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Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Characteristics of KE Basin Sludge Samples Archived in the RPL - 2007

CH Delegard
AJ Schmidt
JW Chenault

November 2011

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Pacific Northwest National Laboratory
Richland, Washington 99352

Revision History

Revision	Date	Reason for Revision
0	November 2007	Initial revision was issued to document a set of well-characterized sludge samples that are suited to support evolving Sludge Treatment Project initiatives. As a part of this effort, like samples of KE Basin sludge were combined and transferred into new containers and some of these samples were characterized to determine the instances and degrees of change that have occurred since their collection at the KE Basin by the K Basin Project. This initial report was issued as a project letter, and the letter was cleared for "limited distribution."
1	November 2011	Revision 1 was issued to clear this report for "unlimited distribution". Changes between Rev 0 and Rev were limited to document formatting changes.

Summary

Samples of sludge were collected from the K East fuel storage basin (KE Basin) floor, contiguous pits (Weasel Pit, North Load Out Pit, Dummy Elevator Pit, and Tech View Pit), and fuel storage canisters between 1995 and 2003 for chemical and radionuclide concentration analysis, physical property determination, and chemical process testing work. Because of the value of the sludge in this testing and because of the cost of obtaining additional fresh samples, an ongoing program of sludge preservation has taken place with the goals to track the sludge identities and preserve, as well as possible, the sludge composition by keeping the sludge in sealed jars and maintaining water coverage on the sludge consistent with the controlling Fluor Hanford (FH) Sampling and Analysis plans and FH contracts with the Pacific Northwest National Laboratory (PNNL).

This work was originally initiated to provide material for planned hydrothermal treatment testing in accordance with the test plan for the Sludge Treatment Project (STP) corrosion process chemistry follow-on testing (Delegard et al. 2007a). Although most of the planned hydrothermal testing was cancelled in July 2007 (as described in the forward of Delegard et al. 2007b), sample consolidation and characterization was continued to identify a set of well-characterized sludge samples that are suited to support evolving STP initiatives. The work described in the letter was performed by the PNNL under the direction of the Sludge Treatment Project, managed by Fluor Hanford.

As described in this report, like samples of KE Basin sludge were combined and transferred into new containers and some of these samples were characterized to determine the instances and degrees of change that have occurred since their collection at the KE Basin by the K Basin Project. For a number of these samples, the physical properties (settled and particle densities and water and solids concentrations), the pH, and the solid phases (crystalline phases as identified by X-ray diffractometry, XRD) also were determined and are reported. The results are compared with results, where available, found in prior testing and laboratory analyses.

Samples from similar origins were combined into new jars in the present work. Three consolidations of like samples were made: sample KC-2/3 (a canister sludge composite) was created from nine assorted KC-2/3 samples; KC-4 Whole (KE floor sludge collected from between canisters) was prepared from five KC-4 samples; and KC-6 (a KE floor sample composed largely of organic ion exchange resin) was prepared from two KC-6 samples. Composites of sludges from different sources also have been created over the past several years for various bench-scale property or process tests. Sludge composites present in usable form in the HLRF archives include 96-13 KE Comp A (a composite of KE canister sludge samples 96-01, 96-05, 96-06 L, 96-06 M/L, 96-08, 96-13, and 96-15), KE Floc Comp (from KE floor and pit sludge samples KC-4 M250, KC-5, and FE-5), KC Floor Comp (KE floor sludge samples KC-4 and KC-5), and KE Pit (from KE Weasel Pit samples KES-P-16, -Q-17, -R-18, -S-19, and -T-20). In the present work, KE Floc Comp sludge was gathered from samples present in two jars, one containing flocculating agent and a much smaller second sample containing no flocculating agent, to create a single item. The other composites, already in single jars, were transferred to new jars. Some individual samples were present in their original jars. Because glass becomes embrittled by extended exposure to high radiation fields, these samples were placed into new jars.

Results of the compositing and characterization are summarized in Table S.1 and show sludge sources, volumes, uranium concentrations, and settled densities. The settled densities of most of the recently measured key samples are within about 20% of their values measured just after sample collection. Also, as expected, settled sludge densities generally increase with uranium concentration while sludge pH generally decreases with increasing uranium concentration. It was also found that where prior data are available, the pH values in the present tests match the prior values within about 1 pH unit. However, one sample, KC-4 Whole, had much lower pH than what was measured initially. The XRD

results (not given in Table S.1), where available, show disappearance of the uranium(IV) phases (various uraninites, UO_2, U_4O_9, and U_3O_7) observed in the original samples to form uranium(VI) compounds including metaschoepite, becquerelite, and uranophane. Further details are provided in the report.

Table S.1. Sources and Properties of Archived KE Basin Sludge Samples

Sample ID	Source	Sample Date	Stld. Vol., ml	[U], dry wt%	Stld. Density, g/cm^3		References
					Present	Original	
96-01	Single closed-bottom canister with good condition fuel	8 Apr 96	15	0.0944	0.98 (cone)	2.09 (1997)	Makenas et al. 1997
96-05	Single closed-bottom canister with very poor condition fuel	9 Apr 96	80	58.5	1.77 (cone)	2.34 (1997)	Makenas et al. 1997
96-08 SSOL	Single canister with poor condition fuel	10 Apr 96	50	31.0	–	1.19 (1997)	Makenas et al. 1997
96-09 SSOL	Single empty open-bottom canister.	11 Apr 96	50	13.1	–	1.07 (1997)	Makenas et al. 1997
96-11 SSOL	Single empty closed-bottom canister	12 Apr 96	<50	6.01	–	1.23 (calc., 1997)	Makenas et al. 1997
96-13 (various)	Single canister with poor condition fuel (Settler Study, Solid Grad, SSOL)	18 Apr 96	125, 100, 50	74.0	–	2.458 (1997)	Makenas et al. 1997
96-13 KE Comp A	Composite of samples 96-01, -05, -06, -08, -13, and -15 from single canisters with good to very poor condition fuel	8-18 Apr 96	125	52.1	1.90 (cone)	–	Makenas et al. 1997; Table 3.2 of Schmidt et al. 1999
96-15 SSOL	Single canister with poor condition fuel	18 Apr 96	100	49.2	–	1.845 (1997)	Makenas et al. 1997
FE-5	Weasel pit including South Loadout Pit sludge	26 Apr & 13 Jan 99	260	5.32	1.66 (cone) 1.68 (jar)	1.50	Composite created in 222-S Lab from KE-9 and KE-10 single-pull samples; Baker & Welsh 2001
KC-1 M500	Canister sludge from highly damaged fuel collected from one sampling location	12 Apr 99	20	68.6	2.05 (cone) 2.66 (jar)	1.5	Sample passing 500-µm sieve; 88.7 wt% of total KC-1 wet solids; Baker & Welsh 2001; Bredt et al. 1999; Bryan et al. 2004
KC-2/3	KC-2; consol. smpl. fr. fuel stor. can. barrels w/ hi. dmgd. fuel fr. all 3 bays	4-13 Mar 99	425	59.0	2.03 (cone) 2.14 (jar)	2.13 (1999)	Composite KC-2/3 created in 325 Lab; Baker & Welsh 2001; Bredt et al. 1999
	KC-3; consol. smpl. fr. can. barrels with mod. dmgd. fuel fr. all 3 bays	1-8 Apr 99					
KC-4 Whole	Consol. smpl. fr. floor btwn. barrels of open bot. can. w/ highly dmgd. fuel fr. all 3 bays	30-31 Mar 99	120	16.6	1.60 (cone) 1.56 (jar)	1.235	Baker & Welsh 2001; Bredt et al. 1999
KC-4-2			165		1.53 (cone) 1.60 (jar)		
KC-6	Consol. smpl. fr. floor area in west bay known to be v. high in ion exchange beads	13 & 26 Mar 99	140	0.314	1.31 (cone) 1.20 (jar)	1.1	Baker & Welsh 2001; Bredt et al. 1999; Bryan et al. 2004
KC-6 carboy			6400		–		
KC Floor Comp	Comp. of 40 vol% KC-4 & 60 vol% KC-5 (stl. sl.); KC-5 consol. deep sl. fr. all 3 bays (smpl. 29 Mar 99)	29-31 Mar 99	25	10.3	1.20 (cone) 1.34 (jar)	1.21 (calc., 2000)	Baker & Welsh 2001; Silvers et al. 2000
KE Container Comp & Floc[(a)]	Composite of KC-2/3, KC-4, KC-5 P250 & FE-5	13 Jan – 26 Apr 99	25, 10	15.7	–	1.65, 1.53 (cone) 1.54, 1.45 (jar)	Delegard et al. 2007a
KE Floc Comp	Composite of KC-4 M250, KC-5, FE-5, and KC Can Comp	13 Jan – 26 Apr 99	260	10.3	1.25 (cone) 1.30 (jar)	1.25 (2004)	Baker & Welsh 2001; Schmidt et al. 2004
KE NLOP	KE North Load Out Pit; top-to-bottom sample composite present in three jars (#1, #2, and #3)	13 & 19 Dec 03	645	2.51	1.06 (cone)	1.23 (2004)	Mellinger et al. 2004; Shelor et al. 2004
KE Pit	Weasel Pit composite of KES-P-16, -Q-17, -R-18, -S-19, & -T-20	15-25 Sep 95	125	7.99	1.77 (cone) 1.92 (jar)	–	Makenas et al. 1996; dry smpls. weigh & mix w/ H_2O, Carlson et al. 1998

(a) Note that this composite composition is near that expected for KE Basin containerized sludge.

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1.0 Introduction

Samples of sludge were collected from the K East fuel storage basin (KE Basin) floor, contiguous pits (Weasel Pit, Load Out Pits), and fuel storage canisters between 1995 and 2003 for chemical and radionuclide concentration analysis, physical property determination, and chemical process testing work. Since their collection, the samples have been stored at hot cell temperatures (~30°C) or room temperature (~20°C, for KE North Loadout Pit, KE NLOP, only). The sludge samples have continued to be of use in the intervening years as methods to process the sludge have been developed and tested and additional information on their properties and chemical reactions is required (Appendix A).

This work was originally initiated to provide material for planned hydrothermal treatment testing in accordance with the test plan for the Sludge Treatment Project (STP) corrosion process chemistry follow-on testing (Delegard et al. 2007a). Although most of the planned hydrothermal testing was cancelled in July 2007 (as described in the forward of Delegard et al. 2007b), sample consolidation and characterization was continued to identify the broad set well-characterized sludge samples that are suited to support evolving STP initiatives. The work described in the letter was performed by the PNNL under the direction of the Sludge Treatment Project, managed by Fluor Hanford.

Because of the value of the sludge in this testing and because of the cost of obtaining additional fresh samples, an ongoing program of sludge preservation has taken place with the goals to track the sludge identities and preserve, as well as possible, the sludge composition by keeping the sludge in sealed jars and maintaining water coverage on the sludge. Even with this active care, it is certain that the uranium metal within the sludge samples has continued to oxidize to UO_2. Further, the product UO_2 plus other U(IV) oxide (such as uraninite, $UO_{2.x}$, where x ranges from 0 to 0.33) within the sludge samples likely have continued to air-oxidize to form U(VI) oxyhydroxides (such as metaschoepite, $UO_3 \cdot 2H_2O$) and more mineralized phases such as becquerelite, soddyite, and uranophane, among others.[(1)] In addition, iron and perhaps aluminum hydroxides [$Fe(OH)_3$ and $Al(OH)_3$] may have continued to dehydrate to form oxyhydroxides (e.g., FeOOH and AlOOH) during the storage, despite occasional water replenishment, due to natural tendencies to chemical equilibrium.

At the same time, sludge in the KE Basin itself has undergone aggressive agitation, mixing, and aeration in sludge transfer and containerization operations at ~12°C. Therefore, both the sludge present at the K Basins and the sludge samples archived within hot cell and laboratory storage have been altered since sampling and are tending to the same state of oxidation and dehydration, though potentially at different rates. With time, sludge from both sources would proceed to complete equilibrium by oxidation, mineralization, and dehydration reactions.

The sludge samples have been kept in closed and labeled jars and the jar contents monitored periodically to ensure that the sludges are wetted with visible supernatant water. Water levels have been maintained, though not without fail, using either distilled deionized (DI) water or, if possible, with K Basin water also kept in archive in the Radiochemical Processing Laboratory, RPL. Most of the sludge samples have been handled and archived in shielded radiochemical facilities (hot cells). However, because of their low contained radionuclide content, the KE NLOP sludges were received and tested in a room-temperature glovebox for initial characterization in 2003. Once the characterization was completed, the remaining KE NLOP sludge was transferred to a sample storage room in the RPL basement. The KE NLOP samples were stored in the basement (~20°C) from the summer of 2003 until they were transferred

(1) Becquerelite is $Ca(UO_2)_6O_4(OH)_6(H_2O)_8$, soddyite is $(UO_2)_2SiO_4 \cdot 2H_2O$, and uranophane is $Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O$.

to hot cell storage in the High-Level Radiochemistry Facility, HLRF, of the RPL during the summer of 2007.

The objectives of the work described in this report were to collect and consolidate like samples of KE Basin sludge into new containers and to characterize some of the sludge to determine the instances and degrees of change that have occurred since their collection. The quantities and properties of the archived sludge materials are described. The physical properties (bulk and particle density and water and solids concentrations), the pH, and the solid phases present in a number of these samples also were determined and are reported. The results are compared with results, where available, found in prior testing.

2.0 Sludge Storage Conditions in the RPL and Rationale for Gathering Similar Sludge Samples

Base chemical and radiochemical analyses have been performed on all of the sludge samples currently archived in the RPL. Since characterization, some of the sludge samples have been kept in reserve without perturbation for additional characterization or process testing. Gas generation testing at hot cell temperatures also was performed to monitor changes to the sludge (e.g., uranium metal corrosion) that would have occurred at the same rate, without monitoring, in storage.[(1)] Other tests having negligible impact on sludge properties compared with ordinary hot cell storage included thermal conductivity and shear strength measurements (Poloski et al. 2002) and long-term (~2.4-year) settling/consolidation and water evaporation rate tests run for sub-samples of FE-5, KC-2/3, KC-4, KC-5, and 96-13 (Delegard et al. 2005). Other sludge sub-samples were sieved and the sieve fractions weighed and stored separately (e.g., Bredt et al. 1999). Because these sludges were generally kept wetted (except as noted) and thus under conditions that they would otherwise have experienced as archive material, they were not physically or chemically altered by virtue of the characterization testing or by dry-out. However, like the undisturbed archive samples, they were not kept under anoxic conditions (except for the relatively short-term gas generation test materials) and therefore may have been susceptible to oxidation by air. Sub-samples that were judged not to have been altered by testing could be candidates for consolidation with other intact sludge sub-samples from the same source which had been held in archive.

To simplify storage and maintenance, gather like materials in a single container for better inventory, and make more durable by replacing the original glass containers that can become embrittled by irradiation, samples from similar origins therefore were combined into new jars in the present work. Three such consolidations of like samples were made – sample KC-2/3 Comp was created from nine assorted KC-2/3 samples, KC-4 Whole was prepared from five KC-4 samples, and KC-6 was prepared from two KC-6 samples.

