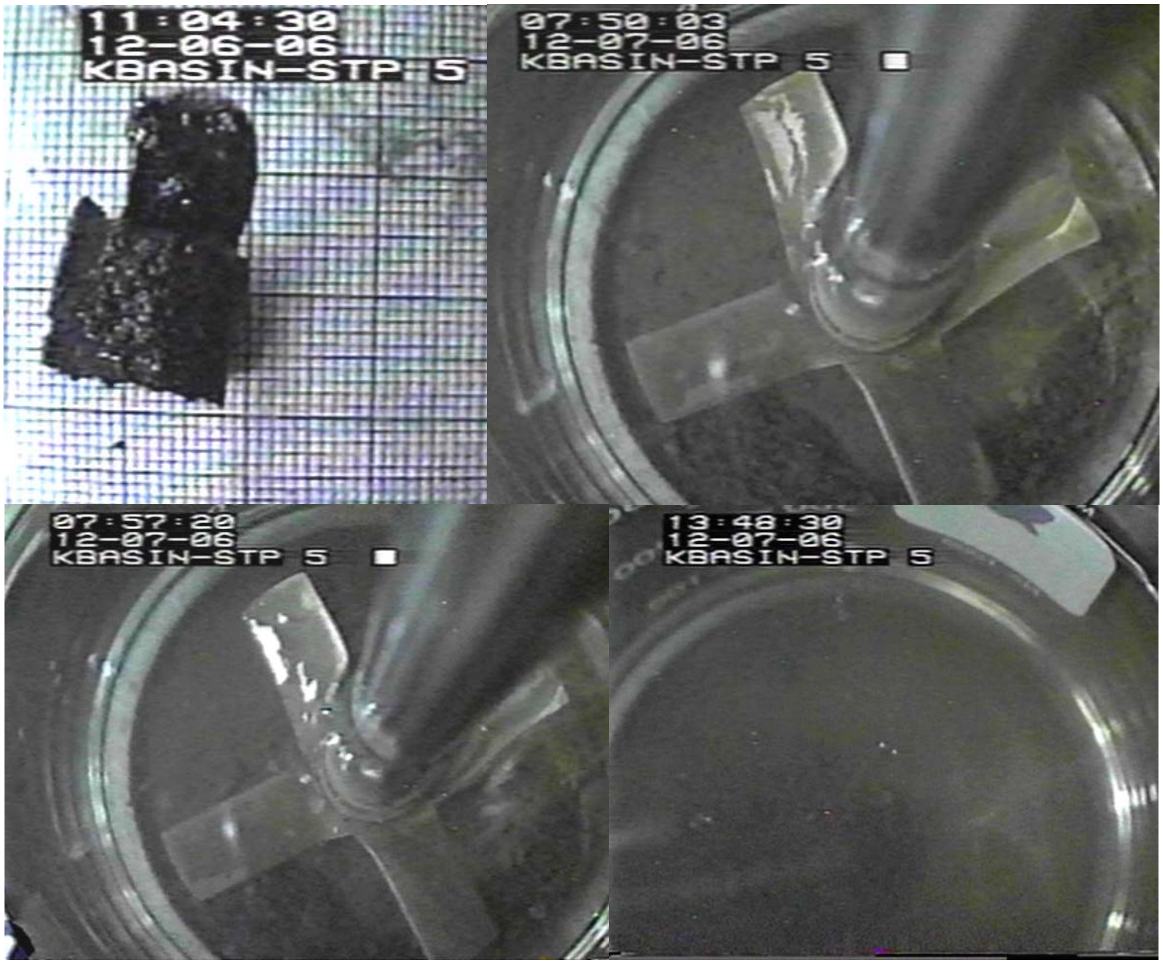

Figure 3.19. KE Container Composite Sludge and OIER from Test 5 During Erosion Testing
Top left – Extruded partial core from Test 5.
Top right – The ejected core partially disintegrated upon adding water from squirt bottle.
Bottom right – After mixing at 40 rpm for 5 minutes. No obvious erosion at 40 rpm.
Bottom left – After 100 rpm for 8 minutes. No larger agglomerates remaining.

4.0 Considerations for Future Testing Supporting STP Processing

Consistent with the guiding Data Quality Objectives (Schmidt et al. 2006, Section 2.2), the bench-scale tests described in this report were scoping in nature and were designed to evaluate and understand:

1) the basic chemical changes to actual K Basin sludge occurring under the hydrothermal conditions of the STP corrosion process, and
2) the effects of sludge composition on sludge rheological properties.

The tests investigated the effects of selected compositional changes (Container composite and Settler sludge; presence of uranium fuel particles, flocculating agent, and OIER) on product sludge rheological properties after unstirred (static) STP process temperature conditions. The testing showed that significant increase in sludge strength (i.e., agglomeration) occurred, particularly for the sludge formulations modeling the Settler tube compositions. These strength increases were accompanied by observable changes in the uranium chemical phases and in dehydration reactions that may have played significant roles in increasing sludge strength. At the same time, the testing showed that the presence of uranium metal fuel particles, flocculating agent, and OIER had little effect on sludge strength.

However, the current tests were not designed to test the engineering aspects of the process, which are typically performed at a pilot scale and require larger sample volumes and more complex and prototypical test apparatus (Schmidt et al. 2006).

Based on the test results, some of the identified concerns associated with the STP corrosion process were largely resolved (e.g., effects of flocculent and OIER, and potential impacts of other K Basin sludge constituents on the theoretical uranium metal corrosion rate) while other concerns (e.g., cementation, sludge adherence to surfaces, the effects of more widely varied sludge composition, and the formulation of pilot-scale test simulants) warrant further investigation. Remaining concerns associated with sludge behavior in the corrosion vessel thus are related to the underlying chemical reaction phenomena and the associated engineering and design implications. Although many of the engineering issues will require pilot-scale testing or design verification and thus be outside of the scope of laboratory investigations, bench-scale test results can provide meaningful data to the engineering work and are considered in the following questions.

Chemistry Questions

- During the STP corrosion process, how is the behavior of sludge affected by the concentration and speciation of key components (e.g., how do uranium and aluminum hydroxides and other compounds affect sludge cementation)?

  In the scoping tests, effectively only two nominal compositions with varied additives (flocculating agent, OIER, and uranium metal) were tested. In contrast, the sludge batch compositions in the STP corrosion vessel are likely to vary significantly. In the scoping tests, sludge that contained 70 wt% U total formed high strength agglomerates at STP conditions. At lower uranium concentrations, (16 wt% uranium), the extent and strength of agglomeration was significantly less. The test results show that the uranium behavior under STP corrosion conditions may largely be controlled by U(VI) in the form of metaschoepite. However, both Settler and KOP sludge have the potential to contain appreciable concentrations of U(IV) phases (e.g., $UO_{2.x}$). Data on the behavior of sludges with high U(IV) oxide concentrations at STP conditions does not currently exist beyond that provided from the current scoping tests.

