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Sludge Treatment Project Engineered Container Retrieval and Transfer System: Status Report for Long Term Monitoring of K Basin Sludge Samples

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
under Contract DE-AC06-08RL14788

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0	Document issued to STP project files	N/A 1/23/2012 ☒
1 RS	Incorporated shear strength measurements obtained in FY 2012 thru FY 2015 for archived KW Basin sludge samples. Reorganized Table 1 to list shear strength results by engineered container. In Table 1, deleted sample results for shear strength measurements that were too close to bottom of sample container or insufficient sludge to immerse shear vane. Updated references per ECR-15-000450	MEJ 5/4/2015 ☒
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1.0 Introduction

The Engineered Container Retrieval and Transfer System (ECRTS) subproject encompasses providing a disposition for the K Basin floor and pits (i.e. Engineered Container) sludge and Settler sludge that is contained in Engineered Containers SCS-CON-210, -220, -230, -240, -250 and -260. The Sludge Treatment Project (STP) recommended and DOE-RL approved a two-phase approach for the disposition of Engineered Container and Settler sludge. Phase 1 comprises retrieval and transported of Engineered Container and Settler sludge to T Plant for interim storage, thus removing the sludge from the River Corridor and transferring it to the Central Plateau. Phase 2 comprises the future sludge retrieval from interim storage, treatment and packaging, and conducting associated preparations required for placing packaged sludge into interim storage pending shipment to the Waste Isolation Pilot Plant (KBC-30811).

The ECRTS subproject plans to retrieve K Basin sludge from the six Engineered Containers and transfer this sludge into Sludge Transport and Storage Containers (STSCs). A flocculant, Clarifloc™ N3300-P may be added during sludge retrieval to promote sludge settling in an STSC and reduce the time for clarification of the supernatant. The excess supernatant will be decanted from an STSC, filtered to remove entrained solids, and then returned to the K West (KW) Basin. Additional sludge will be loaded into an STSC following this same method until the payload limits are reached in the STSC. After loading sludge, the STSC will be transported to T Plant for interim storage. The K Basin sludge will be stored underwater within the STSCs. T Plant can experience a canyon temperature between minus 7°C to 32°C (HNF-SD-SNF-TI-015, Volume 2 Table 4-37). Following the interim storage period, the STSCs will be removed from T Plant and transported to a treatment and packaging facility. The removal and transport of the STSCs to the sludge treatment and packaging facility, as well as the design, construction and operation of this facility, are Phase 2 activities. However, demonstration of a general method to remove sludge from the STSC is part of Phase 1 activities.

The potential for K Basin sludge to form agglomerates is being evaluated due to the influence on the planned future sludge retrieval and treatment activities. Existing information on sludge aging mechanisms (e.g. chemistry, rheology, and agglomerate formation) has been summarized in PRC-STP-00274. A synopsis of information in PRC-STP-00274 is provided in Section 2.0. Section 3.0 discusses additional tests that were conducted using simulated sludge samples to further understand the oxidation of sludge components. Additionally, the STP has initiated a long-term monitoring program to evaluate the potential for agglomerate formation in archived sludge samples stored in the hot-cells (nominally 30 ± 5°C) at the Pacific Northwest National Laboratory (PNNL). Sludge samples selected for long-term monitoring include samples obtained in 2009 and 2010 from all six Engineered Containers and sludge samples that have been treated with the flocculant Clarifloc N3300-P. Section 4.0 summarizes analytical measurements collected during long-term monitoring of sludge samples through February 2015.