Composites of sludges from different sources also have been created over the past several years for various bench-scale property or process tests. The sludge composites present in usable form in the HLRF archives include 96-13 KE Comp A (a composite of 96-01, 96-05, 96-06 L, 96-06 M/L, 96-08, 96-13, and 96-15 samples), KE Floc Comp (from KC-4 M250, KC-5, and FE-5 samples), KC Floor Comp (from KC-4 and KC-5 samples), and KE Pit (from KES-P-16, -Q-17, -R-18, -S-19, and -T-20). In the present work, KE Floc Comp sludge was gathered from samples present in two jars, one containing flocculating agent, the other containing no flocculating agent, to create a single item. The other composites, already in single jars, were transferred to new jars.

Some individual samples were present in their original jars. Again, because glass becomes embrittled by extended exposure to high radiation fields, these samples were placed into new jars. The individual samples that were re-jarred include KC-1 M500 and KC-4-L Dup (which was renamed KC-4-2).

Sludge samples in quantities attractive for future testing also have recently been transferred into new individual jars and transferred from the Shielded Analytical Laboratory (SAL) of the RPL to the HLRF. These samples include 96-01, 96-05, 96-08 SSOL, 96-09 SSOL, three 96-13 samples (Settler Study, Solid Grad, and SSOL), and 96-15 SSOL. The term SSOL means settled solids.

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(1) Some of the characterization testing would have altered the sludge composition. For example, gas generation testing performed at elevated temperatures (Delegard et al. 2000, Bryan et al. 2004) would accelerate or even alter the aging that otherwise might occur at hot cell temperature.

3.0 Work Objectives and Procedures

Aside from retrieval of the KE NLOP sludge from archive storage in the RPL basement, retrieval of other samples from the SAL, and preparation of sample containers, the work activities occurred in the HLRF. The testing was performed under a Test Instruction approved by the Fluor Hanford KBC/STP Project and PNNL project manager, scientists, shielded facility management, quality engineering, and hot cell operations[(1)] under the existing RPL research operation procedure.[(2)] Existing operation-specific procedures for hot cell operations were also used in performing this work.

The objectives of the work were to gather and simplify the KE Basin sludge inventory, to replace the potentially embrittled old glass jars with new glass jars, to mechanically blend the sludge to decrease self-cementation and improve contact with water, to determine the quantities of usable sludge available for future testing, and to characterize the sludge by its physical properties (bulk and particle density, water and solids concentration) and pH. Selected sludge samples also were taken for analysis of their contained crystalline phases using X-ray diffractometry (XRD). The samples were prepared[(3)] and the XRD scans gathered[(4)] according to existing RPL procedures.

Combining sub-samples arising from common sources was done to achieve the goals of simplifying the sample management and maintenance, gathering sufficient materials for future characterization or process testing, and removing sub-samples from storage that did not contain retrievable quantities or were dried out or otherwise compromised. The high radiation fields within the hot cells and from the sludges themselves cause the glass containers and the plastic lids to weaken and become brittle and identification markings to fade or flake off the containers. Therefore, another goal of the sludge sample management was to place samples in new and more durable labeled jars. The re-jarring was done for samples that were recombined but also for single, large quantity, samples being kept in old or degraded containers. Samples recently (2007) placed in new jars were not repackaged.

Once the sludges were recombined, simply re-jarred, or gathered, water was added, if needed, and the sludge materials were blended using an overhead electric drink mixer (3.6-cm diameter blade turning at ~720 RPM to give ~140 cm/sec tip speed). The time of blending varied according to the goals of breaking agglomerates and re-suspending the sludge solids in water but not going beyond this degree of agitation. Blending times did not exceed four minutes for any sludge and blending was not necessary for some sludges.

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(1) Delegard CH. 2007. *Re-Jarring and Preparation of K East Basin Sludge Composites from Archived Samples*, Test Instruction 53451 TI01, Rev. 0, Pacific Northwest National Laboratory, Richland, WA.

(2) RPL Independent Review Committee. 2007. PNNL Operating Procedure, *Routine Research Operations*, RPL-OP-001, Rev. 5, Pacific Northwest National Laboratory, Richland, WA.

(3) Scheele RD and CH Delegard. 2005. *Preparing Sealed Radioactive Samples for XRD and Other Purposes*, RPL-PIP-4, Pacific Northwest National Laboratory, Richland, WA.

(4) Schaef, HT. 2004. *Operation of Scintag Pad-V X-Ray Diffractometer*, RPL-XRD-PIP, Pacific Northwest National Laboratory, Richland, WA.

4.0 Compositing Strategy and Constituent Sludge Descriptions

The sludges selected for compositing and re-jarring were KC-2/3, KC-4, KC-6, and KE Floc Comp. The rationales for their compositing are provided in the following respective sections. The qualities and quantities of the constituent sub-samples used in the compositing are given in Table 8.1. The sources and properties of the sludges are described in the following narrative and summarized in Table 8.2.

KC-2/3 Comp

The sub-samples from KC-2/3 were gathered with the objective to form a single composite representative of the original KC-2/3 sample. The contents of ten sample jars from nine different labeled designations were collected. The samples KC-2/3 Settling Study, KC-2/3 Whole, KC-2/3 SS, and KC-2 SSOL include the entire particle size distribution of the KC-2/3 sludge sample. Based on prior studies of KC-2/3 sludge, ~70 wt% of the settled KC-2/3 sludge is derived from KC-2 (Bredt et al. 1999). Therefore, sample KC-2 SSOL from KC-2 well represents KC-2/3. The KC-2/3 sludge was sieved into fractions passing and retained on a 250-μm sieve (M250, meaning minus 250 μm, and P250, or plus 250 μm, respectively, in prior operations). When combining the sub-samples KC-2/3 M250 (~40 ml), another KC-2/3 M250 (~70 ml), and KC-3 + KC-2 Rec 2 (40 ml) with KC-2/3 P250 (25 ml), a total of 175 ml of sludge were obtained, of which ~86 vol% is in the M250 fraction. This distribution is near that of the original KC-2/3 sludge in which about 78 wt% (wet) passed the 250-μm sieve given that the M250 (2.129 g/cm^3) and P250 (2.109 g/cm^3) fractions had similar densities (Bredt et al. 1999).

The sample KC-2/3 is itself a composite of consolidated samples taken from canister barrels containing highly damaged fuel (sample KC-2) and moderately damaged fuel (sample KC-3) from all three KE Basin bays (Baker and Welsh 2001). The composite was prepared in the 325 Laboratory shortly after the KC-2 and KC-3 samples were received. The dry-basis composition of the KC-2/3 sludge given in Table 8.3 (Baker and Welsh 2001) shows that the sludge contains relatively high uranium concentration (59.0 wt%, dry basis).

KC-4 Whole

The sub-samples KC-4 (labeled KC-4 on the jar body but with a lid labeled KC-5), KC-4 LPG, KC-4 Dup LPG, and KC-4 include the entire sludge particle size distribution. The sub-sample KC-4 Rec contains only sludge passing a 250-μm sieve. However, since 90 wt% of the sludge is in the M250 fraction (Bredt et al. 1999), inclusion of this sub-sample has little impact on the composite composition. These five samples were combined to make the KC-4 composite, KC-4 Whole. The KC-4 sludge was a consolidated sample taken from between barrels of open-bottom canisters containing highly damaged fuel from all three KE Basin bays (Baker and Welsh 2001). The dry-basis composition of KC-4 presented in Table 8.3 (Baker and Welsh 2001) shows that the sludge contains 16.6 wt% uranium on a dry basis. In contrast to the behaviors of other sludge samples, this composite has a slimy consistency, did not settle well, and the supernatant liquid remained turbid. Also, the sludge pH, as will be seen, was uncharacteristically low.

KC-6

Only two sub-samples, KC-6 and KC-6 SSOL A, are combined to make the KC-6 composite. This material was taken from an area of the floor in the KE Basin west bay known to be high in ion exchange resin beads (Baker and Welsh 2001). The sample KC-6 was not analyzed. The composition presented in

Table 8.3 for KC-6 is that reported for the similar sample, KES-H-08 (Makenas et al. 1996) collected from the same KE floor location. The dry-basis uranium concentration in this sludge is low, ~0.3 wt%.

KE Floc Comp

The sub-sample KE Floc Comp (feed) was used as the source material for KE Basin sludge flocculent testing (Schmidt et al. 2004). The sub-sample KE Floc Sludge was the same as KE Floc Comp (feed) but also contained Nalco 7194 Plus flocculating agent. The KE Floc Comp feed sludge contained KC-4 M250 sludge (50.6 wt %, settled basis), KC-5 sludge (29.6 wt%), and FE-5 sludge (19.4 wt%) with a very small quantity (0.35 wt%) of a combined set of canister sludge samples (Schmidt et al. 2004). Combining the flocculated (~200 ml) and non-flocculated (~70 ml) portions provides a larger volume of sludge of known composition in a form suitable for subsequent testing.

The sample KC-4 M250 comprises 90.2 wt% of the total settled KC-4 sludge (Table 6, Bredt et al. 1999) so the KC-4 M250 composition, which was not analyzed, may be represented by that of KC-4 itself. As noted above, KC-4 and KC-5 arose, respectively, from the floor between barrels of open bottom canisters and from areas of deep sludge in the KE Basin (Baker and Welsh 2001). The FE-5 sludge was a single-pull sample taken from the Weasel Pit and also contains South Loadout Pit sludge (Baker and Welsh 2001). The compositions of the individual KC-4 M250 (represented by KC-4), KC-5, and FE-5 portions were combined to determine the composition of the KE Floc Comp sample reported in Table 8.3. Because of its low (0.35 wt%, settled basis) concentration, the contribution of the combined canister sludge was not accounted. Based on these calculations, the KE Floc Comp sludge contains approximately 10 wt% uranium on a dry basis.

5.0 Single Sludge Sample Descriptions

The qualities and quantities of single samples that were re-jarred (KC-1 M500, FE-5 Comp 1, KC-4-2, KC Floor Comp, KE Pit, and 96-11 SSOL), the samples in new jars from SAL that were only blended (96-01, 96-05, and 96-13 KE Comp A), samples from SAL that were not blended (96-08 SSOL, 96-09 SSOL, the 96-13 samples Settling Study, Solid Grad, and SSOL, and 96-15 SSOL), the two KE NLOP samples, KE NLOP Jar #1 and Jar #3 (which had been stored in the RPL basement, transferred to the HLRF, and opened for sampling; Jar #2 also was transferred to the HLRF but was not opened), and the samples that were already in the HLRF and were not re-jarred or blended (KC-6 in the carboy and KE Container and KE Container Comp Floc) are shown in Table 8.1. The sources and properties of the sludges are described in the following narrative and summarized in Table 8.2.

96-01

Sample 96-01 was taken from a stainless steel canister containing fuel in relatively good condition. This sludge was agitated and sampled for bulk and pH analyses. In May 2007, this sample was placed into a new jar in SAL. Chemical concentrations for potassium, chromium, nickel, sodium, and uranium obtained in the analysis of this sludge are of doubtful quality and the plutonium and americium values also appear to be anomalously low. As will be seen, five different uranium concentration values were reported, ranging from <0.02 wt% to over 80 wt% (Makenas et al. 1997). The analytical results are provided in Table 8.3 for completeness but are not reliable for the named analytes.

96-05

Sample 96-05 is 58.5 wt% uranium (dry basis) and was taken from a stainless steel canister containing fuel observed to be in very poor condition (Makenas et al. 1997). In May 2007, this sample was placed into a new jar in SAL and then transferred to the HLRF where it was agitated and sampled. The analytical results are shown in Table 8.3.

96-08 SSOL

Sample 96-08 SSOL is moderately high in uranium concentration (31.0 wt%, dry basis) and was taken from an aluminum canister containing fuel observed to be in poor condition (Makenas et al. 1997). In May 2007, this sample was placed into a new jar in SAL. The sample was not agitated in the present testing. The analytical results are given in Table 8.4.

96-09 SSOL

Sample 96-09 SSOL is relatively low in uranium concentration (13.1 wt%, dry basis) and was taken from an aluminum canister containing fuel of unknown condition (Makenas et al. 1997). The sample was not re-jarred or agitated in the present testing. The analytical results are reported in Table 8.4.

96-11 SSOL

Sample 96-11 SSOL is a settled solids portion of sample 96-11, taken from an empty stainless steel canister (Makenas et al. 1997). Accordingly, the uranium concentration is relatively low (~6 wt%, dry basis) for a canister sludge. The sample 96-11 was divided into upper (96-11 U) and lower (96-11 L) portions before the portions were individually analyzed (Makenas et al. 1997). The upper portion comprised 7 volume% and the lower 93 volume% of the total sludge. The compositions of the individual portions were combined to determine the composition of the total 96-11 sample reported in Table 8.4. In

May 2007, this sample was placed into a new jar in SAL, and then transferred to HLRF, but was not agitated in the present testing.

96-13 Settling Study, Solid Grad, and SSOL

Sample 96-13 is available in three jars (labeled Settling Study, Solid Grad, and SSOL) and is high in uranium concentration (74.0 wt%, dry basis). The sample was taken from an aluminum canister containing poor condition fuel (Makenas et al. 1997). None of the three samples was re-jarred or blended in the present testing. The sample analyses are summarized in Table 8.4.

Sample "96-13 Solid Grad" was collected after completion of a multi-year settling test (Delegard et al. 2005). In this test, ~100 ml aliquots of various sludge samples were placed into capped 250-ml graduated cylinders with excess water and their settled volumes were monitored with time to look for evidence of long-term compaction. At the completion of the testing, all other sludge samples were readily slurried and poured from their respective graduated cylinders into sample jars. However, the 96-13 sample self-cemented and could only be recovered by breaking the graduated cylinder. For this reason, a sample of the agglomerated "96-13 Solid Grad" recovered from the settling test, was included in the present study for XRD analysis.

96-13 KE Comp A

The sample 96-13 KE Comp A contains sludge from sample 96-13 but also contains other canister sludges. It is a composite prepared from canister sludge samples 96-01 (61.92 g), 96-05 (62.92 g), 96-06 L (74.05 g), 96-06 M/L (57.37 g), 96-08 (39.03 g), 96-13 (124.54 g), and 96-15 (57.37 g). The first two were from stainless steel canisters and the others from aluminum canisters. The sludges, which were composited for bench-scale validation testing of nitric acid dissolution processing, were dry before their compositing and the noted weights are their dry weights (Schmidt et al. 1999). The composite sludge is called "KE Canister Sludge Composite" in Schmidt et al. (1999) and its previously analyzed composition is given in a footnote to Table 8.3 in the present report.

The sample 96-06 was split into 96-06 M and 96-06 L fractions (representing 53 and 47 vol%, respectively, of the total settled 96-06 sample) before analyses of the individual fractions. The individual 96-06 M and 96-06 L sludge compositions (Makenas et al. 1997) then were combined to determine the composition of the total 96-06 M/L portion contributing to the 96-13 KE Comp A composite. The compositions of the seven sludge constituents were combined in a similar manner (including those of 96-01, which contains many concentration values of suspect quality) to calculate the composition of the 96-13 KE Comp A provided in the body of Table 8.3. The dry-basis uranium concentration is 52.1 wt%. This composite was re-jarred, sampled, and agitated in the present testing.

96-15 SSOL

Sample 96-15 is moderately high in uranium concentration (49.2 wt%, dry basis). The sample was taken from an aluminum canister containing poor condition fuel (Makenas et al. 1997). In May 2007, this sample was placed into a new jar in SAL. The sample analytical results are given in Table 8.4.