Non-radioactive simulant tests showed that gibbsite (an aluminum hydroxide phase found in sludge) formed a firm solid monolith at STP processing conditions. However, in testing with an actual K Basin Container sludge composite containing about 25% less aluminum than the non-radioactive simulant, a firm monolith was not formed. The effects of aluminum hydroxide on processed sludge strength are ambiguous. Will KE floor/pit/canister sludges with high aluminum concentrations form high strength products under STP conditions?

- Can STP process operating conditions, or the composition of the process feed, be adjusted to minimize sludge agglomeration in anticipated zones of no/low agitation in the STP corrosion vessel? For example, do temperature and pH adjustment, sludge stream blending, and addition of diluents affect product strength? Are adjustments to these process parameters feasible?

- Will sludge adhere or form scale along the inner process vessel surfaces? Will the adherence or scaling be exacerbated by the anticipated higher wall temperature of the STP process corrosion vessel compared with the wall temperatures experienced in the scoping tests?

  In the scoping tests, the vessel temperature was controlled at 185°C at the outer vessel wall and the sludge was in contact with the Teflon vessel liner. In the STP corrosion vessel, the stainless steel wall temperature in contact with sludge generally will exceed 185°C to ensure heat transfer and drive water evaporation. Tests should be performed to understand the effects of enhanced wall temperature on sludge behavior.

- Can a non-radioactive (and non-uranium containing) simulant that generally mimics the chemical and physical behavior of Settler sludge under static hydrothermal processing conditions be developed for use in scaled-up corrosion vessel testing?

  Based on the limited volume of actual sludge materials and the engineering challenges associated with the interpretation of a scaled-down radioactive test (~15,000 L corrosion vessel vs. ~500 ml hot cell test), corrosion vessel validation testing would be more accurate and defensible if conducted at a larger scale.

- Will the nitrogen sparge in the STP corrosion vessel cause localized precipitation?

  The nitrogen sparge will strip water from the sludge and produce localized cooling. Will the cooler and more concentrated solutions engendered by the nitrogen purge act to precipitate dissolved phases and increase or decrease sludge agglomeration?

Engineering/Design Questions

- What is the effect of the planned agitation and reactor (corrosion vessel) design and geometry on the extent and location of concretion formation and scaling that occurs under nominal mixing and sparging operations? Note that these questions may need to be addressed on an engineering scale.

- Is the current design concept and operating approach of the STP corrosion vessel adequately robust (or are contingent operations planned) to address expected cementation (i.e., shear strength >100 kPa) in a loss-of-agitation event?

- Can design features/approaches be incorporated to minimize potential impacts from scaling and concretions that do form? For example, can increasing product strength during processing be detected and, if so, what are effective mitigations (e.g., injecting additives, decreasing temperature, increasing mixing rate) that can be implemented within the process?

Testing Approach

Table 4.1 provides a comparative overview of laboratory testing approaches that can be used to address some of the proposed outstanding questions associated with the behavior of sludge in the STP corrosion process. To provide a disciplined approach for the direction of the future testing, the KBC Sludge Treatment Project has initiated a DQO process to articulate the STP Project processing concerns (problem statements) and identify the key decisions and the required input (including test data) to address these questions. The DQO approach was also used for the current scoping tests. The present report will serve as key input to this DQO process.

Table 4.1. Options for Further Laboratory Testing and Tradeoffs

Test Approach/Option	Questions and Information/Data Generated	Advantages/Concerns
Small Scale Static Cold Tests (no agitation), (<600 ml) Similar/identical equipment to that used in the Scoping tests.	Identify problematic phases. For example, what are the key non-uranium phases affecting sludge strength (e.g., gibbsite → boehmite)? Modify non-uranium chemistry/behavior. What are the effects of blending, additives, and pH control? Design and validate simulants for larger scale lab testing with agitation and for vendor pilot-scale testing. Compare static vs. mixed systems. Determine if hydrogen scavenging reactions occur for non-U compounds [e.g., $Fe(OH)_3 + H_2 \rightarrow Fe_3O_4$]	Lowest cost testing, and can be executed quickly. Initial and product non-uranium phases in K Basin sludge in the present tests were largely not identifiable by XRD. Significant batch-to-batch sludge compositional variability is expected.
Small to Bench-Scale Cold Tests with Agitation/Evaporation (300 ml to 2 gal)	Better evaluate mixing and evaporation. Give insight into fate of dissolved species on hot reactor wall and precipitation on solids during evaporation. Validate non-uranium simulant for vendor testing.	Can be done relatively quickly. Can examine several agitator or impeller designs. Will be challenging to extrapolate results to full scale system.
Small Scale Warm Static Tests with Natural Uranium. (< 600 ml) Similar/identical equipment to that used in current testing. Must be conducted in rad lab.	Identify problematic U oxide phases. What are the key uranium phases affecting sludge strength? Investigate H_2 scavenging by oxidized U phases. Determine if behaviors observed in current hot tests be duplicated. Modify chemistry/behavior by blending, additives, or pH control. Provide data for comparison with data for mixed system. If stainless vessel used, provide insight into scale formation.	Less costly than hot testing. Current data show that U oxide phases are biggest concern with respect to changing rheology. Assumes natural uranium metal and oxides behave like uranium from N-Reactor fuel/corrosion.
Small Scale Warm Test (Natural Uranium) with Agitation/ Evaporation (300 to 1000 ml)	Compare static and mixed systems. Provide additional insight into fate of dissolved species during evaporation (hot wall deposition vs. precipitation on solids). Provide closer representation of Settler/KOP sludge under process conditions.	Can serve as shakedown activity for hot cell tests. Value of results depends on ability to duplicate chemistry and behavior during warm static tests.
Small Scale Static Hot Test (no Agitation) Similar/identical equipment to that used in current testing.	Further explore chemistry changes that may be of concern. Expand range of actual sludge compositions tested. Evaluate benefits of blending, additives, or pH adjustment.	Equipment, methods, approvals are in hand. Provides additional data on the effects of sludge variability and increases confidence in findings. May provide options to limit shear strength in loss-of-agitation event or in low-agitation reactor regions.
Small Scale Hot Test with Agitation and Evaporation (300 to 1000 ml)	Compare static vs. mixed system for actual sludge. Provide additional insight into fate of dissolved species during evaporation (hot wall deposition vs. precipitation on solids).	Tests are close to actual STP system conditions. Equipment, methods, and approvals would need to be developed; hot cell tests with both agitation and evaporation will likely require >6 months to prepare and run. Archived K Basin sludge materials available for testing are limited.

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Appendix A

Bases for Uranium Metal Quantity in Tests 1, 2, and 3; Flocculent Loading in Tests 3 and 4; and OIER Concentration in Test 5

Appendix A

Bases for Uranium Metal Quantity in Tests 1, 2 and 3 and Flocculent Loading in Tests 3 and 4 and OIER Concentration in Test 5

Basis for Uranium Metal Loading in Tests 1 through 3

The uranium metal concentrations in Tests 1, 2, and 3 are targeted to be 5 wt% (settled sludge basis) and, thus, similar to that of Safety Basis KE Canister and KW Canister sludge (i.e., Settler tank sludge). Tests 1 through 3 include approximately 50 ml of as-settled sludge. The settled density of the sludges being used range from about 1.4 to 2.2 g/cm^3. Assuming a density of 2 g/cm^3, each test will contain approximately 100 g of as-settled sludge. In Tests 1 - 3, about 4 to 5 g of irradiated metallic fuel will be added to the sludge. Therefore, on a settled sludge mass basis, the uranium metal content will be approximately 4 to 5 wt%. [Note: It is assumed that the sludge used in these tests contain insignificant quantities of uranium metal. In support of this assumption, the uranium metal content of KC-2/3 M250 (Fine KE Canister sludge) was 0.049 wt% (settled sludge basis) in 2000 (Delegard et al. 2000).]