2.0 Understanding of Sludge Aging Mechanisms

PNNL personnel have observed the agglomeration of K Basin sludge under laboratory conditions. PNNL personnel conducted tests from May 2002 to September 2004 to characterize six K East (KE) Basin sludge samples during long-term storage and quantify the rate of supernatant loss (PNNL-15092). These tests were conducted over a 28-month period to predict sludge drying rates under hot cell storage conditions, which were ~32° to 38°C, ~30 to 41% relative humidity, and ~5 rad/hour radiation field. The hot cell conditions are similar to T Plant storage conditions; maximum temperature 32°C and ambient humidity. One of the KE sludge samples (sample 96-13) had previously dried-out during storage and was reconstituted by mixing with water for these tests. The 96-13 sample self-agglomerated during the dry-out test. The other five sludge samples remained fluid slurries at the end of the dry-out test. The agglomerated 96-13 sludge sample, shown in Figure 1, consisted of "paste" and "chunks" with shear strengths of approximately 3 to 5 kPa and 380 to 770 kPa, respectively. High-uranium-content sludge samples subjected to hydrothermal testing (e.g., 185°C for 10 hours) have also been observed to form agglomerates with shear strength up to 170 kPa (PNNL-16496).

Figure 1 Agglomerated Sample 96-13
Sample in a 3.5 cm inner diameter graduated cylinder after settling test[1].

Further investigation of the available K Basin sludge sampling and characterization reports show that high strength sludge agglomerates have been observed in four laboratory samples and sub-samples that were stored in the PNNL hot cells, and indirectly during six KE basin sampling events. These sludge samples had been collected from 1995 through 1999. For the purpose of this discussion agglomerates are defined as sludge of sufficient strength such that mobilization and transfer of the sludge is significantly impeded. The four samples and sub-samples that

[1] Figure courtesy of PNNL-15092, page 3.10

agglomerated during storage in the PNNL hot cells (i.e., conditions similar to T Plant) were identified as KE Pit (composite of five KE Weasel Pit sludge samples), KC-2/3 SS (settled solids fraction from settling test conducted with KC-2/3 sample), KC-2/3 M250 (less than 250 μm sieved fraction of KE canister sludge composite sample) and 96-13 (KE canister sludge sample). All of these samples and sub-samples formed high strength agglomerates that proved difficult to remove from their respective storage containers. With the exception of sample KE Pit, all the samples that exhibited agglomerate formation while stored in the PNNL hot cells have total uranium concentrations (dry wt. % basis) greater than 59 wt. %. Sample KE Pit had a total uranium concentration of ~8 wt. % and was determined to have moderate concentrations of Zeolite minerals and high iron concentration, which possibly caused dissolution and re-precipitation reactions resulting in the formation of uranium silicate agglomerates (PRC-STP-00274 page 6). The KE-Pit sample also contained relatively high iron concentration at 36.4 wt. %.

The results of this investigation on sludge agglomeration suggest that the cause of agglomerate formation in K basin sludge is a combination of the following conditions:

- High total uranium content (i.e., sample homogeneity and influence from other constituents)
- Distribution of uranium phases (i.e., extent of conversion from uraninite to uranium oxide or hydroxide compounds)
- Sample dry-out (loss of cover water)
- Elevated temperature
- Solubility of U(IV) phases vs. U(VI) phases
- Long storage times

The potential agglomerate formation mechanism is dissolution of uranium oxides (e.g. uraninite) and re-precipitation. This dissolution and re-precipitation occurs at the sludge bed – water interface and can form layering of uranium oxide hydrates such as metaschoepite. For example, metaschoepite [$UO_3 \cdot 2H_2O$], the dominant uranium phase found in highly oxidized K Basin sludge, has been shown to dehydrate, and react with silica (from soil and concrete) to form the uranium silicate soddyite [$(UO_2)_2SiO_4 \cdot 2H_2O$]. Section 3.0 provides additional information on agglomeration of sludge from uraninite oxidation to metaschoepite. K Basin sludge will be stored at T Plant inside STSCs. Water will be contained above the settled sludge layer in each STSC. T Plant will have a means to measure water loss and provide for replenishment, which will significantly lower the risk of agglomeration associated with sludge dry-out.