FE-5 Comp 1

The sample FE-5 Comp 1 is from sample FE-5, itself a composite prepared in the 222-S Laboratory from the KE-9 and KE-10 samples drawn from the KE Weasel Pit and which also includes South Loadout Pit sludge (Baker and Welsh 2001). Its composition (Baker and Welsh 2001) shows it to be relatively low (5.32 wt%, dry basis) in uranium concentration (Table 8.3). This sample was re-jarred and agitated.

KC-1 M500

The sample KC-1 M500 is the portion of the KC-1 sample that was retained on 500-μm and larger sieves during sieve analyses (Bredt et al. 1999). The M500 fraction comprises 88.1 wt% of the total KC-1 wet (settled) solids. Therefore, the assumed composition of KC-1 M500 is that of non-fractionated KC-1 (given in Table 8.3). The sample KC-1 is a canister sludge taken from an area with highly damaged fuel (Baker and Welsh 2001). The dry-basis uranium concentration is 68.6 wt%. This sample was re-jarred and agitated.

KC-4-2

The sample KC-4-2 is taken from KC-4 and thus is nominally the same as that of KC-4 Whole presented in Table 8.3. The KC-4 sample, 16.6 wt% uranium (dry basis), was obtained between barrels of open-bottomed canisters containing highly damaged fuel (Baker and Welsh 2001). The sample jar label was difficult to read and the jar contents were completely dried. However, the sample readily re-wetted and appeared well behaved after water reconstitution. This sample was re-jarred and agitated.

KC Floor Comp

The KC Floor Comp sample was prepared for TCLP testing in the proportion 40 vol% of sample KC-4 and 60 vol% of sample KC-5 (settled sludge basis; Silvers et al. 2000). Sample KC-4 was a consolidated sample taken from between barrels of open-bottom canisters containing highly damaged fuel from all three KE Basin bays and KC-5 was a consolidated sample taken from deep sludge areas on the main KE Basin floor from all three bays (Baker and Welsh 2001).

The compositions of the individual KC-4 and KC-5 portions were combined to determine the composition of the KC Floor Comp sample reported in Table 8.3. The analyses reported in Baker and Welsh (2001) for this composite (dubbed KC-Flr Comp) were not used because the iron concentration was unrealistically high and no radionuclide concentrations were reported. The calculated uranium concentration is 10.3 wt% (dry basis). The sample was re-jarred and agitated.

KE Container Comp and KE Container Comp Floc

The KE Container Comp sample was prepared as composite of 8.5 vol% KC-2/3, 28.9 vol% KC-4, 34.1 vol% KC-5 P250, and 28.5 vol% FE-5 sludge (all settled-sludge basis). This sludge composite was created to emulate the composition of the KE floor, pit, and canister sludge that was containerized in the KW Basin. A portion of this composite was flocculated. The dry-basis composition, given in Table 8.4, was calculated based on the compositions of the constituent sludges (Delegard et al. 2007a) and applies to both the flocculated and non-flocculated portions. Due to the very small volumes, and the fact the sample jars were less than a year old, neither of these samples was agitated in the present testing. On a dry basis, the sludge contains 15.7 wt% uranium.

KE NLOP

The KE NLOP samples were taken from the K East Basin North Loadout Pit through a top-to-bottom isolation tube in four stratified sub-samples that were individually and collectively analyzed (Mellinger et al. 2004; additional analytical results in Shelor et al. 2004). Three jars, KE NLOP Jar #1, Jar #2, and Jar #3, were prepared from the composite of the top-to-bottom samples. Sample KE NLOP Jar #1 was mixed by a spatula instead of with the overhead drink mixer used to agitate many of the other samples.

Sample KE NLOP Jar #3 was not agitated but a small portion of the top layer was taken for analysis. The KE NLOP sludge contains only 2.51 wt% uranium (dry basis).

KE Pit

The KE Pit sample is a composite of 51.97 g (dry weight basis) of KES-P-16, 12.37 g of KES-Q-17, 111.14 g of KES-R-18, 54.43 g of KES-S-19, and 52.16 g of KES-T-20. All five constituent sludges were taken from the KE Weasel Pit. The composite was prepared for nitric acid dissolution/leach process testing (Carlson et al. 1998) and subsequently was used as a component of "KE Areas Sludge Composite" in further bench-scale leach testing (Schmidt et al. 1999).

Analyses are based on those of all contributing sludges except KES-T-20, for which only the acid-insoluble residue analysis was reported (Makenas et al. 1996). The silicon concentrations in each of the sludges were estimated for purposes of the present report based on the concentrations of acid-insoluble residue in each of the constituent sludges and the assumption that the residue was quartz, SiO_2. The concentration of uranium in KES-T-20 was estimated to be 30.4 wt% (dry basis) based on its $^{239,240}Pu$ concentration and the ratio of uranium to $^{239,240}Pu$ found in the other KE Pit constituent sludges. The uranium concentration in the KE Pit composite is calculated to be 7.99 wt% (dry basis). This sample was re-jarred and agitated.

6.0 Sample pH

The pH values of the sludge samples that were agitated, plus the KE NLOP Jar #1 and Jar #3 samples, were determined using a calibrated pH probe.[1] The pH meter was calibrated with commercial buffers[2] 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 stated values within 0.07 pH units in all cases for the pH 4.01 and 7.00 buffers and within 0.15 pH units for the pH 10.01 buffer. The pH results are presented in Table 8.5 and compared there with pH values, where available, measured in prior testing.

As noted in Table 8.5, the KE NLOP Jar #1 and Jar #3 samples were measured 23 days later than the other samples. By use of the pH buffers, the pH probe was found to be still functional but had drifted from calibration. Therefore, the pH values measured for the KE NLOP sludge samples were adjusted to account for the drift registered by the buffers.

It was found that where prior data are available, the pH values in the present tests matched the prior values within 1 pH unit except for the composite sample, KC-4 Whole. The pH of KC-4 Whole is 3.47 (an average of three measurements; 3.37, 3.52, and 3.51); the sister sample KC-4-2 pH is 7.66, near the previously measured value of 7.8, and in line with the trend of decreasing pH with increasing uranium concentration observed for most other sludges (Figure 6.1). The reason for the unusually low pH of KC-4 Whole is not known.

Another exception to the general trend of decreasing pH with increasing uranium concentration is found for the canister sludge sample 96-01. As noted previously, the analytical data for 96-01, including the data for uranium concentration, are suspect. Therefore, the relatively low pH measured for sample 96-01 may be an artifact of an understatement of the uranium concentration. The dry-basis values for uranium concentration reported for 96-01 (Makenas et al. 1997) were <0.0257 wt% (by ICP), 0.0944 wt% (by phosphorescence), 82.4 and 85.4 wt% (by laser fluorimetry), and 65.0 wt% (by ICP with mass spectrometric detection). If one of the higher uranium concentration values were used, the pH vs. uranium concentration trend observed for most of the other sludges would hold for 96-01.

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[1] Stick-type pH probe and temperature meter, Piccolo model HI 9214, Hanna Instruments, Woonsocket, RI.

[2] Buffers at pH 4.01 and 10.01 from VWR Scientific, West Chester, PA; pH 7.00 buffer from Ricca Chemical, Arlington, TX.

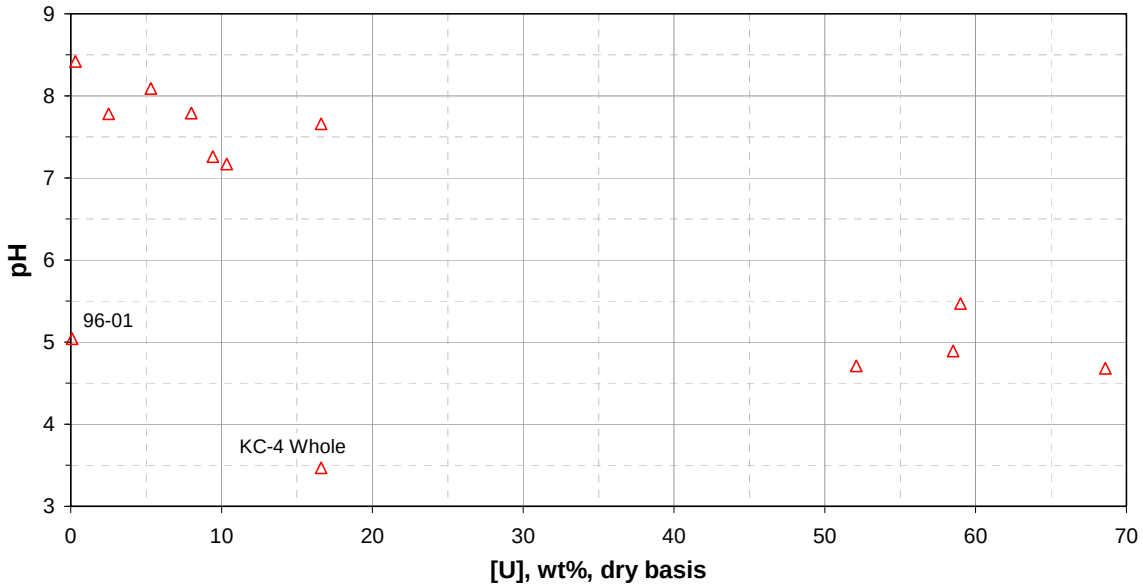

Figure 6.1. Sludge pH as a Function of Dry-Basis Uranium Concentration

7.0 Sludge Bulk Properties

The bulk physical properties of the agitated sludges were measured by weighing well-mixed representative samples into volume-calibrated centrifuge cones, adding DI 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 settled densities of entire sludge samples also were determined by measuring the volumes and net sludge weights for those sludges packaged in new jars in the present tests. The new sample jars were volume-calibrated, before use in the hot cell, by adding 50-ml increments of water to the tare-weighed jars and marking the jar walls at each level. The densities for samples and whole sludge jar items, Table 8.5, match within ~8% or better except for sample KC-1 M500, which differed by 23%. Because of the difficulty of obtaining representative sludge samples, the jar values, where available, likely are more reliable than those obtained by the centrifuge cone method.

The settled density is shown generally to increase with increasing dry-basis uranium concentration in the sludge (Figure 7.1). The KE Pit and FE-5 samples deviate on the high side of this trend, having greater densities than their uranium concentrations would indicate. Both of these samples have relatively high iron concentrations (36.4 and 30.6 wt%, respectively) which may have increased their densities. Because of its aberrant uranium concentration values, the point plotted for sample 96-01 is called out in Figure 7.1. In this case, its density is found to be in line with its (low) uranium concentration. If one of its high uranium concentration values were used in plotting, the 96-01 density would be out of line.

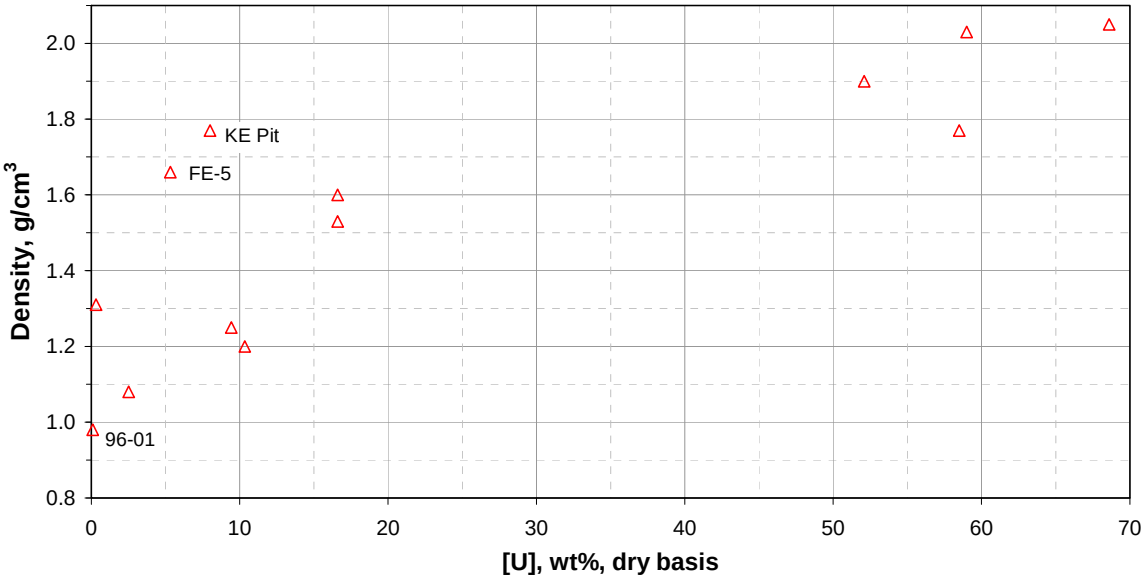

Figure 7.1. Sludge Density as a Function of Dry-Basis Uranium Concentration

8.0 X-Ray Diffraction Analysis Results

A number of the sludges analyzed for density and pH also were analyzed by XRD. The samples included 96-13 KE Comp A, FE-5, KC-2/3 Comp, KC-4-2, KC-4 Whole, KC Floor Comp, and KE NLOP Jar #1 (whole jar sub-sample) and Jar #3 (upper layer sub-sample). One of the non-agitated single samples, 96-13 Solid Grad, also was analyzed by XRD. The XRD scans are presented in Appendix B and the sample results summarized in Table 8.6. For comparison, the phases identified in these sludges in prior characterization tests also are presented in Table 8.6.[(1)] The prior results are based on analyses obtained during the original sludge characterization testing, if possible, or failing that, on analyses conducted during later testing.

As expected, the most prominent phases contained uranium for most samples. The only sample for which uranium was not in a prominent phase was the whole-jar sub-sample of KE NLOP Jar #1. This material contains only ~2.5 wt% uranium (dry basis) whereas the other samples contain from 4.1 to 79.8 wt% uranium (the uranium concentration in the upper layer sub-sample of KE NLOP Jar #3 is not known).

The disappearance of chemically reduced uranium oxide phases (uraninites of the nominal formulas UO_2, U_4O_9, and U_3O_7) in the recent samples is also noteworthy. Canister sludges, for which only uraninite phases were identified in past characterization (96-13 KE Comp A, 96-13 Solid Grad, and KC-2/3 Whole), now contain no identifiable uraninite. Instead, only fully oxidized uranium(VI) phases (metaschoepite for all three samples, and a sodium uranium hydroxide hydrate for 96-13 KE Comp A) are found in the present analyses. No uraninite phase was found in any of the analyzed sludges.

Further mineralization of the uranium(VI) beyond metaschoepite is seen by the appearance of $Ca(UO_2)_6O_4(OH)_6(H_2O)_8$, becquerelite, in the KC-4 samples (which include KC-4 Whole, KC-4-2, and KC Floor Comp, which includes KC-4 and KC-5 sludge). A sodium uranyl oxide hydroxide hydrate also was found in the KC-4 Whole sample. No prior XRD analyses were performed for either KC-4 or KC-5 for comparison.

The FE-5 sample, which previously was found to contain quartz, SiO_2, and two FeO(OH) phases, goethite and lepidocrocite, showed none of these phases in the recent sampling but did show a weak indication of the highly mineralized uranium phase uranophane, $Ca(H_3O)_2(UO_2)_2(SiO_4)_2(H_2O)_2$, the first observation of this phase in K Basin sludge characterization. As noted in the Sludge Treatment Project hydrothermal testing report (Delegard et al. 2007a), uranophane is observed as a uranium alteration phase end member in uranium ore weathering and uranium oxide fuel oxidative degradation studies published in the technical literature.