Basis for Flocculent Loading in Tests 3 and 4

The commercial flocculent Optimer 7194 Plus (Nalco), a polymeric (acylamide co-polymer) cationic flocculent, is being used to improve particle capture during sludge containerization in the KE Basin. This flocculent will also be used to improve particulate capture when sludge is transferred from containers in the KE Basin to containers located in the KW Basin. Emulsion polymers, such as Optimer 7194 Plus, are typically 3 phase products found in roughly equal proportions of polymer, light oil (solvent), and water.

From the MSDS, Optimer 7194 Plus exhibits the following properties:

Specific Gravity of 1.01 to 1.04,
Volatile Organic Content = 24.4%
Total organic carbon: 230 g/L

Moore and Duncan (2005)(a) give projected concentrations of neat flocculent in the as-settled Container sludge (Table A.1).

(a) Moore, FW and DR Duncan. 2005. *K Basin Closure Project KW Sludge Containerization System Calculation to Determine Flocculent Concentrations in KW Containers*. KBC-27977, Rev. 0, Fluor Hanford, Richland, WA.

Table A.1. Projected Flocculent Concentrations in Settled Sludge (Moore and Duncan 2005) [(a)]

Case	Neat Floc Concentration, ml/l of As-Settled Sludge
Low Nominal	4.85
Nominal	5.53
High Nominal	12.9
Bounding	14.8

(a) Moore, FW, and DR Duncan. 2005. *K Basin Closure Project KW Sludge Containerization System Calculation to Determine Flocculent Concentrations in KW Containers.* KBC-27977, Rev. 0, Fluor Hanford, Richland, WA.

Tests 3 and 4 each include 50 ml of as-settled sludge. The neat flocculent target for these tests at the nominal flocculent loading (5.53 ml/liter) = 5.53 ml × (50 ml/1000 ml) = 0.28 ml neat flocculent per 50 ml of sludge. Diluted to a 1 wt% solution, 28 ml (0.28/0.01) of made-down (diluted) flocculent would be added to the 50 ml of sludge.

Alternatively, if the bounding value is used, 75 ml (28 ml × 14.8 ml/5.53 ml) of 1 wt% made-down flocculent would be added. Note, however, that adding 75 ml of neat flocculent to 100 ml of sludge would be difficult in the hot cell environment and not typical of the sludge conditions.

Based on a collaborative decision between PNNL and FH personnel, use of the nominal flocculent loading was recommended and used to prepare the sludge for Tests 3 and 4.

Basis for 15% OIER Loading in Test 5

It is estimated that the West Bay floor of the KE Basin contained between 1.05 m^3 (nominal) and 2.78 m^3 (bounding) of IXM-related OIER beads (Pearce 2001). Based on estimates, this OIER was distributed in a fairly limited area encompassing 12.5 to 25% of the West Bay (though occasional beads are found throughout the other sludges). Because of the high concentrations and the near neutral buoyancy of the OIER, it is likely that pockets of sludge with high concentrations of OIER now exist in the KE sludge containers, and it is likely that high concentrations of OIER (e.g., >10 vol%) will be seen in one or more batches in the STP. Based on previous testing in water at 95°C, OIER beads did not melt or agglomerate. Furthermore, the OIER was found to be little affected by 24 hours of treatment in 15.7 M nitric acid at 95°C (Pool et al. 1998). Based on differential scanning calorimeter/thermogravimetric analysis (DSC/TGA) data, K Basin OIER is relatively unreactive at temperatures below 200°C. The DSC/TGA data also showed that fresh (non-radioactive) OIER is more reactive than OIER collected from the KE Basin.

However, in a February 2006 communication, the OIER vendor (Purolite) stated the following:

"We normally recommend a maximum temperature of 140°F (60°C) for the regenerated forms of these resins that are in the NRW-37. Above this the resin eventually breaks down chemically. At 185°C, softening and agglomeration of the resin is likely."

The propensity for OIER to soften and potentially contribute to sludge agglomeration at STP process conditions lead to the conclusion that this behavior in the K Basin sludge should be investigated.

The amount of OIER in a sludge process batch must be estimated to create a meaningful test condition. The following volumes are based on estimates provided by Woodworth (2006):[a]

- The 40.9 m^3 (i.e., KE and KW sludges) of as-settled Container Sludge will be treated in 12 batches. Therefore each batch contains, on average, ~3.4 m^3 of as-settled sludge.
- The Container Sludge transfer volume is 2764 gal (10.5 m^3) at 10.1% solids for batches 1 through 8 and the original sludge has 25 vol% solids. Therefore, the starting volume of each of the eight batches is 4.2 m^3:

$$2764\text{ gal transfer vol.}\times\frac{0.101\text{ gal solids}}{\text{gal transfer vol.}}\times\frac{\text{gal starting vol.}}{0.25\text{ gal solids}}\times\frac{3.78\text{ liters}}{\text{gal}}\times\frac{\text{m}^3}{10^3\text{ liters}}=4.2\text{ m}^3\text{ starting volume}$$

Nominal OIER Loading:

Assume that 50% of the nominal OIER inventory (i.e., $0.5 \times 1.05\ m^3$) is present in one average batch:

$$100\% \times 0.5 \times 1.05\ m^3/3.4\ m^3 = 15\%\text{ loading.}$$

Assume that 50% of the nominal OIER inventory is in one of the first 8 batches:

$$100\% \times 0.5 \times 1.05\ m^3/4.2\ m^3 = 12.5\%\text{ loading.}$$

Bounding OIER Loading:

Assume 50% of the bounding OIER inventory (i.e., $0.5\times 2.78\ m^3$) is present in one average batch:

$$100\% \times 0.5 \times 2.78 m^3/3.4\ m^3 = 41\%\text{ loading.}$$

Given that the OIER existed in a fairly small area of the KE West Bay Floor, and the fact that it is (based on sampling experience) one of the easiest of all sludge types in the basin to retrieve, it is likely that sludge with a very high concentration of OIER currently exists in one of the KE Sludge Containerization System (SCS) containers. It is also noted that OIER exhibits a relatively narrow distribution in particle size and density. Therefore, when the OIER is transferred from the KE Basin to the KW Basin via the hose-in-hose system, most will likely deposit in a relatively thin (e.g., 6-12 in.) band in a KW container. The best re-distribution of the OIER will likely occur when this containerized sludge in KW is pumped to the Cold Vacuum Drying (CVD) building for thermal processing. The assumption that 50% of the nominal OIER inventory could be present in a single STP Container Sludge batch appears plausible. Therefore, for Test 5, a 15 vol% loading of OIER (settled sludge basis) is recommended and will be used for the laboratory testing.