3.0 Uranium Oxide Oxidation to Metaschopite

PNNL personnel studied the oxidation reaction of uranium oxide (UO_2 or uraninite) to form metaschoepite ($UO_3 \cdot 2H_2O$) to evaluate the formation of agglomerates in sludge samples (PNNL-20100). All other major sludge compounds (e.g., gibbsite, ferrihydrite, sand, ion exchange media) are chemically stable and of low solubility and, therefore, are not expected to alter during extended storage and oxidation reactions. To accelerate potential physical and

chemical changes, PNNL personnel conducted tests at 50°C and oxygen partial pressures significantly greater than those expected in the T Plant canyon cells (maximum 32°C). Uranium-containing simulants used for this work were designed to match the chemical compositions of K West (KW) Engineered Container sludge and Settler sludge. The KW Engineered Container sludge simulant contained uraninite [U(IV)], metaschoepite [U(VI)], aluminum hydroxide, ferrihydrite, Hanford sand, organic ion exchange resin Purolite™ NRW-37, mordenite inorganic ion exchanger, flocculating agent Optimer™ 7194 Plus[2], and water. The compositions simulating Settler sludge contained uraninite and water or uraninite, metaschoepite, and water only. Water covered the settled simulated sludge used in the uraninite oxidation tests.

Excerpts of the specific results from PNNL-20100 and their importance to the potential for K Basin sludge agglomerate formation are:

- Oxidation of settled uraninite slurry to metaschoepite by dissolved oxygen produces no increase in settled volume. Metaschoepite product crystals form from the top-down and then knit together to form a continuous layer through Ostwald ripening. No change in total settled solids volume was observed for the ~300-day experimental duration in accelerated static testing conducted at 51°C under a pure oxygen atmosphere.

- The oxidation of uraninite under static 51°C pure oxygenated conditions progresses very slowly and appears to be diffusion-limited as shown by its kinetic behavior. Only the top 5 mm of the sludge bed was oxidized to metaschoepite after nearly 10 months of exposure. The projected metaschoepite solids layer depth under 20°C atmospheric oxygen conditions (P_{O2} = 0.21 atm) is ~5 mm after 30 years. The product metaschoepite solids layer at this thickness is weak and friable.

- A previous 28-month-long storage test conducted with six K Basin sludge samples at ~30±5°C under hot cell conditions showed that the settled solids volume decreased or remained essentially unchanged with storage time after an initial 4 days of settling. After the 28-month settling, five of the sludge samples were readily re-suspended to pourable slurries by agitation. However, the sixth sludge, a uranium-rich fuel canister sludge sample called 96-13, was estimated to have a bulk shear strength of 15 kPa to 65 kPa and could be retrieved from its glass test vessel only by breaking the vessel.

  These findings indicate that for solids very rich in uranium (≳ 70 to 80 wt%, dry basis), long-term storage under aerated non-agitated conditions will form a thin metaschoepite crust that is readily broken. The underlying material may compact somewhat with time, but, because little appreciable change in settled solids strength was seen after nearly a year of settling at 51°C in laboratory tests, little increase in strength, beyond that associated with any compaction, is anticipated during lower temperature but longer term storage.

[2] Optimer 7194 Plus flocculating agent was used during the consolidation of sludge into containers within the 105-KE Basin and on a limited scale during the transfer of sludge from the 105-KE basin to engineered containers within the 105-KW Basin.

The observations from the 28-month settling test with uranium-rich genuine sludge and the studies with the uraninite oxidation suggest that metaschoepite crystal ripening and intergrowth may have been responsible for the uncommon strength found in the genuine sludge. In this case, the presence of relatively high amounts of metaschoepite within the settled solids layer likely was necessary to produce the strong product material.

Based on these findings, K Basin sludges rich in metaschoepite [≳ 70 to 80 wt% U as U(VI), dry basis] may self-cement by Ostwald ripening to produce strong agglomerates similar to the behavior shown by the 96-13 sludge in the 28-month settling tests. Because of the low solubility of UO_2, similar gains in strength by Ostwald ripening for UO_2-rich sludge cannot occur.

- Under 51°C oxygenated conditions, a full KW containerized sludge simulant containing gibbsite, ferrihydrite, mordenite, organic ion exchange resin, Hanford sand, and ~50%/50% $UO_2/UO_3 \cdot 2H_2O$ decreased in settled solids volume by about 25% over 106 days while a parallel control test run in the absence of oxygen decreased only about 3%. The volume decrease coincided with the oxidation of UO_2 to $UO_3 \cdot 2H_2O$ and may have been due to better solids packing or coagulation of non-uranium solids with the crystallizing $UO_3 \cdot 2H_2O$. However, even though the KW containerized sludge simulant compacted with time, the strength remained low.