The whole-jar sample of KE NLOP (taken from Jar #1) contained a SiO_2 phase and lesser indications of iron and chromium oxyhydroxides, FeOOH and CrOOH. Only metaschoepite was found in the layer of sludge settled on the top of sample KE NLOP Jar #3. Three years previously, only SiO_2 and some unidentified peaks (which were verified to not be assignable to FeOOH, metaschoepite, or other candidate phases) were found in the KE NLOP composite sample.

Together, the XRD analyses show that storage of sludge in the laboratory environment has resulted oxidation and continued mineral alteration of the uranium phases with the disappearance of the reduced uranium oxides of the form $UO_{2.x}$, where x = 0-0.33 (i.e., uraninite), to form fully oxidized hexavalent

(1) Jenson ED. 2007. Letter report, "XRD Examination of Samples," to CH Delegard, August 24, 2007, Pacific Northwest National Laboratory, Richland, WA.

uranium [U(VI)] compounds starting with metaschoepite and proceeding to becquerelite (calcium uranium oxide hydroxide hydrate), sodium uranium oxide hydroxide, and uranophane (calcium uranium silicate oxide hydrate).

Table 8.1. Sludge Archive Samples for Compositing, Re-Jarring, Blending, and Inventory

Sludge Sample	Sludge Sub-sample	Condition	Approx. Vol., ml	Blending Time, s
For compositing, re-jarring, and blending				
KC-2/3 Comp	KC-2/3 Settling Study	Mushy, thick mud, black, no hardpan, with water	100	240
	KC-2/3 Whole	Stiff saturated mud, green, with water, easily dispersed with water	70	
	KC-2/3 SS	Very stiff, glass broken to collect sample, with water	100	
	KC-2 SSOL B	Very little solids with abundant water	5	
	KC-3 + KC-2 Rec 2	Two jars with similar labels; solids wet but stuck to bottom	40	
	KC-2/3 M250	Hard chunks, very black, with water, easily dispersed with water	40	
	KC-2/3 P250	Can be scooped out	25	
	KC-2/3 M250	Very good with abundant water; source material for STP Tests 1 and 2	40-100	
KC-4 Whole	KC-4	Abundant water	50	120
	KC-4-L P6	Sludge plug recovered, abundant water	70-100	
	KC-4 Dup LPG	Well settled solids, with water	30-50	
	KC-4	Dry, but black, some retrieved as puck and some as powder	30-40	
	KC-4 Rec	Soft and readily suspendible	40	
KC-6	KC-6	Fully saturated, beads are clumped but readily break up	100	30
	KC-6 SSOL A	Some clumping but fully wet	125	
KE Floc Comp	KE Floc Sludge (floc'd.)	Saturated, original plug fell apart with shaking	200	60
	KE Floc Comp (not floc'd.)	Saturated, original plug fell apart with shaking but not as easily as flocculated sludge	70	
For re-jarring and blending only				
KC-1 M500	KC-1 M500	Stiff but readily sluiced, suspended, and re-settled	50-70	20
FE-5 Comp 1	FE-5 Comp 1	Reddish brown, can be penetrated and scooped	200	120
KC-4-2	KC-4*	Dry chunks, water added and chunks broke up	300	120
KC Floor Comp	KC Floor Comp	Wet, saturated, readily suspendible	30-50	0
KE Pit	KE Pit	Wet chunks, jar broken to recover	150-200	60
Transferred to HLRF and blended only				
96-01	96-01	Very black solids	15	30
96-05	96-05	Big chunks	80	120
96-13 KE Comp A	96-13 KE Comp A	May contain some glass	125	90
Re-jarred in SAL and currently staged in SAL				
96-08 SSOL		Watered, dry before	50	NA
96-15 SSOL		Watered, dry before	100	NA
Transferred to HLRF and not re-jarred or blended				
96-09 SSOL		None	50	NA
96-11 SSOL		Very little sample	<50	0
96-13 Settler Study		Not watered, wet	125	NA
96-13 Solid Grad		Solids not watered, not wet	100	NA
96-13 SSOL		Not watered	50	NA
KE NLOP Jar #1		Good, with water	165	NA
KE NLOP Jar #2		Good, with water	240	NA
KE NLOP Jar #3		Good, with water	240	NA
In HLRF and not re-jarred or blended				
KC-6 carboy		Good condition; 6-liter	6400	NA
KE Container Comp		Moist, 70 ml supernatant	25	NA
KE Container Comp Floc		Moist, 30 ml supernatant	10	NA
* KC-4 written on jar; other markings, written below KC-4, were difficult to discern and may be M250 or Rec-2.				

Table 8.2. Source Information for Archived KE Basin Sludge Samples

Sample ID	Source	Sampling Locations	Barrel Type & Material	Sample Date	Preparation and References
96-01	Single closed-bottom canister with good condition fuel	1845	Mark II, SS	8 Apr 96	Makenas et al. 1997
96-05	Single closed-bottom canister with very poor condition fuel	3128	Mark II, SS	9 Apr 96	Makenas et al. 1997
96-08 SSOL	Single canister with poor condition fuel	2350	Mark I, Al	10 Apr 96	Makenas et al. 1997
96-09 SSOL	Single empty open-bottom canister.	4638	Mark I, Al	11 Apr 96	Makenas et al. 1997
96-11 SSOL	Single empty closed-bottom canister	6073	Mark I, SS	12 Apr 96	Makenas et al. 1997
96-13 (various)	Single canister with poor condition fuel (Settler Study, Solid Grad, SSOL)	5055	Mark I, Al	18 Apr 96	Makenas et al. 1997
96-13 KE Comp A	Composite of samples 96-01, -05, -06, -08, -13, and -15 from single canisters with good to very poor condition fuel	1845 (96-01) 2711 (96-05) 5465 (96-06) 2350 (96-08) 5055 (96-13) 6070 (96-15)	Mark II, SS Mark II, SS Mark I, Al Mark I, Al Mark I, Al Mark I, Al	8-18 Apr 96	Makenas et al. 1997; Table 3.2 of Schmidt et al. 1999
96-15 SSOL	Single canister with poor condition fuel	6070	Mark I, Al	18 Apr 96	Makenas et al. 1997
FE-5	Weasel pit including South Loadout Pit sludge	One near south wall 8 ft from east end; other near center, 11 ft from west end	–	26 Apr & 13 Jan 99	Composite created in 222-S Lab from KE-9 and KE-10 single-pull samples; Baker & Welsh 2001
KC-1 M500	Canister sludge from highly damaged fuel collected from one sampling location	4569E	Mark 0, Al	12 Apr 99	Sample passing 500-µm sieve; 88.7 wt% of total KC-1 wet solids; Baker & Welsh 2001; Bredt et al. 1999
KC-2/3	KC-2; consol. smpl. from fuel storage can. barrels w/ highly dmgd. fuel from all 3 bays	668E & W 2229E 4571E 6071W	Mark 0, Al Mark 0, Al Mod. Co-Prod., Al Mark 0, Al	4-13 Mar 99	Composite KC-2/3 created in 325 Lab; Baker & Welsh 2001; Bredt et al. 1999
	KC-3; consol. smpl. fr. can. barrels with mod. dmgd. fuel fr. all 3 bays	4850W 4869E 3125W 2905E 450E 455W	Mark 0, Al Mark 0, Al Mark 0, Al Mark 0, Al Mark 0, Al Mark 0, Al	1-8 Apr 99	
KC-4	Consol. smpl. fr. floor btwn. barrels of open bot. can. w/ highly dmgd. fuel fr. all 3 bays	0550 4573 5465	Mod. Co-Prod., Al Mod. Co-Prod., Al Mod. Co-Prod., Al	30-31 Mar 99	Baker & Welsh 2001; Bredt et al. 1999
KC-6	Consol. smpl. fr. floor area in west bay known to be v. high in ion exchange beads	6758	Mark 0, Al	13 & 26 Mar 99	Baker & Welsh 2001; Bredt et al. 1999
KC Floor Comp	Comp. of 40 vol% KC-4 & 60 vol% KC-5 (stl. sl. basis); KC-5 consol. deep sl. fr. all 3 bays	See above; KC-5 4648, 3133, 0548	Mod. Co-Prod., Al	29-31 Mar 99	Baker & Welsh 2001; Silvers et al. 2000
KE Container Comp (& Floc)	Composite of KC-2/3, KC-4, KC-5 P250 & FE-5	See above	See above	See above	Delegard et al. 2007a
KE Floc Comp	Composite of KC-4 M250, KC-5, FE-5, and KC Can Comp	See above	See above	See above	Baker & Welsh 2001; Schmidt et al. 2004
KE NLOP	KE North Load Out Pit; top-to-bottom sample composite present in three jars (#1, #2, and #3)			13 & 19 Dec 03	Mellinger et al. 2004; Shelor et al. 2004
KE Pit	Weasel Pit composite of KES-P-16, -Q-17, -R-18, -S-19, & -T-20			15-25 Sep 95	Makenas et al. 1996; dry samples weighed & mixed w/ water, Carlson et al. 1998

Table 8.3. Chemical and Radiochemical Compositions of Archive Sludge Analyzed for Bulk Properties

Sludge	96-01[a]	96-05	96-13 KE Comp A[b]	FE-5	KC-1 M500[c]	KC-2/3	KC-4 Whole	KC-6[d]	KC Floor Comp[e]	KE Floc Comp[f]	KE NLOP[g]	KE Pit[h]
Dry Basis												
Element	**Concentration, Wt%**											
Al	2.99	1.32	2.08	2.66	2.04	5.16	6.82	1.87	12.0	7.70	3.93	3.34
Ca	0.0412	0.0779	0.0751	1.2	0.125	0.134	1.04	1.22	0.696	0.945	0.937	1.21
Fe	0.0459	0.698	0.880	30.6	0.339	1.84	24.3	1.51	19.3	24.2	6.83	36.4
Mg	BDL[i]	0.221	0.194	0.146	0.0200	0.0462	0.33	0.225	0.236	0.230	0.122	0.194
Na	BDL	0.0416	0.0395	BDL	0.237	0.24	0.36	3.26	0.368	0.365	BDL	0.0732
Si	NR[j]	NR	NR	0.330	0.160	0.752	4.91	NR	5.24	3.57	36.3	8.00
U[k]	0.0944	58.5	52.1	5.32	68.6	59.0	16.6	0.314	10.3	10.3	2.51	7.99
Compound[l]	8.95	79.4	73.9	77.1	93.5	94.8	101.7	16.9	98.8	92.6	108.0	110.3
Radionuc.	**Concentration, µCi/g**											
^{60}Co	BDL	0.892	1.27	0.875	0.209	0.441	1.08	0.185	1.09	1.02	0.280	1.59
^{137}Cs	329	1140	748	170	392	860	1680	144	731	783	34.6	412
^{154}Eu	BDL	18.6	11.3	0.985	8.62	8.14	2.6	BDL	1.69	1.68	0.542	2.41
^{238}Pu	0.00541	16.2	36.6	2.06	21.5	16.2	4.91	0.0618	3.12	3.22	0.280	1.37
$^{239/240}$Pu	0.0501	153	197	13.1	142	114	39.2	0.403	23.2	23.9	9.00	19.4
^{241}Am	BDL	133	90.3	10.4	122	90.5	29.2	0.397	19.3	18.9	7.82	14.6
Settled Sludge Basis												
El. / H_2O	**Concentration, Wt%[m]**											
Al	1.66	0.706	1.22	1.56	1.38	3.04	3.83	0.802	5.72	2.53	0.562	2.03
Ca	0.0229	0.0417	0.0439	0.704	0.0844	0.0791	0.584	0.523	0.331	0.310	0.134	0.737
Fe	0.0255	0.373	0.515	18.0	0.229	1.09	13.7	0.648	9.17	7.92	0.977	22.1
Mg	BDL	0.118	0.114	0.0857	0.0135	0.0273	0.185	0.0965	0.112	0.0755	0.0174	0.118
Na	BDL	0.0223	0.0231	BDL	0.160	0.142	0.202	1.40	0.175	0.120	BDL	0.0445
Si	NR	NR	NR	0.194	0.108	0.444	2.76	NR	2.50	1.17	5.19	4.86
U	0.0524	31.3	30.5	3.12	46.3	34.8	9.33	0.135	4.92	3.37	0.359	4.85
H_2O	44.5	46.5	41.5	41.3	32.5	41.0	43.8	57.1	52.4	67.2	85.7	39.3
Radionuc.	**Concentration, µCi/g[m]**											
^{60}Co	BDL	0.477	0.743	0.514	0.141	0.260	0.607	0.0794	0.519	0.334	0.0400	0.962
^{137}Cs	183	610	438	100	265	507	944	61.8	348	257	4.95	250
^{154}Eu	BDL	9.95	6.59	0.578	5.82	4.80	1.46	BDL	0.802	0.552	0.0775	1.46
^{238}Pu	0.00300	8.67	21.4	1.21	14.5	9.56	2.76	0.0265	1.49	1.06	0.0400	0.832
$^{239/240}$Pu	0.0278	81.9	115	7.69	95.9	67.3	22.0	0.173	11.1	7.84	1.29	11.8
^{241}Am	BDL	71.2	52.9	6.10	82.4	53.4	16.4	0.170	9.21	6.20	1.12	8.89
Reference[n]	1	1	1, 2	3	3, 4	3	3	3, 4, 5	3, 7	3, 6	8	5, 9

Table 8.3. Chemical and Radiochemical Compositions of Archive Sludge Analyzed for Bulk Properties (Cont'd)

Note that for sludge composites, the concentrations were weighted based on the contributions of only those individual components having reportable concentration values.

(a) The analytical data associated with sample 96-01 are of suspect quality but are reported for completeness. According to page 4 of Makenas et al. (1997), "Sample 96-01 had significantly higher reported K, Cr, Ni, Na, and P concentrations than the other samples" and "Sample 96-01 was again anomalous with a reported spread in uranium concentration from essentially 0 to 63 wt% of centrifuged sludge depending on the analysis method". Also, the plutonium and americium values are unusually low.

(b) Sample 96-13 KE Comp A is a composite of 61.92 g of 96-01, 62.92 g of 96-05, 74.05 g of 96-06 L, 57.37 g of 96-06 M/L, 39.03 g of 96-08, 124.54 g of 96-13, and 57.37 g of 96-15 (all dry basis). The composition was calculated from the compositions of the constituent sludges. For comparison, the dry basis composition of this composite, called "KE Canister Sludge Composite" in the report on validation testing of nitric acid treatment of sludge, is 1.84 wt% Al, 0.118 wt% Ca, 1.20 wt% Fe, 0.118 wt% Si, 68.5 wt% U, 809 μCi ^{137}Cs/g, 121 μCi ^{239,240}Pu/g, and 95.3 μCi ^{241}Am/g (Table 3.3 of Schmidt et al. 1999; other analytes not reported). The calculated total compound weight based on the Schmidt et al. (1999) values represents 95.3 wt% of the total mass (see footnote l).

(c) KC-1 M500 is 88.1 wt% of total KC-1 wet solids; composition given for KC-1 M500 is that of KC-1.