(a) Woodworth, M. 2006. *Sludge Retrieval and Transfer System Material Balance*. CALC-5477-PR-R-0001, Rev. 1, BNG America.

Appendix B

Vessel Loading and Post-Test Heating Data

Appendix B

Table B.1. Vessel Loading and Post Heating Data

Line	Value	Calculation (by line number)	Test 1	Test 2	Test 3	Test 4	Test 5
Loading Measurements and Calculations							
1	Empty vessel bottom, g		381.57	381.32	380.46	380.89	380.17
2	Empty vessel lid, g		55.14	54.78	54.64	54.74	54.75
3	Full sludge transfer vessel, g		141.00	140.96	121.15	122.01	90.20
4	Emptied sludge transfer vessel, g		21.48	26.48	29.50	31.17	23.41
5	Full OIER transfer vessel, g						16.41
6	Emptied OIER transfer vessel, g						7.91
7	Net OIER wt., g	7=5-6					8.50
8	Volume settled OIER, cm^3						7.50
9	Volume OIER beads, cm^3	9=8×(0.667 pack factor)					5.00
10	Wt. OIER beads, g	10=7-(8-9)×1.00 g/cm^3					6.00
11	Water wt. added, g		13.50	12.20	0.00	2.00	9.65
12	Metal vial(s) full, g		21.98	88.83	22.11		
13	Metal vial(s) empty, g		16.93	83.74	16.96		
14	Metal wt., g	14=12-13	5.05	5.09	5.15		
15	Volume metal, cm^3 (U fuel & clad)	15=14/(16.8 g/cm^3)	0.30	0.30	0.31		
16	Volume metal sludge, cm^3 (U fuel, clad, & H_2O)	16=15/(0.6 cm^3 fuel/cm^3 sludge) **(a)**	0.50	0.30	0.51		
17	Sludge lost by wiping & stirring, g		0.17	0.00	0.66	0.27	0.09
18	Net sludge wt., g	18=3-4-17	119.35	114.48	90.99	90.57	66.70
19	Settled sludge density, g/cm^3		2.68	2.68	1.53	1.53	1.65
20	Volume settled sludge, cm^3	20=18/19	44.53	42.72	59.47	59.20	40.42
21	Vol. settled sludge/metal/OIER mix, cm^3	21=8+16+20	45.03	43.02	59.98	59.20	47.92
22	Settled mixture density, g/cm^3	22=(10+14+18)/21	2.76	2.78	1.60	1.53	1.52
23	Gross loaded pre-oven wt., g		572.04	565.91	530.72	526.06	519.48
24	Gross wt. by calculation, g	24=1+2+7+11+14+18	574.61	567.87	531.24	528.20	519.77
25	Water loss in loading, g	25=24-23	2.57	1.96	0.52	2.14	0.29
26	Net added water, g	26=11-25+7-10	10.93	10.24	-0.52	-0.14	11.86
27	Supernatant water, g	27=26-(16-15)	10.73	10.24	-0.72	-0.14	11.86
28	Water in starting settled sludge, wt%		25.0	25.0	50.5	50.5	46.9
29	Water in starting settled sludge, g & cm^3	29=0.01×18×28	29.8	28.6	46.0	45.8	31.3
30	Adj'd. water in starting settled sludge, g & cm^3	30=29+16-15-25**(b)**+7-10	30.0	28.6	46.2	45.8	33.8
31	Water in starting settled mixture, wt%	31=100%×30/[10+14+16-15+18-25**(b)**]	24.1	23.9	48.2	51.8	44.9
32	Water in starting settled mixture, vol%	32=100%×30/21	66.7	66.5	77.0	77.3	70.4
33	Mixture solids particle density, g/cm^3	33=22×(1-0.01×31)/(1-0.01×32)	6.29	6.31	3.61	3.26	2.83
34	Solids in mix & supernatant water, vol%	34=100%-100%×(27+29)/(26+21)	28	27	24	23	28

Table B.1. Vessel Loading and Post Heating Data (cont'd)

Line	Value	Calculation (by line number)	Test 1	Test 2	Test 3	Test 4	Test 5
Post-Heating Measurements and Calculations							
35	Gross loaded wt. post-oven, g		571.69	565.70	530.08	525.24	518.94
36	Gross decanted wt., g		553.43	550.60	526.48	525.24	516.90
37	Depth to sludge layer, mm		55	56	57	40	50
38	Water loss in oven, g	38=23-35	0.35	0.21	0.64	0.82	0.54
39	Decanted water wt., g	39=35-36	18.26	15.10	3.60	0.00	2.04
40	Net drained sludge wt., g	40=36-1-2	116.72	114.50	91.38	89.61	81.98
41	Measured drained sludge volume, cm^3	**(c)**	52.3	50.8	49.2	75.6	60.1
42	Settled product sludge density, g/cm^3	42=40/41	2.23	2.25	1.86	1.19	1.36
43	Expected reacted fuel weight, g	43=0.93×(274/238)×14+0.07×14	5.76	5.81	5.87	0.00	0.00
44	Expected reacted fuel sludge volume, cm^3	44=43/[(9.4 g/cm^3)(0.35 cm^3/1.00 cm^3)] **(d)**	1.75	1.76	1.79	0.00	0.00
45	Water in reacted fuel sludge, g & cm^3	45=44-43/(9.4 g/cm^3) **(d)**	1.14	1.15	1.16	0.00	0.00
46	Expected drained sludge volume, cm^3	46=8+20+26+(44-45)-38-39	37.5	38.3	55.3	58.2	57.2
47	Expected drained sludge density, g/cm^3	47=40/46	3.12	2.99	1.65	1.54	1.43
48	Void volume of drained sludge, cm^3	48=41-46	14.9	12.5	-6.1	17.3	2.9
49	Water in drained product sludge, g & cm^3	49=26+28-38-39	22.1	23.5	41.2	44.8	40.5
50	Water in drained product sludge, wt%	50=100%×49/40	19.0	20.6	45.1	50.0	49.5
51	Settled solid & gas volume, cm^3	51=41-49	30.2	27.3	8.0	30.7	19.5
52	Drained sludge packed volume, cm^3	52=41-48	37.5	38.3	55.3	58.2	57.2
53	Drained sludge packed density, g/cm^3	53=40/52	3.12	2.99	1.65	1.54	1.43
54	Drained packed sludge water, vol%	54=100%×49/52	59.1	61.5	74.5	77.0	70.9
55	Void volume in product sludge, vol%	55=100%×48/41	28.4	24.7	-12.4	22.9	4.8
56	Product solids particle density, g/cm^3	56=(40-49)/(51-48)	6.17	6.18	3.56	3.34	2.49
57	Solids in product & supernatant water, vol%	57=100%-100%×(26+29)/(26+21)	27	28	24	23	28

(a) For finely particulate fuel used in Tests 1 and 3 only.

(b) Water loss from sludge accounted for Tests 3 and 4 only because they had no supernatant water. Evaporative water losses for other tests occurred from their supernatant liquids.