- Under warm (30±5°C) semi-oxic conditions, the uraninite in uranium-rich K Basin sludge samples oxidized to metaschoepite and other U(VI) phases after 9 years of hot cell storage.

  These findings mean that, unlike uraninite-rich sludges that form continuous layers or networks of product metaschoepite upon reaction with oxygen or which already have high metaschoepite concentrations, sludges more dilute in uraninite or metaschoepite likely will be unable to produce continuous metaschoepite layers that inhibit further oxidation or which self-cement to form high strength agglomerates. Instead, the metaschoepite may act to coagulate non-uranium sludge solids and produce settled solids that are more tightly packed and have a lower settled-solids volume and a lower volume fraction of void water.

  The effect of decreased water-void volume may be to increase the settled-sludge strength. However, the long-range binding of sludge solids through metaschoepite recrystallization with itself will not be possible because of insufficient metaschoepite. Marked strength increases were not noticeable for the simulated sludge materials tested after ~100 days of reaction.

- Under strongly stirred oxygenated room temperature conditions, uraninite oxidation produces ~50%/50% (mole basis) uraninite/metaschoepite settled solids mixtures of significantly higher solids loading (~24 volume %) and shear strength than the starting

uraninite material and the product metaschoepite. A shear strength in excess of 26,000 Pa was noted for one such mixture, and shear strengths of 2,000 Pa were routinely observed for similar mixtures. In contrast, pure uraninite and metaschoepite settled slurries had shear strengths measured in the hundreds of Pa. The higher solids loading likely is because of better packing of the finer uraninite settled solids within the interstitial pores of the larger metaschoepite crystals.

- The shear strengths of duplicate simulated KW containerized sludge, which contains a variety of sludge components, ranged from 500 to 700 Pa.

- Previous K Basin sludge shear-strength measurements establish the 1 to 8,200 Pa range provided in the Sludge Technical Databook (HNF-SD-SNF-TI-015, Volume 2 revision 14B). The shear strength is affected by sample history and generally increases with increasing undisturbed settling time. Within settling times ranging from several days to several weeks, shear strengths ranged from less than 100 Pa to about 3,000 Pa and had 240, 4,000, 1,000, 400, and 8,200 Pa shear strengths after 20 to 30 days settling while containing, respectively, 1.7, 5, 6, 17, and 60 dry basis wt. % uranium.

- Shear strengths measured in 2009 for samples from the KW containers SCS-CON-240, 250, and 260 that passed through 500-μm sieves and settled for several days to several weeks were about 300, 300, and 80 Pa, respectively (PNNL-19035 Section 5.6). The total uranium concentrations for the same respective materials were 4.91, 5.25, and 6.61 wt. % on a dry basis (PNNL-19035 Section 5.5.4). The shear strength for the settled <500-μm fraction from SCSCON-220 were ~90 Pa and ~500 Pa, but the measurements were of low reliability (PNNL-19035 Section 7.6).

  [Note: The shear strength was subsequently measured for three of the archived sludge core samples from SCS-CON-220 that had settled for ~66 days. The shear strength was 3800 Pa, 8400 Pa, and 3100 Pa for SCS-CON-220 sludge core samples A1, B3, and B4, respectively (PNNL Memorandum 5278-2011-M01). The dry-basis total uranium concentration was a maximum of 34.6 wt. % in the SCS-CON-220 sludge samples (PNNL-19035 Section 7.5.1)].

- *The better packing of the 50%/50% uraninite/metaschoepite mixtures to ~24 vol% volumetric solids fraction is typical of those observed for genuine sludges containing the several other key sludge constituents (e.g., ferrihydrite, gibbsite, sand). Simulated KW containerized sludge samples are relatively weak compared with the 50%/50% uraninite/metaschoepite mixtures. However, measurements of actual sludge show no clear trend relating shear strength to uranium concentration, but do indicate increasing shear strength with increased settling time. Shear strengths of genuine sludge can alter because of continued uraninite oxidation and mixing by remobilization and transfer.*

- Results from SCS-CON-220, 240, 250, and 260 containerized sludge sample characterization show that the uranium oxide in the sludge is about 50 to 70% U(IV),

such as uraninite, with the balance being U(VI), such as metaschoepite or other more mineralized U(VI) phases (PNNL-19035 Section 4.7 and Section 6.7).