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

(e) KC Floor Comp is a composite that is 40 vol% KC-4 and 60 vol% KC-5 (settled basis). The composition was calculated from the compositions of the constituent sludges converted to a dry weight basis. The analyzed composition (Baker & Welsh 2001) was not used because the iron concentration was unreasonable and no sodium or radchem values were reported.

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

(g) KE NLOP composition applies to all three KE NLOP jars (#1, #2, and #3).

(h) KE Pit is a composite of 51.97 g of KES-P-16, 12.37 g of KES-Q-17, 111.14 g of KES-R-18, 54.43 g of KES-S-19, and 52.16 g of KES-T-20, all from the KE Weasel Pit. All are dry sludge weights. Analyses are based on those of all contributing sludges except KES-T-20, for which only acid-insoluble residue analysis was reported. The silicon concentration was determined based on the concentrations of acid-insoluble residue in each of the constituent sludges and the assumption that the residue was SiO_2. The uranium value for KES-T-20 (30.4 wt%) was based on the ^{239,240}Pu value and the observed ratio of uranium-to-^{239,240}Pu concentrations for the other KE Pit sludge contributors.

(i) BDL means below detection limit.

(j) NR means not reported.

(k) Uranium concentrations generally were those reported by phosphorescence, or by ICP if phosphorescence values were not available. KE NLOP values are based on laser fluorimetry.

(l) Based on assignment of the elements to the compounds $Al(OH)_3$, $CaCO_3$, $Fe(OH)_3$, $MgCO_3$, Na_2O, SiO_2, and $UO_{2.63}\cdot H_2O$. The compounds $Al(OH)_3$, $CaCO_3$, and SiO_2 have been observed in genuine sludge. The compound $Fe(OH)_3$ generally is X-ray indifferent but represents the likely state of the wet iron hydroxide solids present in sludge (though Fe_2O_3 and other crystalline iron compounds have been observed by 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 except KE Pit (acid digest) are based on fusion digests.

(m) Settled sludge analyses are calculated based on the water concentrations of the respective sludges. Note that drying and wetting in storage and during sample maintenance will alter these values and that water concentration values should be determined upon use to re-establish the component concentrations.

(n) References: 1 – Makenas et al. 1997; 2 – Schmidt et al. 1999; 3 – Baker and Welsh 2001; 4 – Bredt et al. 1999; 5 – Makenas et al. 1996; 6 – Silvers et al. 2000; 7 – Schmidt et al. 2004; 8 – Shelor et al. 2004; 9 – Carlson et al. 1998.

Table 8.4. Chemical and Radiochemical Compositions for Archive Sludges That Were Not Re-Jarred

Sludge	96-08 SSOL	96-09 SSOL	96-11 SSOL	96-13	96-15	KE Cont. Comp
Dry Basis						
Element	**Concentration, Wt%**					
Al	7.86	13.9	6.66	1.45	1.60	7.82
Ca	0.141	0.161	0.245	0.0698	BDL[a]	0.770
Fe	7.27	21.0	25.4	0.281	0.656	20.3
Mg	0.168	0.198	0.0318	0.19	0.193	0.171
Na	0.0728	0.0825	0.0595	0.043	0.0471	0.219
Si	NR[b]	NR	NR	NR	NR	2.81
U	31.0	13.1	6.01	74.0	49.2	15.7
Compound[c]	76.5	98.0	76.3	98.3	68.2	89.9
Radionuc.	**Concentration, µCi/g**					
^{60}Co	0.694	2.44	1.98	BDL	BDL	0.912
^{137}Cs	1180	276	223	648	795	521
^{154}Eu	10.6	4.18	2.57	9.12	9.40	2.44
^{238}Pu	17.4	5.89	3.59	BDL	8.20	4.78
$^{239/240}Pu$	93.5	34.0	17.6	110	95.4	33.7
^{241}Am	90.8	32.6	18.3	72.0	70.4	27.3
Reference[d]	1	1	1	1	1	2

(a) BDL means below detection limit.
(b) NR means not reported.
(c) Based on assignment of the elements to the compounds $Al(OH)_3$, $CaCO_3$, $Fe(OH)_3$, $MgCO_3$, Na_2O, SiO_2, and $UO_{2.63}\cdot H_2O$. The compounds $Al(OH)_3$, $CaCO_3$, and SiO_2 have been observed in genuine sludge. The compound $Fe(OH)_3$ generally is X-ray indifferent but represents the likely state of the wet iron hydroxide solids present in sludge (though Fe_2O_3 and other crystalline iron compounds have been observed by 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). Sample analyses based on fusion digests.
(d) References: 1 – Makenas et al. 1997; 2 – Delegard et al. 2007a.

Table 8.5. Bulk Physical Properties and pH of Agitated Sludge

Values	96-01	96-05	96-13 KE Comp A	FE-5 Comp 1	KC-1 M500	KC-2/3 Comp	KC-4 Whole	KC-4-2	KC-6	KE Floc Comp	KC Floor Comp	KE NLOP Jar #1[a]	KE NLOP Jar #3[a]	KE Pit
Starting Weight and Volume Values														
Tube tare, g	5.52	5.55	5.62	5.51	5.54	5.54	5.54	5.56	5.55	5.49	5.44	5.53	5.55	5.54
Tube + cap tare, g	6.83	6.82	6.90	6.78	6.83	6.85	6.81	6.86	6.83	6.77	6.71	6.80	6.68	6.82
Gross sludge & H_2O, g	17.27	20.43	23.36	21.81	21.35	22.99	20.33	20.67	16.49	20.60	20.43	18.86	18.49	21.76
Settled sludge vol., ml	0.25	2.30	5.60	5.45	2.45	5.10	4.70	4.05	2.00	6.50	1.10	9.90	3.80	3.95
Sludge & H_2O vol., ml	10.45	11.85	11.40	11.45	11.95	10.90	10.70	11.65	9.05	12.20	13.50	11.45	11.45	11.90
Dry wt., g	5.65	7.72	11.86	10.81	8.93	11.64	9.76	8.69	6.67	8.15	6.07	7.03	6.25	9.78
Net Weight and Volume Values														
Settled sludge wt., g, in H_2O	0.25	4.06	10.66	9.03	5.02	10.34	7.52	6.21	2.61	8.13	1.32	10.51	4.16	6.99
Dry solid wt., g	0.14	2.17	6.24	5.30	3.39	6.10	4.23	3.13	1.12	2.66	0.63	1.51	0.70	4.24
Dry solid vol., ml	0.14	0.41	1.18	1.72	0.82	0.86	1.40	0.97	0.51	1.04	0.41	0.90	0.34	1.20
Total H_2O wt., g	10.31	11.44	10.22	9.73	11.13	10.04	9.30	10.68	8.54	11.16	13.09	10.55	11.11	10.70
H_2O in settled sludge, g or ml	0.11	1.89	4.35	3.73	1.63	4.24	3.30	3.08	1.49	5.46	0.69	9.00	3.46	2.75
Densities and Water/Solids Concentrations														
Stl. sludge ρ, sample, g/cm^3	0.98	1.77	1.90	1.66	2.05	2.03	1.60	1.53	1.31	1.25	1.20	1.06	1.09	1.77
Sludge jar ρ, g/cm^3	NM[b]	NM	NM	1.68	2.66	2.14	1.56	1.60	1.20	1.30	1.34	NM	NM	1.92
Solids in settled sludge, vol%	56.4	18.0	21.0	31.5	33.5	16.8	29.9	24.0	25.4	15.9	37.0	9.1	8.9	30.5
Solids in settled sludge, wt%	55.5	53.5	58.5	58.7	67.5	59.0	56.2	50.4	42.9	32.8	47.6	14.3	16.7	60.7
Solids particle ρ, g/cm^3	0.96	5.26	5.30	3.08	4.13	7.10	3.01	3.23	2.21	2.57	1.55	1.67	2.05	3.52
H_2O in settled sludge, vol%	43.6	82.0	79.0	68.5	66.5	83.2	70.1	76.0	74.6	84.1	63.0	90.9	91.1	69.5
H_2O in settled sludge, wt%	44.5	46.5	41.5	41.3	32.5	41.0	43.8	49.6	57.1	67.2	52.4	85.7	83.3	39.3
pH														
pH	5.04	4.89	4.71 (avg. 2)	8.09	4.68	5.47	3.47 (avg. 3)	7.66	8.42 (avg. 2)	7.26 (avg. 2)	7.17	7.82[c]	7.75[c]	7.79
Prior pH values	6.06	4.4-6.8	NM	7.9	5.1	5.0-5.4	7.8		7.4	NM	NM	8.31		NM
Reference[d]	1	1	–	2	2	3	3		2	–	–	3		–
Sludge Quantities														
Volume settled sludge, ml	15	80	125	260	20	425	120	165	140	260	25	165[e]	240	125

(a) KE NLOP Jar #1 from whole-jar mixed sample; KE NLOP Jar #3 from sample of top layer.
(b) NM means not measured.
(c) KE NLOP Jar #1 and Jar #3 pH values meas'd. July 19, 2007; other samples meas'd. 23 days earlier on June 26, 2007, immediately after loading the calibrated pH meter. The pH meter response, checked using pH 7.00 and 10.0 standards, showed 6.64 (avg. of 6.62 and 6.66) and 9.43, respectively. Therefore, the pH values meas'd. for KE NLOP Jar #1 and Jar #3 were adjusted upwards 0.41 pH units (interpolated from the low measured pH bias found for the buffers) each to give the reported values.
(d) References: 1 – Makenas et al. 1997; 2 – Bryan et al. 2004; 3 – Delegard et al. 2000 ; 4 – Mellinger et al. 2004.
(e) Sludge volume in KE NLOP Jar #2 is 240 ml.

Table 8.6. Summary of XRD Findings for Archived Sludge Samples

Phase	Formula	PDF #	Prominence in Sludge [(a)]								
			96-13 KE Comp A	96-13 Solid Grad	FE-5	KC-2/3 Comp	KC-4-2	KC-4-Whole	KC Floor Comp	KENLOP Jar #1	KENLOP Jar #3
Present Testing											
Metaschoepite	$(UO_2)_4O(OH)_6(H_2O)_5$	70-4765	H	H		H	M				M
	$UO_3 \cdot 2H_2O$	43-3634									H
Schoepite [(b)]	$UO_3 \cdot 2H_2O$	13-241	H	M		H		M			M
	$((UO_2)_8O_2(OH)_{12})(H_2O)_{12}$	86-1383					?				
Sodium uranium hydroxide hydrate	$Na_2(UO_2)_6(OH)_{14} \cdot 4H_2O$	36-117	M								
Sodium uranyl oxide hydroxide hydrate	$Na_2(UO_2)_6O_4(OH)_6 \cdot 8H_2O$	53-876						M			
Becquerelite	$Ca(UO_2)_6O_4(OH)_6(H_2O)_8$	84-1505					H		H		
	$Ca(UO_2)_6O_4(OH)_6(H_2O)_8$	84-513						H			
Uranophane	$Ca(H_3O)_2(UO_2)_2(SiO_4)_2(H_2O)_2$	83-1847			L						
Quartz	SiO_2	82-511							M		
	SiO_2	65-466								?	
Cristobalite	SiO_2	89-3606								M	
Bayerite	$Al(OH)_3$	74-119							L		
Iron oxide hydroxide	FeOOH	73-2326								L	
Guyanaite	CrOOH	70-1115								L	
Nichromite	$NiCr_2O_4$	85-935							?		
Prior Testing											
Uraninite	UO_2, U_4O_9, U_3O_7		X	X		X	NM		NM		
Metaschoepite	$UO_3 \cdot 2H_2O$		X			X					
Quartz	SiO_2				X					X	
Gibbsite, bayerite, nordstrandite	$Al(OH)_3$					X					
Goethite, lepidocrocite	FeO(OH)				X						
References[(c)]			1	1	2	3	–		–	4	

(a) Prominence: H = high; M = medium; L = low; ? = questionable; X = present; NM = not measured.

(b) The schoepite phase $UO_3 \cdot 2H_2O$ has the formula of metaschoepite. The phase $(UO_2)_8O_2(OH)_{12})(H_2O)_{12}$ is equivalent to $UO_3 \cdot 2.25H_2O$ and is a true schoepite.

(c) References: 1 – Makenas et al. 1997; 2 – Baker and Welsh 2001; 3 – Delegard et al. 2000; 4 – Melllinger et al. 2004.

9.0 Conclusions

Samples of sludge were collected from the K East fuel storage basin (KE Basin) floor, contiguous pits (Weasel Pit, North Load Out Pit, Dummy Elevator Pit, and Tech View Pit), and fuel storage canisters between 1995 and 2003 for chemical and radionuclide concentration analysis, physical property determination, and chemical process testing work. Because of the value of the sludge in this testing and because of the cost of obtaining additional fresh samples, an ongoing program of sludge preservation has taken place with the goals to track the sludge identities and preserve, as well as possible, the sludge composition by keeping the sludge in sealed jars and maintaining water coverage on the sludge.

In the present work, like samples of KE Basin sludge were consolidated into new containers, other sludges put into new containers, and other sludge samples from the SAL and from storage in the RPL basement were gathered into the HLRF to maintain better sample tracking. The quantities of the various sludge samples were measured. The physical properties (bulk and particle density and water and solids concentrations), the pH, and the solid phases present in a number of these samples were determined and are reported. The results are compared with results, where available, found in prior testing.

Results of the compositing and characterization are summarized in Table 9.1 and show sludge sources, volumes, uranium concentrations, and densities. It was found that settled sludge densities generally increase with increasing uranium concentration while sludge pH generally decreases with increasing uranium concentration. The X-ray diffraction results (not shown in Table 9.1), where available, show disappearance of uranium(IV) phases (various uraninites, UO_2, U_4O_9, and U_3O_7) observed during prior characterization testing and the appearance of uranium(VI) compounds including metaschoepite, becquerelite, and uranophane.