(c) Sludge volume, $\text{cm}^3 = 137.5\ \text{cm}^3 - \pi \times (\text{line 37, mm}) \times (22.2\ \text{mm})^2 \times \dfrac{\text{cm}^3}{1000\ \text{mm}^3}$ where vessel volume is 137.5 cm^3 (to the brim less the volume in the top bevel region) measured by both geometry and water displacement and 22.2 mm is the vessel radius.

(d) Reacted fuel sludge particle density is 9.4 g/cm^3; product fuel sludge is 65 vol% water and 35 vol% solids.

Appendix C

Results from Sludge Treatment Project Process Chemistry Validation Tests – Cold Shake-Down Testing

Appendix C

Results from Sludge Treatment Project Process Chemistry Validation Tests – Cold Shake-Down Testing

Prepared by: CH Delegard, AJ Schmidt, PK Berry, and SA Bryan

Scoping process tests with archived K Basin sludge and irradiated N Reactor fuel samples at prototypical Sludge Treatment Project (STP) time and temperature (72 hours at 185°C) are scheduled to begin in October 2007. Planning and preparation activities, including establishing test apparatus and procedures for hot cell application, are covered under FY 2006 funding. Accordingly, two non-radioactive simulated K Basin sludges were prepared and tested as part of these "shake down" activities. The primary objective was to design and evaluate the test apparatus and protocols for hot cell application with the archived K Basin sludge samples. A secondary objective was to gain some insight on whether the textures of the two simulant non-radioactive sludge types would be altered by the thermal treatment. Concerns have been expressed that the process conditions could alter sludge rheological characteristics to form aggregates or clumps that would be difficult to remove from the STP reactor vessel.

Through this non-radioactive shake-down testing effort, the general test approach and equipment was validated as appropriate for the intended hot cell testing application. Staff members were able to become familiar with handling and disassembling the test hardware and retrieving sample materials from test vessels. Protocols were also developed for post-test analyses of treated sludge. The results from this testing also provide early insights into the behavior of sludge components under STP conditions. Detailed results of the cold shake-down testing are provided below.

Non-Radioactive Sludge Simulants Used in Shake-Down Tests

The non-radioactive K Basin sludge simulants, whose compositions are shown in Table C.1, were prepared to generally mimic properties of genuine Container Sludge at the end of a STP corrosion cycle. One simulated sludge contained organic ion exchange resin (OIER; mixed anion/cation polystyrene divinylbenzene resin as used in the K Basins) and blow sand. The second sludge simulant contained aluminum hydroxide, ferric oxide hydroxide, and blow sand at mass ratios roughly proportional to those expected for nominal KE Container Sludge. The second simulant also contained the commercial flocculent Optimer 7194 Plus (Nalco) that is being used to improve particle capture during sludge containerization in the KE Basin. The neat flocculent was prepared (inverted) as a 1 wt% solution before being added to the simulant slurry. The preparation and testing of the OIER and Flocculated Sludge simulants were performed under specific Test Instructions approved by the KBC Project.(a)

(a) Test Instruction 51623-TI01, Rev. 0, "Non-Radioactive Test (Cold) with Resin Beads to Validate Sludge Treatment Process (STP) Chemistry Validation Test," AJ Schmidt, June 2006.
Test Instruction 51623-TI01-Addendum 1, Rev. 0, "Non-Radioactive Test (Cold) with K Basin Simulant + Flocculent to Validate Sludge Treatment Process (STP) Chemistry Validation Test," AJ Schmidt, August 2006.

Table C.1. Simulated Sludge Compositions

OIER Simulant		**Flocculated Sludge Simulant**[(a)]	
Component	**Value**	**Component**	**Value**
Blow sand, wt%	40.6	Blow Sand, wt%	20.5
NRW-100 (anion), wt%	13.2	$Al(OH)_3$ (gibbsite) , wt%	20.5
NRW-400 (cation), wt%	6.9	$Fe_5O_7(OH)\cdot 4H_2O$, wt%	27.4
Water, wt%	39.3	Water, wt%	31.5
		Flocculating agent, wt%	0.0269
Total, wt%	100.0	Total, wt%	100.0
Water, vol%	51.2	Water, vol%	55.2
Total volume (simulant + water), mL	62.5	Total volume (simulant + water), mL	62.5
Total mass (simulant + water), g	81.4	Total mass (simulant + water), g	109.6
Settled density, g/mL	1.30	Settled density, g/mL	1.75

(a) The flocculated sludge simulant is 10.4 wt% aluminum, 23.3 wt% iron, and 14.0 wt% silicon, dry basis, assuming the blow sand is SiO_2.

Test Equipment and Operation

Testing with the two simulants was conducted in parallel with two Parr Model 4748 vessels. Each vessel is comprised of a ~125-mL capacity Teflon vessel liner encased in a screw-topped steel sleeve and fitted with an overpressure rupture disk (Figure C.1). The vessels were loaded to 50% of the vessel volume (62.5 mL settled sludge) to allow head space for gas generation. The water vapor pressure at 185°C is ~162 psig, which, with the contained air, brought total pressure to ~184 psig. The Teflon/steel vessel apparatus, rated for operation up to 1900 psig at 250°C, were heated externally by placement in a thermostat-controlled oven. Tests were run up to ~185°C, or 85°C above the normal boiling point of water at 1 atmosphere, with a temperature profile envisioned for STP process operations. Heating from room temperature to 140°C required about 14 hours and was followed by a dwell at 140°C for 12 hours. Heating from 140°C to 185°C required about 12 hours and was followed by a 72-hour dwell at 185°C. Cooling from 185°C to 40°C required about 33 hours. Thermocouples monitored the oven air temperature and each vessel's outer wall temperature. The observed temperature profiles are shown in Figure C.2. The heating tests were initiated on August 28 and completed on September 1, 2006.

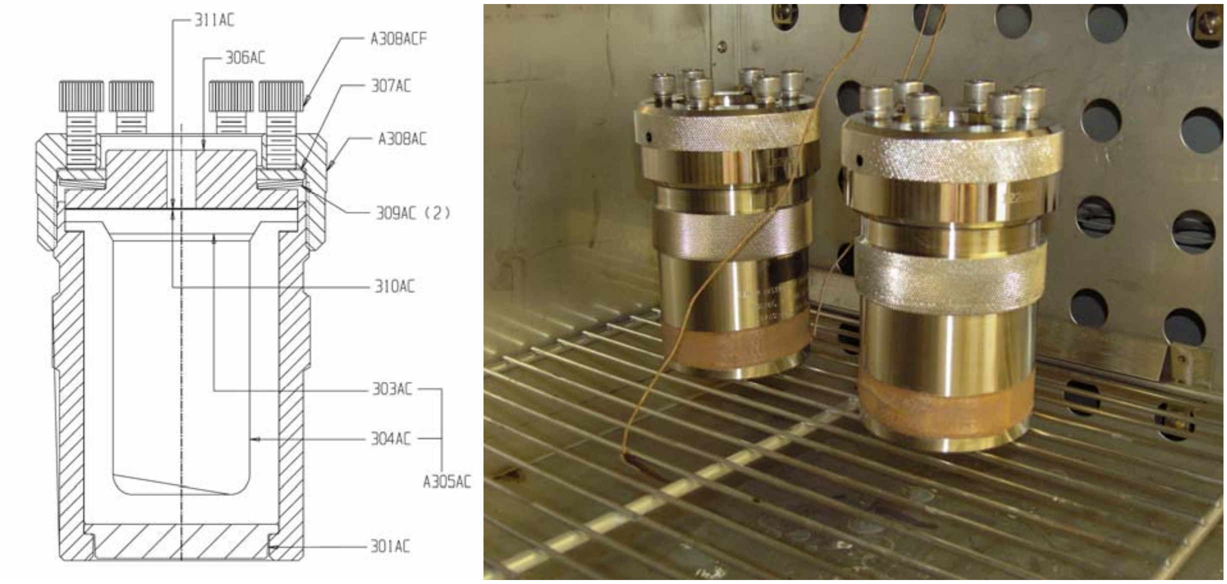

Figure C.1. Cross-Sectional View of Parr Model 4748 Reaction Vessel and Vessel Arrangement in Oven