Table 9.1. Sources and Properties of Archived KE Basin Sludge Samples

Sample ID	Source	Sample Date	Stld. Vol., ml	[U], dry wt%	Stld. Density, g/cm^3		References
					Present	Original	
96-01	Single closed-bottom canister with good condition fuel	8 Apr 96	15	0.0944	0.98 (cone)	2.09 (1997)	Makenas et al. 1997
96-05	Single closed-bottom canister with very poor condition fuel	9 Apr 96	80	58.5	1.77 (cone)	2.34 (1997)	Makenas et al. 1997
96-08 SSOL	Single canister with poor condition fuel	10 Apr 96	50	31.0	–	1.19 (1997)	Makenas et al. 1997
96-09 SSOL	Single empty open-bottom canister	11 Apr 96	50	13.1	–	1.07 (1997)	Makenas et al. 1997
96-11 SSOL	Single empty closed-bottom canister	12 Apr 96	<50	6.01	–	1.23 (calc., 1997)	Makenas et al. 1997
96-13 (various)	Single canister with poor condition fuel (Settler Study, Solid Grad, SSOL)	18 Apr 96	125, 100, 50	74.0	–	2.458 (1997)	Makenas et al. 1997
96-13 KE Comp A	Composite of samples 96-01, -05, -06, -08, -13, and -15 from single canisters with good to very poor condition fuel	8-18 Apr 96	125	52.1	1.90 (cone)	–	Makenas et al. 1997; Table 3.2 of Schmidt et al. 1999
96-15 SSOL	Single canister with poor condition fuel	18 Apr 96	100	49.2	–	1.845 (1997)	Makenas et al. 1997
FE-5	Weasel pit including South Loadout Pit sludge	26 Apr & 13 Jan 99	260	5.32	1.66 (cone) 1.68 (jar)	1.50	Composite created in 222-S Lab from KE-9 and KE-10 single-pull samples; Baker & Welsh 2001
KC-1 M500	Canister sludge from highly damaged fuel collected from one sampling location	12 Apr 99	20	68.6	2.05 (cone) 2.66 (jar)	1.5	Sample passing 500-µm sieve; 88.7 wt% of total KC-1 wet solids; Baker & Welsh 2001; Bredt et al. 1999; Bryan et al. 2004
KC-2/3	KC-2; consol. smpl. fr. fuel stor. can. barrels w/ hi. dmgd. fuel fr. all 3 bays	4-13 Mar 99	425	59.0	2.03 (cone) 2.14 (jar)	2.13 (1999)	Composite KC-2/3 created in 325 Lab; Baker & Welsh 2001; Bredt et al. 1999
	KC-3; consol. smpl. fr. can. barrels with mod. dmgd. fuel fr. all 3 bays	1-8 Apr 99					
KC-4 Whole	Consol. smpl. fr. floor btwn. barrels of open bot. can. w/ highly dmgd. fuel fr. all 3 bays	30-31 Mar 99	120	16.6	1.60 (cone) 1.56 (jar)	1.235	Baker & Welsh 2001; Bredt et al. 1999
KC-4-2			165		1.53 (cone) 1.60 (jar)		
KC-6	Consol. smpl. fr. floor area in west bay known to be v. high in ion exchange beads	13 & 26 Mar 99	140	0.314	1.31 (cone) 1.20 (jar)	1.1	Baker & Welsh 2001; Bredt et al. 1999; Bryan et al. 2004
KC-6 carboy			6400		–		
KC Floor Comp	Comp. of 40 vol% KC-4 & 60 vol% KC-5 (stl. sl.); KC-5 consol. deep sl. fr. all 3 bays (smpl. 29 Mar 99)	29-31 Mar 99	25	10.3	1.20 (cone) 1.34 (jar)	1.21 (calc., 2000)	Baker & Welsh 2001; Silvers et al. 2000
KE Container Comp & Floc[(a)]	Composite of KC-2/3, KC-4, KC-5 P250 & FE-5	13 Jan – 26 Apr 99	25, 10	15.7	–	1.65, 1.53 (cone) 1.54, 1.45 (jar)	Delegard et al. 2007a
KE Floc Comp	Composite of KC-4 M250, KC-5, FE-5, and KC Can Comp	13 Jan – 26 Apr 99	260	10.3	1.25 (cone) 1.30 (jar)	1.25 (2004)	Baker & Welsh 2001; Schmidt et al. 2004
KE NLOP	KE North Load Out Pit; top-to-bottom sample composite present in three jars (#1, #2, and #3)	13 & 19 Dec 03	645	2.51	1.06 (cone)	1.23 (2004)	Mellinger et al. 2004; Shelor et al. 2004
KE Pit	Weasel Pit composite of KES-P-16, -Q-17, -R-18, -S-19, & -T-20	15-25 Sep 95	125	7.99	1.77 (cone) 1.92 (jar)	–	Makenas et al. 1996; dry smpls. weigh & mix w/ H_2O, Carlson et al. 1998

(a) Note that this composite composition is near that expected for KE Basin containerized sludge.

10.0 References

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Appendix A

Sludge Sample Uses for Characterization and Process Testing

Table A.1. Use of Sludge Samples for Property and Process Testing

Activity	Samples Used	Composites Generated		Reference
Uranium and radionuclide leaching from KE Pit sludges	KES-P-16, -Q-17, -R-18, -S-19, and -T-20	KE Weasel Pit: 51.97 g of P-16, 12.37 g of Q-17, 111.14 g of R-18, 54.43 g of S-19, and 52.16 g of T-20 (dry basis)		Carlson et al. 1998
Validation testing of nitric acid treatment of sludge	96-01, 96-05, 96-06 L, 96-06 M/L, 96-08, 96-13, 96-15; KES-A-02, -B-03, -C-04, -F-10, -G-07, -I-15, -K-12, -L-01, -N-05, -E-11, -J-06, -D-14, -P-16, -Q-17, -R-18, -S-19, and -T-20; KES-H-08	KE Canister Sludge: 61.92 g of 96-01, 62.92 g of 96-05, 74.05 g of 96-06 L, 57.37 g of 96-06 M/L, 39.03 g of 96-08, 124.54 g of 96-13, and 57.37 g of 96-15 (dry basis)	KE Area Sludge: 0.39 g of A-02, 1.41 g of B-03, 0.39 g of C-04, 10.54 g of F-10, 1.25 g of G-07, 1.60 g of I-15, 1.65 g of K-12, 0.36 g of L-01, 6.48 g of N-05, 17.67 g of E-11, 30.31 g of J-06, 7.75 g of K-14, 18.93 g of P-16, 4.51 g of Q-17, 40.49 g of R-18, 19.83 g of S-19, and 19.00 g of T-20 (dry basis)	Schmidt et al. 1999
Receipt, recovery, and physical characterization (recovery, settling, sieving, % water, shear strength, and acid calorimetry)	KC-1, KC-2/3, KC-4, KC-5, and KC-6	None		Bredt et al. 1999
Chemical characterization	KC-1, KC-2/3, KC-4, and KC-5	None		Elmore et al. 2000
TCLP testing and ICP	KC-1, KC-2/3, KC-4, and KC-5	KC Can Comp: 10.6 wt% KC-1 + 69.8 wt% KC-2/3 + 19.6 wt% KC-2/3 P250 (settled)	KC Floor Comp: 41.1 wt% KC-4 and 58.9 wt% KC-5	Silvers et al. 2000
Shipped to 222-S for testing	KC-1, KC-2/3, and KC-4	Shipped as KC Can Comp and KC-4		Steen 2000
Gas Generation Series I	KC-2/3, KC-4, KC-5	None		Delegard et al. 2000
Gas Generation Series II	KC-1, KC-6, FE-1, FE-3, FE-5, FE-6, and 96-06	None		Bryan et al. 2004
Gas Generation Series III	KC-1, KC-2/3, KC-4, and KC-5	KC Can Comp and KC Floor Comp used (see Silvers et al. 2000)		Schmidt et al. 2003
Thermal conductivity and shear strength testing	KC-1, KC-2/3, KC-4, and KC-5	KC Can Comp and KC Floor Comp used (see Silvers et al. 2000)		Poloski et al. 2002
Flocculation testing	KC-4, KC-5, FE-5, and KC Can Comp	Flocculation composite (Floc Comp) and flocculated sludge is 50.6 wt% KC-4 M250, 29.6 wt% KC-5, 19.4 wt% FE-5, and 0.35 wt% KC Can Comp (see PNNL-13280)		Schmidt et al. 2004
Gas generation testing of sludge and grouted and absorbent forms	KE NLOP	Composite of top-to-bottom collection from isolation tube sampling		Mellinger et al. 2004
Long-term compaction studies	FE-5, KC-1, KC-2/3, KC-4, KC-5, 96-13, and KE NLOP	SNF Comp came from residues of gas generation tests “SNF + Can 60L” and “SNF + Floor 60L”, reported in PNNL-14346, using 64 vol% KC Floor Comp + 36 vol% KC Can Comp plus crushed & part-corroded fuel		Delegard et al. 2005
Sludge Treatment Process testing	KC-2/3, KC-4, KC-5, and FE-5	KE Container Comp = KE Floc Container Comp = 12.5 wt% KC-2/3, 25.3 wt% KC-4, 32.2 wt% KC-5 P250, and 30.0 wt% FE-5. Also used KC-2/3 M250.		Delegard et al. 2007a

Appendix B

XRD Scans

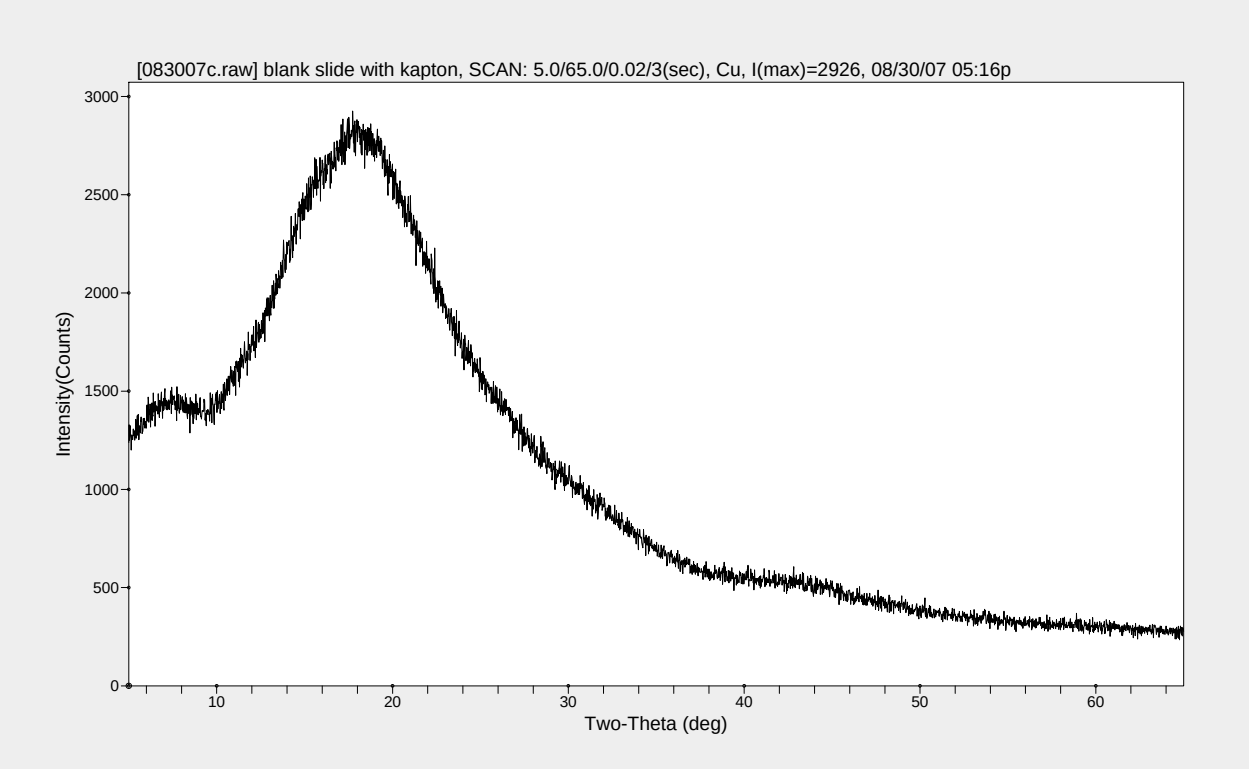

Figure B.1. Raw X-Ray Diffraction Scan for a Blank Slide

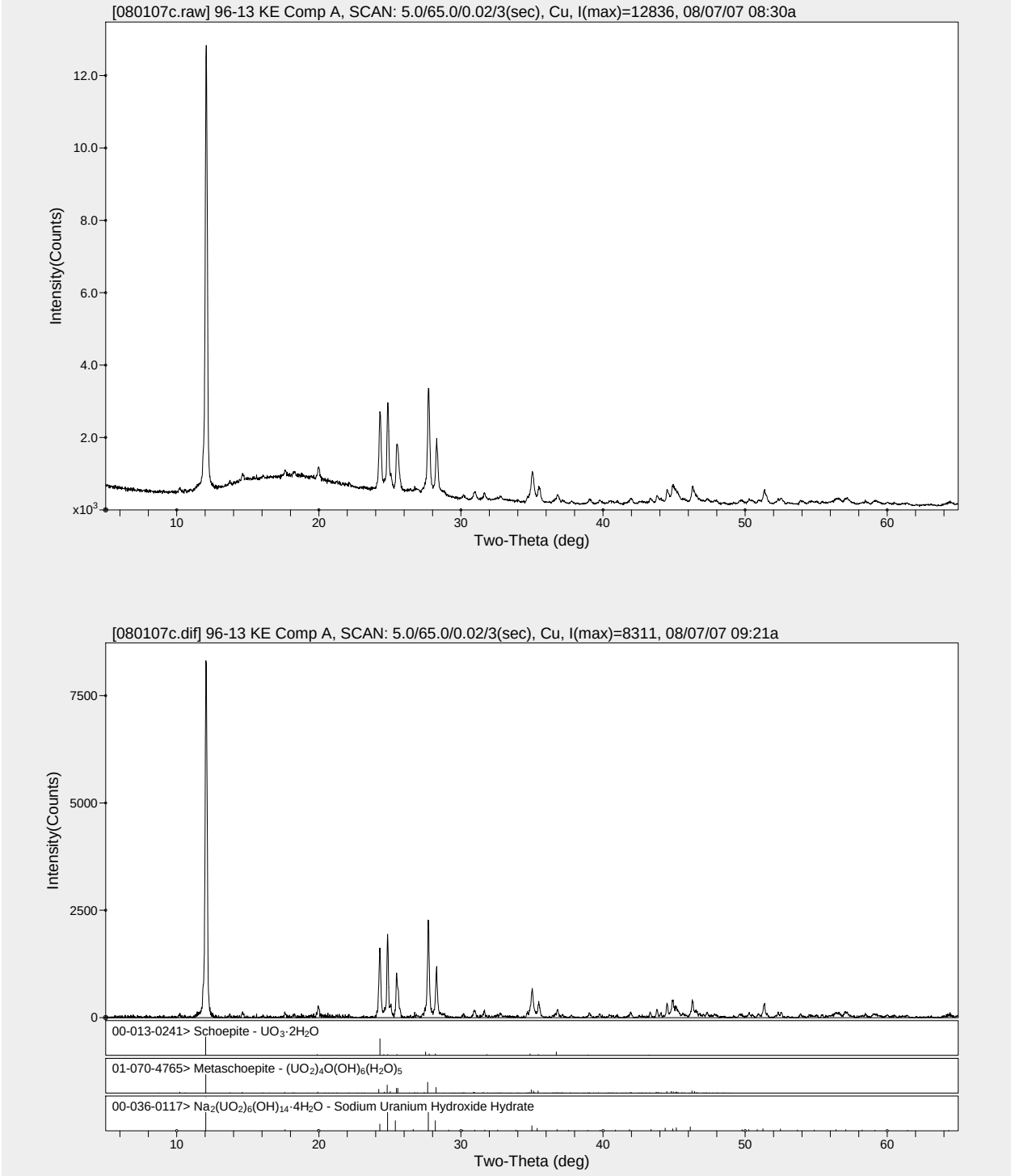

Figure B.2. Raw and Background-Corrected X-Ray Diffraction Scan for 96-13 KE Comp A

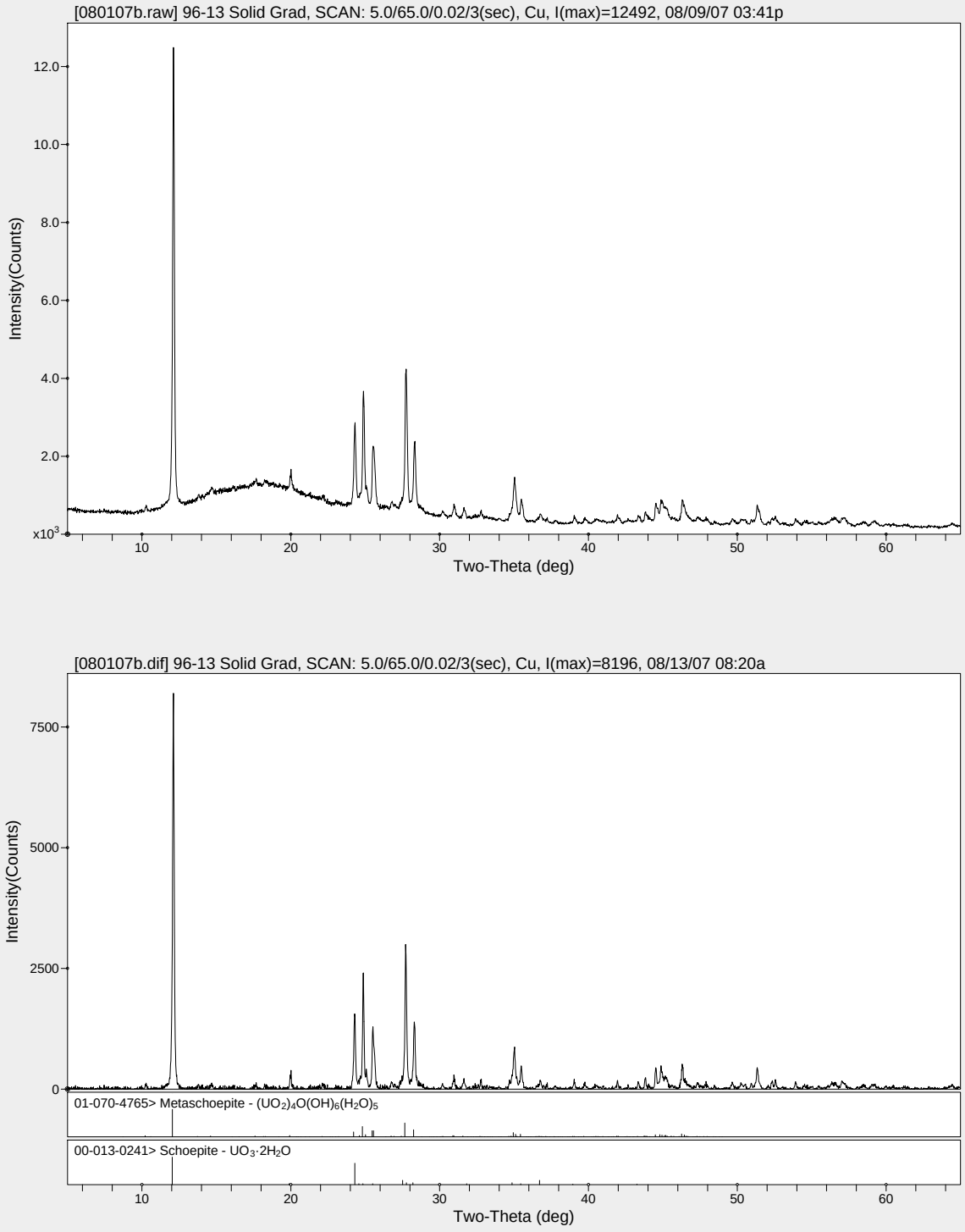

Figure B.3. Raw and Background-Corrected X-Ray Diffraction Scan for 96-13 Solid Grad