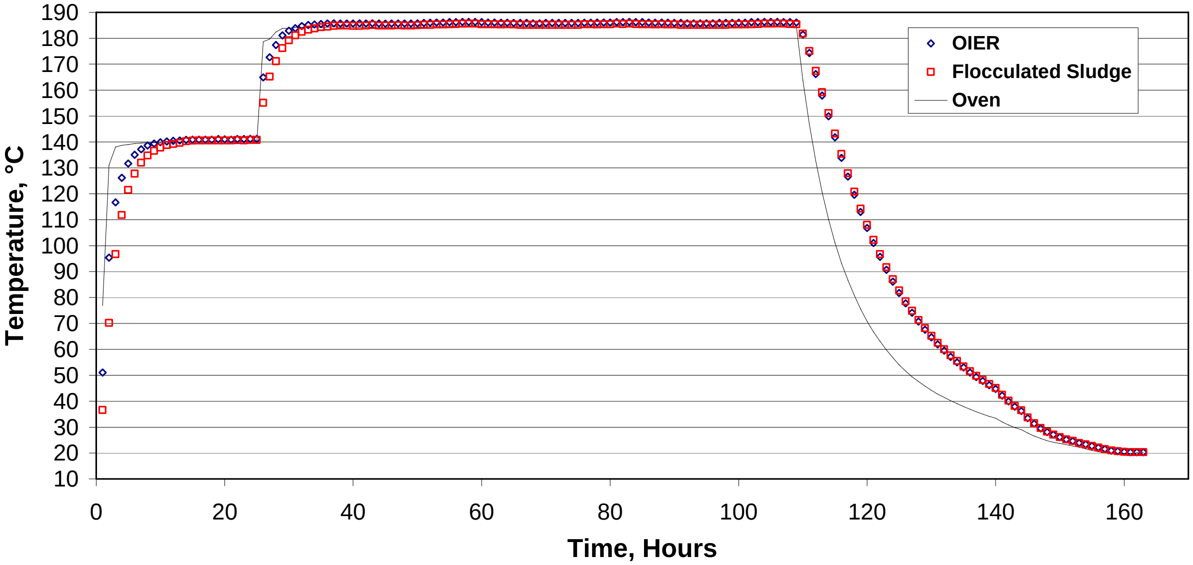

Figure C.2. Temperature Profile of Testing

Initial Results and Observations through September 8, 2006

The contents of the test vessels were examined after the simulated STP process treatment. Water losses were 0.44 g and 0.16 g for the OIER and flocculated sludge tests, respectively, or 1.4 wt% and 0.5 wt% of the initial water. A layer (~0.5-cm or less) of free water observed upon opening each vessel indicated that the simulants remained saturated during testing. The OIER and flocculated sludge solution pHs (~7.06 and 8.80, respectively) were not affected by the thermal testing.

The OIER simulant showed no signs of agglomeration and poured readily from the Teflon vessel. Prior to the testing, it was suspected that the organic resin might soften or melt at the 185°C test temperature and fuse with itself or with the sand. However, as shown in Figure C.3, no evidence of melting or fusing was observed. The OIER sludge color and texture appeared to be unaffected by the heating. Initial sieving tests confirmed that no agglomeration occurred.

Figure C.3. OIER Sludge After Testing (left, in Teflon reactor vessel; right, dumped into weighing boat)

The texture of the flocculated sludge simulant that contained the mixed aluminum hydroxide, ferric oxide hydroxide, and sand was greatly affected by the heating. Before heating, the flocculated simulant exhibited a pudding-like consistency. Instead of pouring from the reaction vessel as in its original slurry condition, the flocculated sludge was removed from the vessel as a monolithic block that had significant structural integrity (Figure C.4). As shown by probing with a spatula, the flocculated sludge was strongly cemented but weaker in the horizontal direction. Considerable pressure was required to penetrate the bottom of the sludge block with a steel spatula. However, the sludge split when pressed by a spatula from the side (Figure C.4, right side image).

Figure C.4. Flocculated Sludge After Testing
Left – with spatula
Right – cracked in original horizontal axis by spatula

As of September 8, further characterization testing was being planned for the Flocculated Sludge with strength tests (by soil penetrometer) and controlled stirring tests in water being considered. The originally planned sieve testing was judged to be unsuitable to the monolithic character of the Flocculated Sludge. Both of these tests are designed to determine the degree of resistance the agglomerated sludge might offer to re-mobilization in the STP reactor. Phase analysis by X-ray diffractometry (XRD) also was planned to determine whether the beginning aluminum and iron phases [gibbsite, $Al(OH)_3$, and primarily FeOOH, respectively] were significantly altered by heating. It was expected that phase dehydration occurred during the 185°C treatment to form AlOOH (boehmite) and Fe_2O_3 (hematite).

Results from Supplementary Characterization of Thermally Treated Simulants Completed September, 22, 2006

Additional testing was performed to characterize the OIER and Flocculated Sludge Simulant products. The OIER sludge was wet-sieved through a sieve stack containing 1000, 500, and 250 µm mesh sizes and a receiver pan. As noted previously, the sieving showed no apparent agglomeration of the OIER with itself or with the sand particles. The weight distribution of the wet-sieved material is shown in Table C.2.