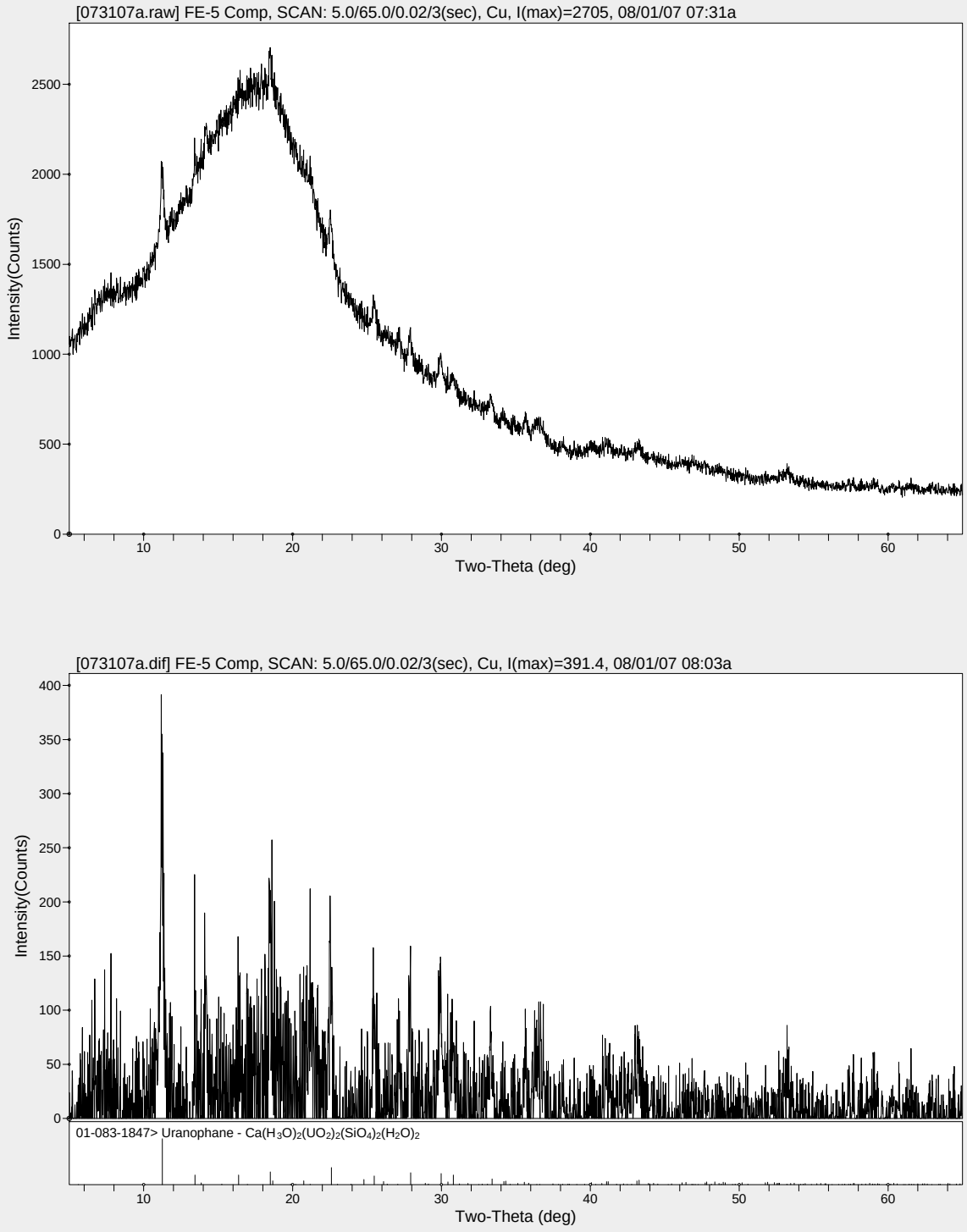

Figure B.4. Raw and Background-Corrected X-Ray Diffraction Scan for FE-5 Comp

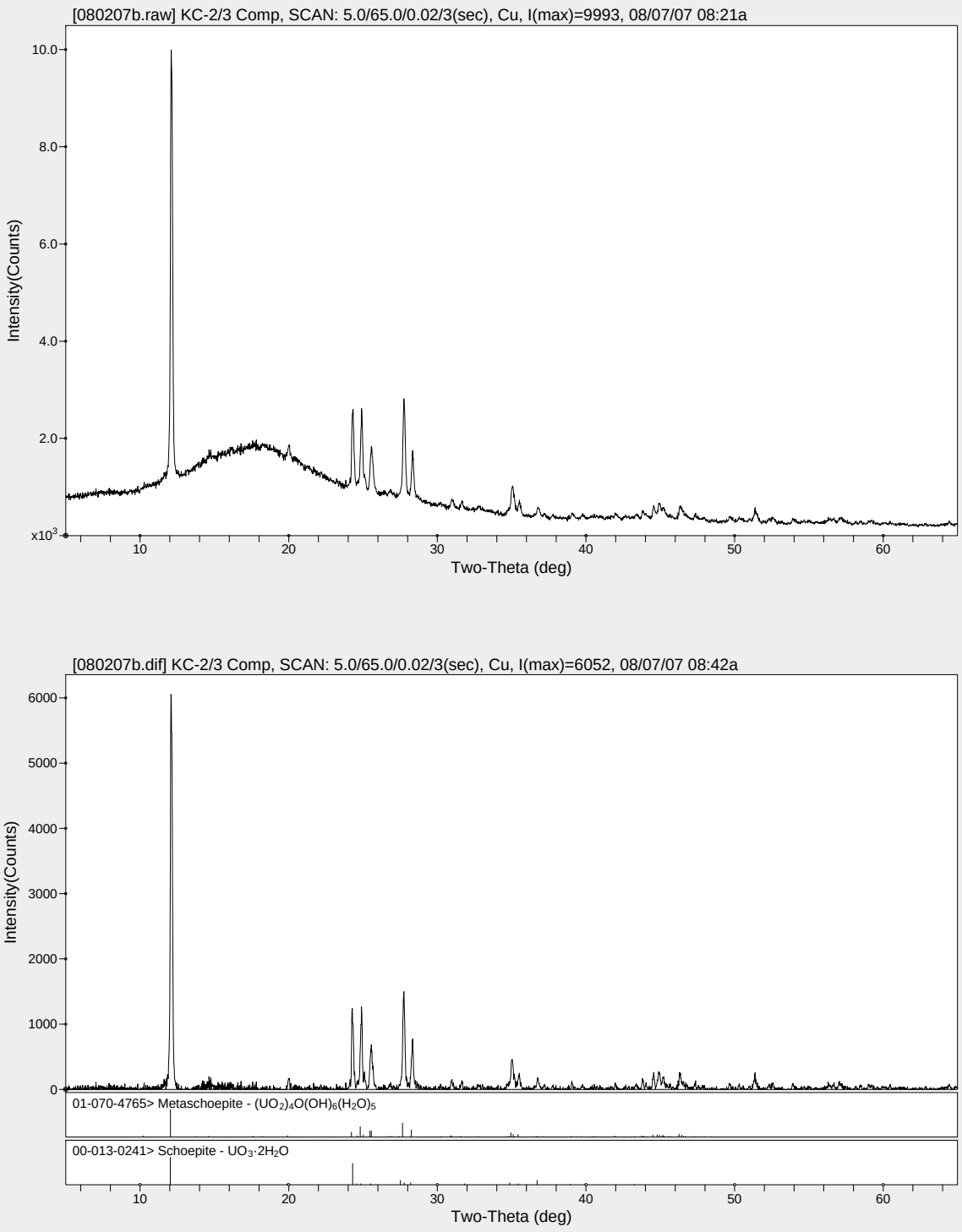

Figure B.5. Raw and Background-Corrected X-Ray Diffraction Scan for KC-2/3 Comp

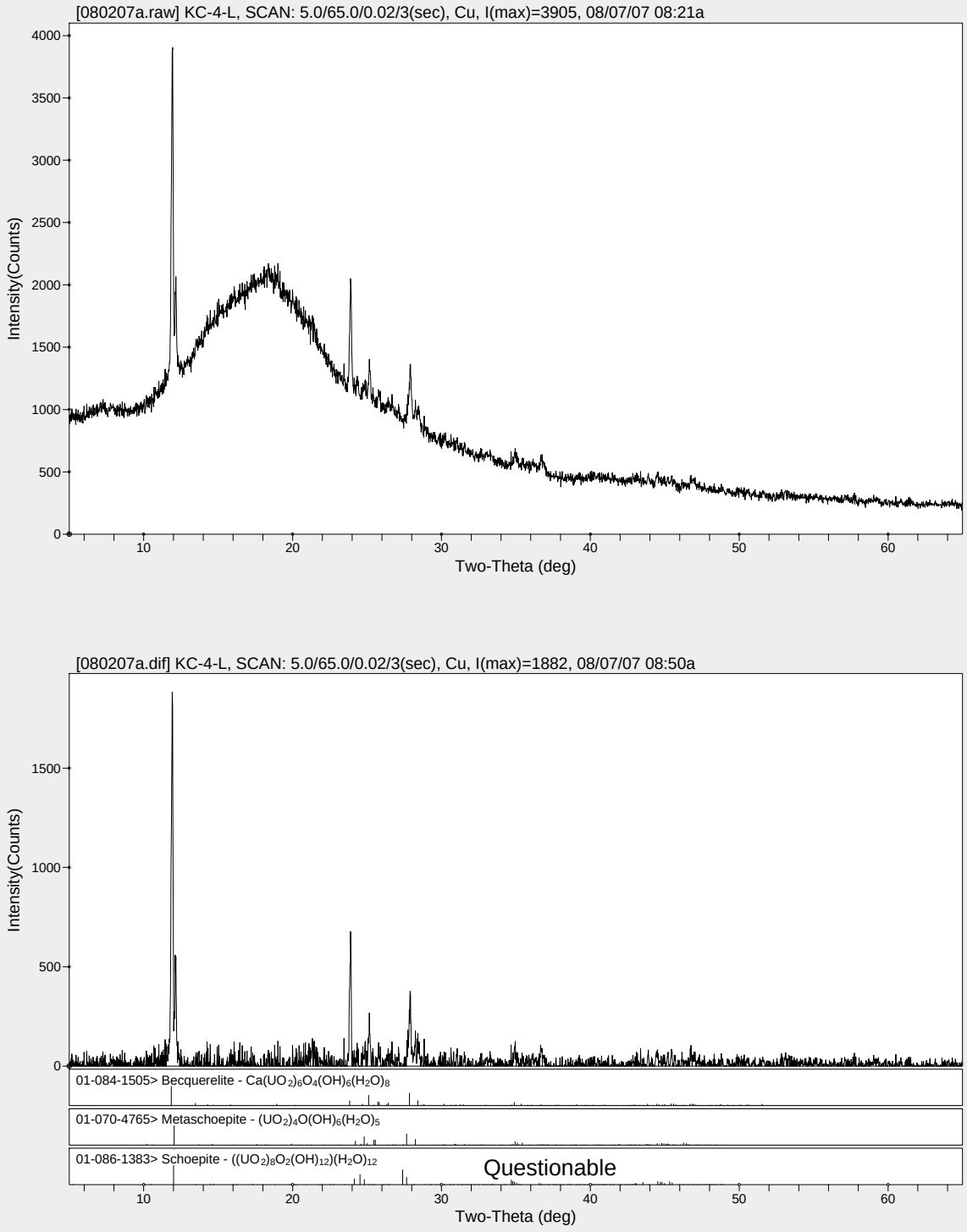

Figure B.6. Raw and Background-Corrected X-Ray Diffraction Scan for KC-4-L

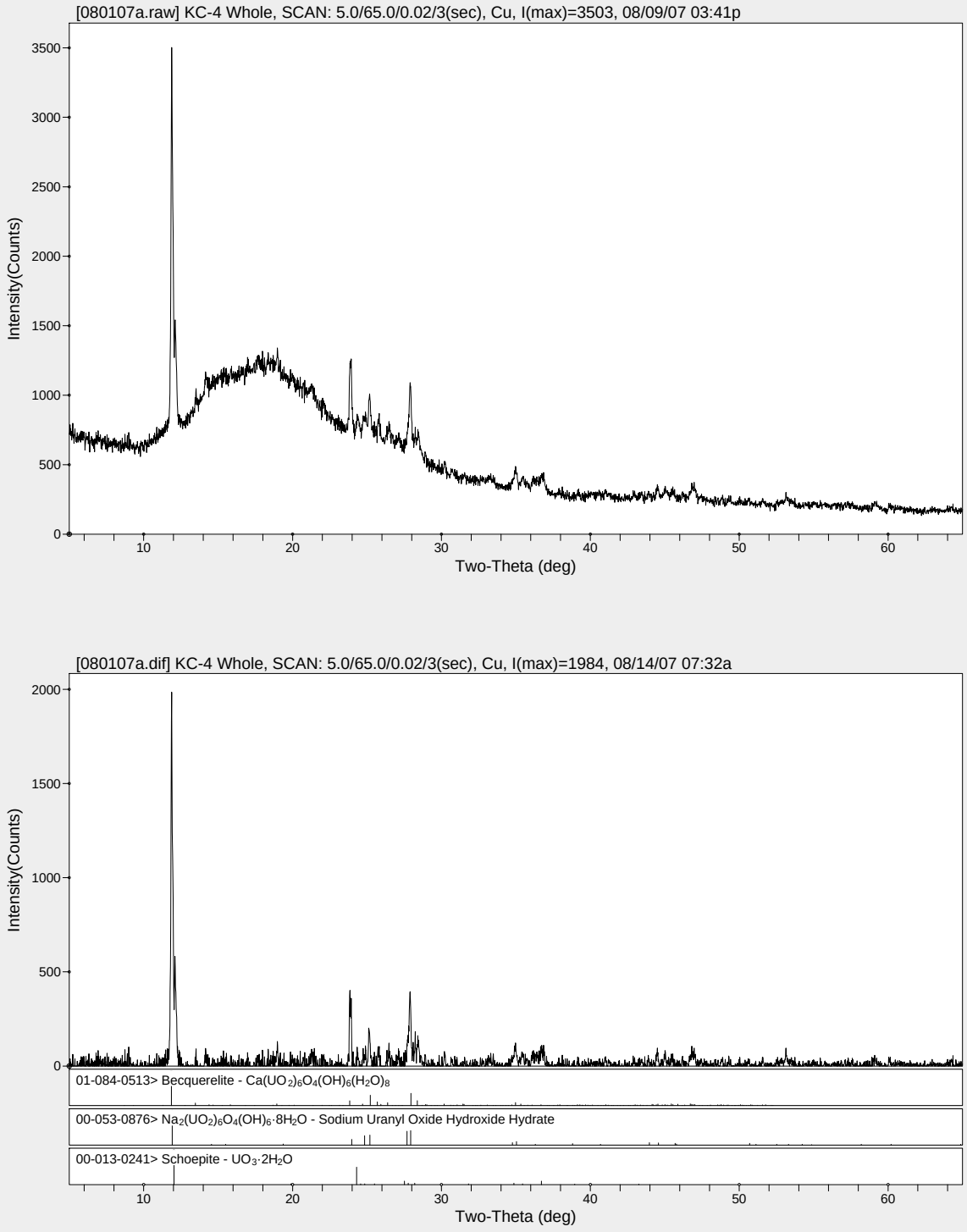

Figure B.7. Raw and Background-Corrected X-Ray Diffraction Scan for KC-4 Whole

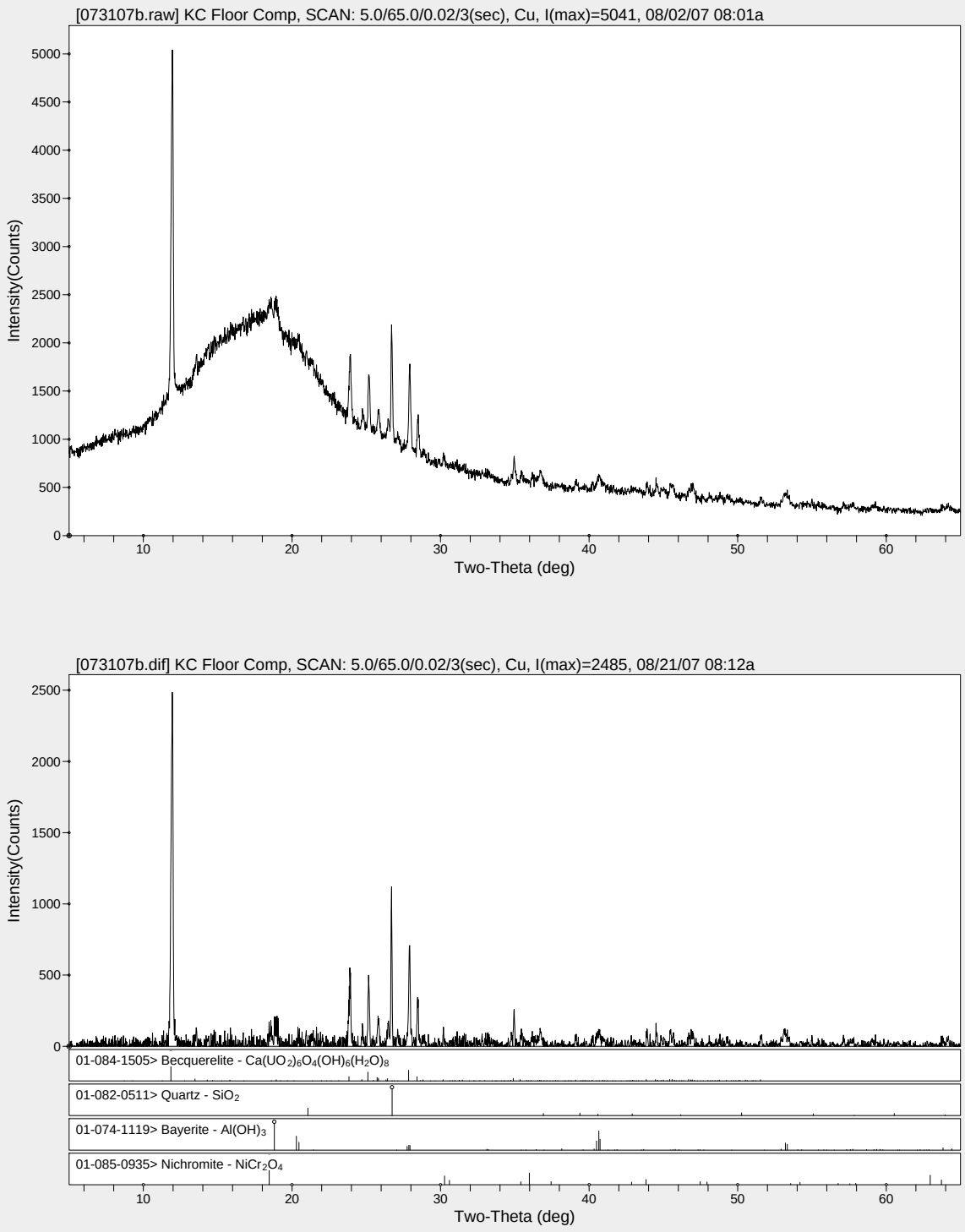

Figure B.8. Raw and Background-Corrected X-Ray Diffraction Scan for KC Floor Comp

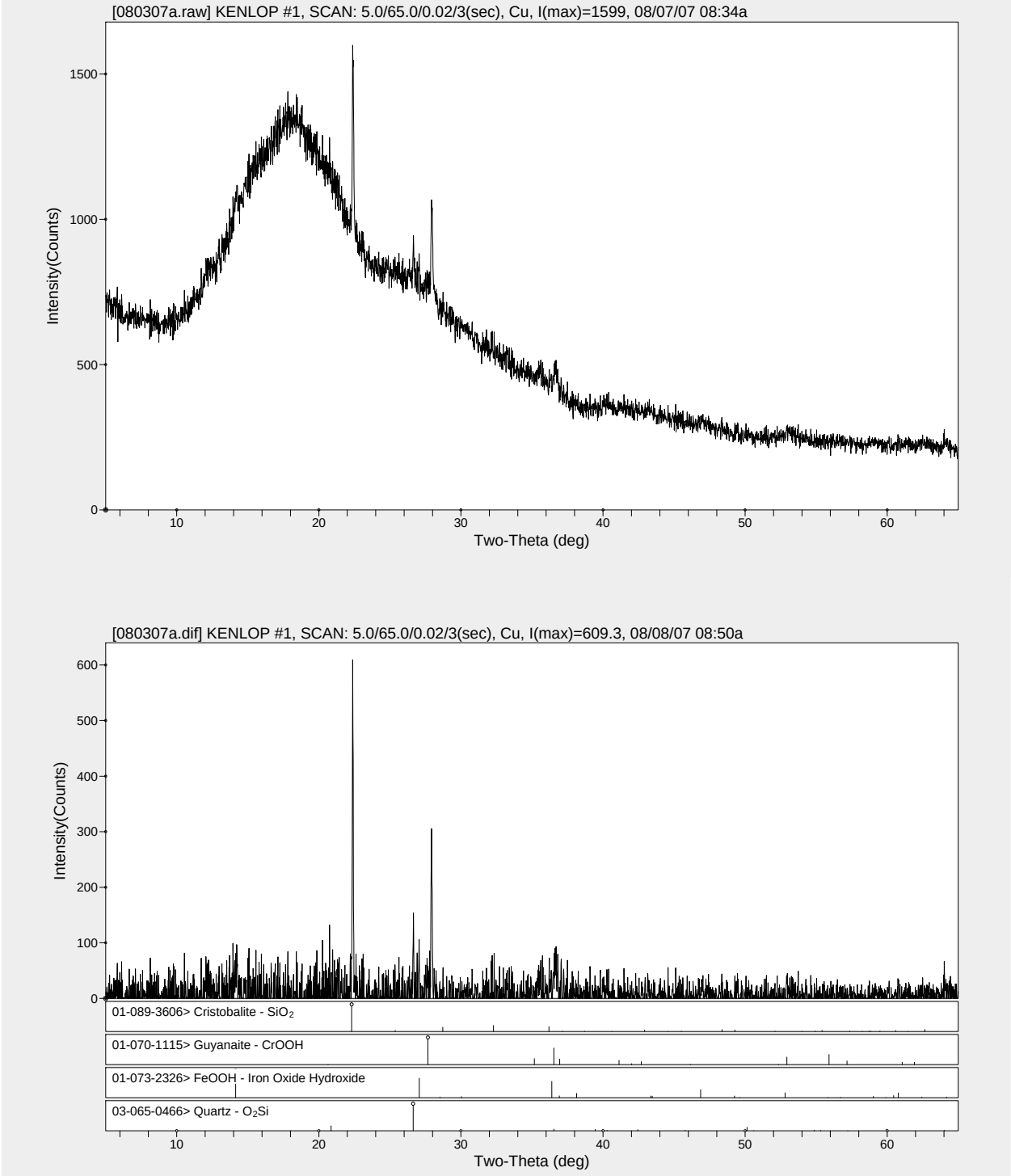

Figure B.9. Raw and Background-Corrected X-Ray Diffraction Scan for KENLOP #1 (Jar #1)

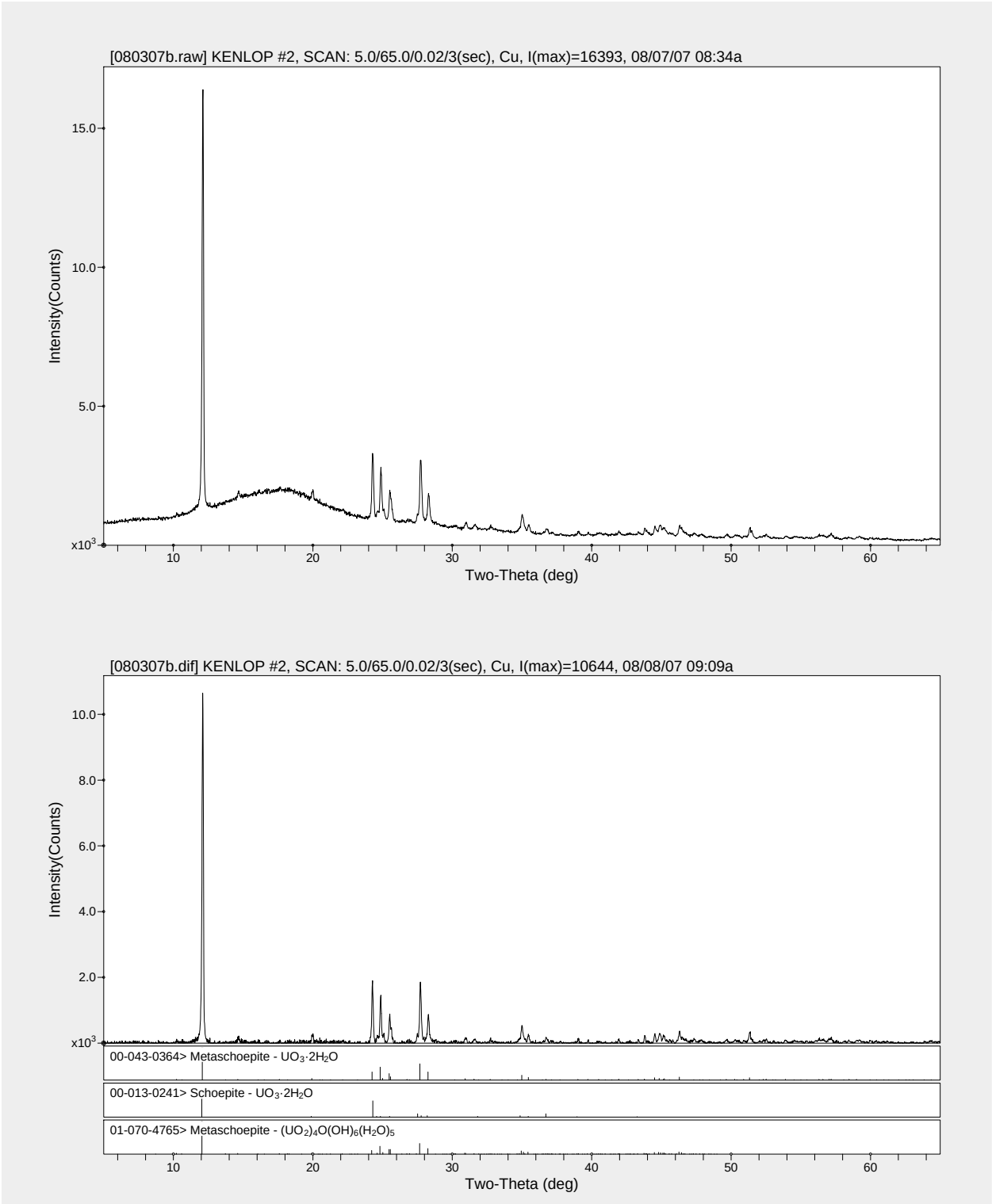

Figure B.10. Raw and Background-Corrected X-Ray Diffraction Scan for KENLOP #2 (Jar #3)

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