Table C.2. Wet Sieve Analysis of Thermally Processed OIER Sludge Simulant

Sieve Fraction, µm	Weight Percentage
+1000	4.8
-1000 +500	45.0
-500 +250	36.3
- 250	13.9

Analyses of the thermally processed Flocculated Sludge simulant performed by XRD confirmed the expected thermal processing phase alteration. XRD analyses of the starting aluminum and iron hydroxide phases had been done previously. The aluminum hydroxide was found to be pure gibbsite [γ-$Al(OH)_3$; density (ρ) 2.42 g/cm^3] while the iron hydroxide was found to be poorly crystalline "6-line" ferrihydrite [$Fe_5O_7(OH){\cdot}4H_2O$; $\rho \cong 3.9$ g/cm^3] with lesser amounts of goethite [α-$FeO(OH)$] and hematite (α-Fe_2O_3). After heating, the gibbsite in the sludge had transformed entirely to boehmite [γ-$AlO(OH)$; $\rho=3.01$ g/cm^3] while the ferrihydrite had transformed almost entirely to hematite ($\rho=5.24$ g/cm^3) with only some residual, but better crystallized, ferrihydrite as shown by its narrower diffraction lines (Figure C.5). The observed predicted reactions are dehydrations, producing about one mole of water per mole of metal, with the products having higher particle density than their respective starting materials:

$$Al(OH)_3 \rightarrow AlO(OH) + H_2O$$

$$2\ Fe_5O_7(OH){\cdot}4H_2O \rightarrow 5\ Fe_2O_3 + 9\ H_2O$$

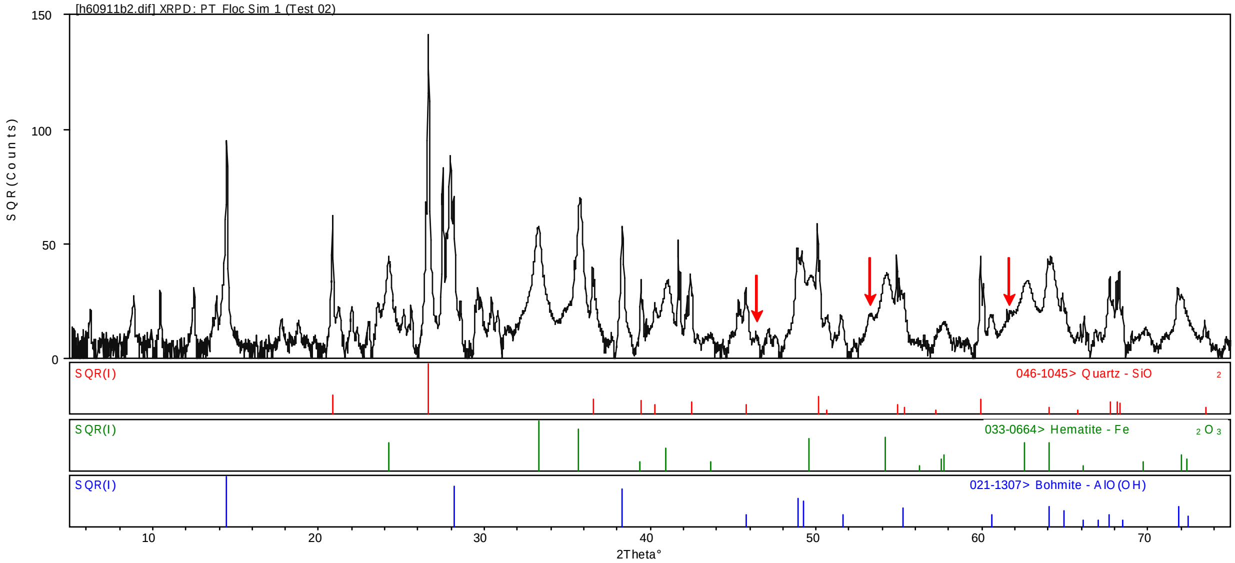

Figure C.5. XRD Pattern for Thermally Treated Flocculated Sludge Simulant [Note: Red arrows indicate locations of peaks due to ferrihydrite.]

Alterations of phases in the blow sand are, as yet, not known because a diffraction pattern of the starting material has not been obtained. The phases in the blow sand, in order of prominence, are quartz (SiO_2), anorthite ($CaAl_2Si_2O_8$), albite [$Na(Si_3Al)O_8$], clinochlore [$(Mg,Fe,Al)_6(Si,Al)_4O_{10}(OH)_8$], phlogopite [$KMg_3(Si_3Al)O_{10}(OH)_2$], and pargasite [$NaCa_2Mg_4Al(Si_6Al_4)O_{22}(OH)_2$]. All but the last mineral (and perhaps even the last mineral) is known to be found in Hanford Site soil.

The mechanical strength of the flocculated sludge simulant was tested on September 22, 2006, three weeks after the completion of the hydrothermal experiment. The first test was to measure the strength using a soil penetrometer (Geotester). To use the soil penetrometer, a circular foot of a known diameter (10 mm in the present case) is pressed to a depth of 1/4-inch into the sludge. The mass load necessary to achieve the penetration is registered on a dial gauge. The unconfined compressive strength of the soil (sludge), UCS in kg/cm^2, is obtained by the equation:

$$\mathrm{UCS} = 0.182 \times \frac{\mathrm{Q}}{\mathrm{A}}$$

where Q is the load, in kg of force [kg(f)], and A is the area of the foot, in square centimeters. The shear strength of the sludge, τ in kilopascals (kPa), is obtained by the equation:

$$\text{Shear strength, } \tau\text{, kPa} = \frac{\mathrm{UCS,\ kg(f)/cm^2}}{2} \times \frac{9.81\ \mathrm{m}}{\mathrm{sec^2}} \times \frac{10^4\,\mathrm{cm^2}}{\mathrm{m^2}} \times \frac{\mathrm{kPa}}{(10^3\ \mathrm{kg/m \cdot sec^2})}$$

where the gravitational constant, g, is 9.81 m/s^2.

The larger portion of the Flocculated Sludge product, after the initial examinations depicted in Figure C.3, was returned to the Teflon test vessel and maintained in a wetted state until the strength testing was conducted three weeks after the conclusion of the thermal process testing. Using the soil penetrometer, three determinations of the cohesion were made on the top surface of the sludge. The sludge piece developed fractures during the penetrometer testing which became even more evident when the sludge concretion was removed from the test vessel and, once inverted, returned to the test vessel to test the strength on the bottom surface. A single measurement of the bottom surface was made. Further tests were not done as severe fractures occurred from the first measurement and meaningful results could not be obtained. The results of the soil penetrometer testing are shown in Table C.3.

Table C.3. Soil Penetrometer Test Results for the Flocculated Sludge Simulant

Test Location	**Loading, kg**	**Unconfined Compressive Strength, kg(f)/cm^2**	**Shear Strength, kPa**
Top, 1	2.8	0.64	32
Top, 2	3.6	0.83	41
Top, 3	3.1	0.71	35
Average, top	3.2 ± 0.4	0.73 ± 0.09	36 ± 5
Bottom	1.7	0.39	19

In a final test of the integrity of the Flocculated Sludge, ~1-cm cubes were cut by scalpel from what were visually judged to be intact (non-fractured) portions of the sludge. Two such portions were obtained and one portion each added to a 600-ml beaker (~85-mm diameter) near the bottom edge. Four hundred (400) ml of distilled water then was added to each beaker (~70-mm depth), care being taken not to disturb the sludge cubes. The beaker water then was agitated using a Phipps and Bird JarTester stirrer. The 1-inch by 3-inch (horizontal) stirrer blades were set to rotate 4-cm from the beaker bottom. The Phipps and Bird stirrer apparatus is shown in Figure C.6.

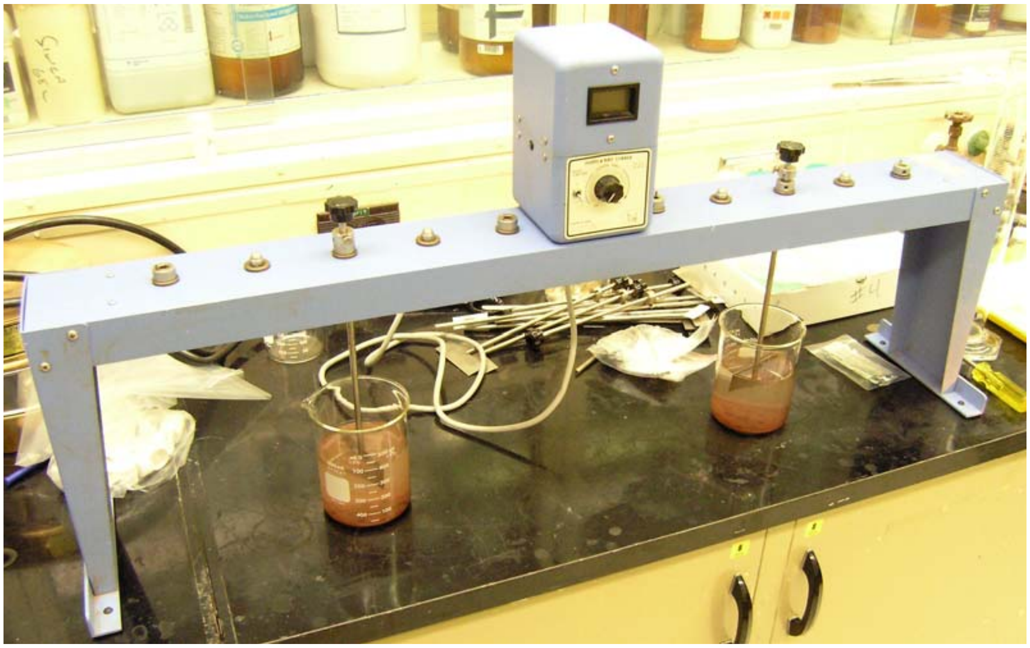

Figure C.6. Phipps and Bird JarTester with Samples After Stirring

Despite the care taken in adding the water, the sludge cubes immediately showed severe crumbling such that the remaining intact sludge pieces were reduced to about 7-8 mm and were surrounded by smaller particulate sludge. The stirrers were set to rotate at 20 revolutions per minute (RPM) for 5 minutes. This stirring had little further effect. The stirrer speed then was set to 50 RPM. After 5 minutes at 50 RPM, the largest agglomerates were about 3-6 mm across and the water had become turbid with sludge fines. The stirrer was set to 100 RPM for a final 5 minutes with marked increase in turbidity. After this stirring, the largest particles in each container were about 1-6 mm across. The observations are summarized in Table C.4. Overhead images of the settled sludge solids in the two tests are shown in Figure C.7.

Table C.4. Effects of Agitation on Agglomerate Size and Integrity

Agitation Time, min	RPM	Tip Speed, cm/sec	Description
0	0	0	Starting ~10-mm agglomerate cubes crumbled to ~7-8 mm upon addition of water to beaker
5	20	8.0	No appreciable effect on agglomerate dimension
5	50	19.9	Agglomerate dimensions reduced to 3-6 mm
5	100	39.9	Agglomerate dimensions reduced to 1-6 mm

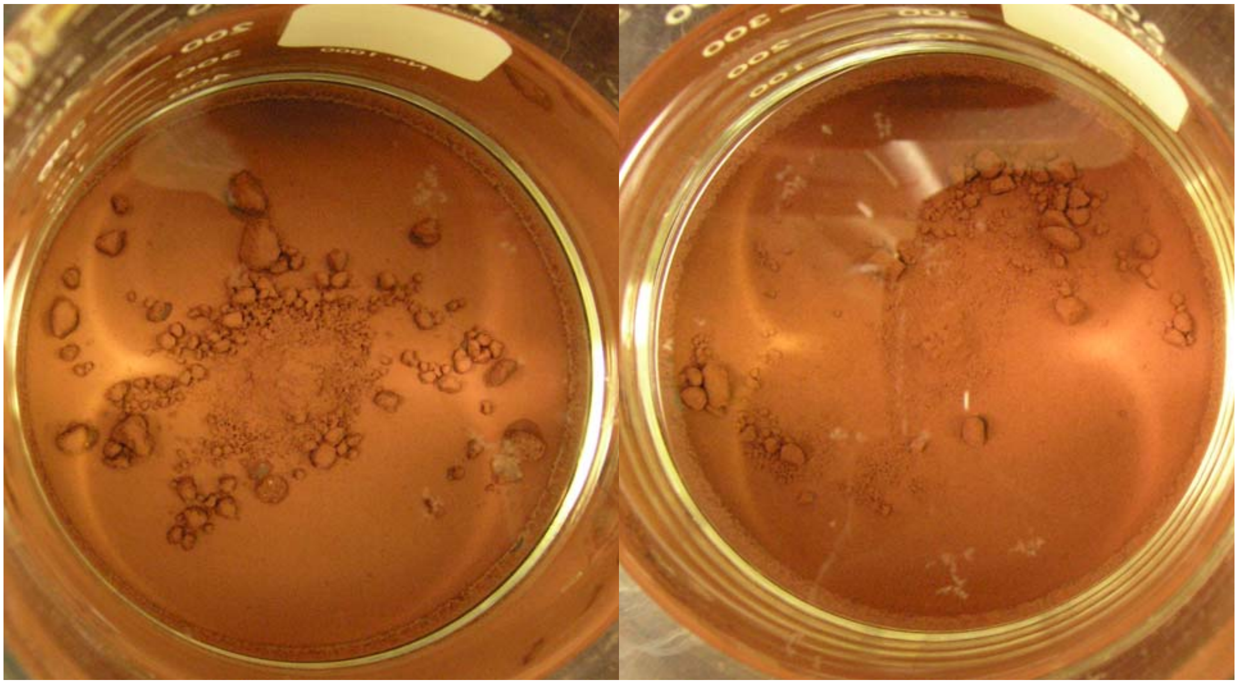

Figure C.7. Overhead Images of Flocculated Sludge Simulant After JarTester Stirring and Settling Tests [Note: For reference, the beaker diameters are 85 mm.]

The sludge strengths as measured by the soil penetrometer and by the Phipps and Bird stirrers were much lower than would have been anticipated had the measurements occurred immediately after opening the test vessels. The validity of the stirrer tests likely also was compromised by the prior penetrometer testing which introduced fractures into the sludge monolith. Based on these observations, the following recommendations are made for future post-test evaluations of sludge monoliths:

- Perform strength tests as soon as possible after completion of the thermal processing.
- Cut the monolith in half horizontally.
- Retrieve cubes for stirrer testing from the top half of the monolith.
- Return the lower half of the monolith to the Teflon test vessel and perform the penetrometer testing.
- If the above-listed operations are too difficult to perform in the hot cell, or are judged to compromise the strength integrity of the monolith, perform only the penetrometer testing without displacing the monolith from the Teflon vessel.
- If the Phipps and Bird stirrer testing is performed, estimate agglomerate particle sizes by video imaging using the beaker diameter, or an adjacent measuring scale, for reference dimensions.