Subsequent to PNNL having published these findings, PNNL completed characterization of the KW Engineered Container sludge in SCS-CON-210 (PNNL-20650) and Settler sludge in SCS-CON-230 (PNNL-20470). Shear strengths measured in 2010 for sludge samples from SCS-CON-210 (minus 500-μm fraction) and SCS-CON-230 minus 600-μm fraction) that had settled for several weeks were a maximum of 280 Pa and 810 Pa, respectively (PNNL-20650 Section 5.2 and PNNL-20470 Section 5.4).

The total uranium concentrations for the less than 500-μm fraction sieved SCS-CON-210 sludge samples were 16 to 17.2 wt. % on a dry basis (PNNL-20650 Table 5.20). The total uranium concentration was an average of 7.7 wt. % on a dry basis in the SCS-CON-210 sludge core subsamples (includes contribution in undissolved solids from acid digest of samples). The total uranium concentrations for the SCS-CON-230 sludge core subsamples were 34.9 to 61.1 wt. % on a dry basis (PNNL-20470 Table 4.10). The total uranium concentration was an average of 49.6 wt. % on a dry basis in the SCS-CON-230 core subsamples (includes contribution in undissolved solids from acid digest of samples). Results from SCS-CON-210 and SCS-CON-230 sludge sample characterization show that the uranium oxide in the sludge is about 86 to >99% U(IV) in SCS-CON-230 sludge samples (PNNL-20470 Section 4.10) and 80 to 86% U(IV) in SCS-CON-210 sludge samples (PNNL-20650 Section 5.7), such as uraninite, with the balance being U(VI), such as metaschoepite or other more mineralized U(VI) phases. It is possible that the uranium oxidation state ratios could be confounded by reduction of U(VI) due to the presence of Fe(II) in these sludge samples.

The above findings relating to sludge stored in Engineered Containers SCS-CON-220, 240, 250, and 260 are also applicable to sludge stored in Engineered Containers SCS-CON-210 and SCS-CON-230 based on comparison of these characterization results. The sludge stored in the six Engineered Containers SCS-CON-210, 220, 230, 240, 250, and 260 contain on average less than 50 wt. % total uranium on a dry basis, which is primarily uraninite. This sludge likely will be unable to produce continuous metaschoepite layers that inhibit further oxidation or which self-cement to form high strength agglomerates. Instead, the metaschoepite may act to coagulate non-uranium sludge solids and produce settled solids that are more tightly packed and have a lower settled-solids volume and a lower volume fraction of void water. The effect of decreased water-void volume may be to increase the settled-sludge strength. However, the long-range binding of sludge solids through metaschoepite recrystallization with itself will not be possible because of insufficient metaschoepite. Marked strength increases were not noticeable for the simulated sludge materials tested after ~100 days of reaction.

4.0 Shear Strength Results for Archived Sludge Samples

PNNL personnel have measured the shear strength of archived sludge samples that have been stored under hot cell conditions with minimal disturbance of the settled sludge within the sample container. Shear strength measurements for sludge samples obtained in 2009 and 2010 from all

six Engineered Containers and sludge samples that have been treated with the flocculant Clarifloc N3300-P are discussed in Section 4.1. Section 4.2 discusses shear strength measurements obtained from archived KE Basin sludge samples.

4.1 Shear Strength Results for Long-Term Monitoring of Sludge Samples

The STP has also initiated a long-term monitoring program to evaluate the potential for agglomerate formation in archived sludge samples stored in the hot-cells (nominally 30 ± 5°C) at PNNL (Test Instruction 52578-TI027). Sludge samples selected for long-term monitoring include samples obtained in 2009 and 2010 from all six Engineered Containers and sludge samples that have been treated with the flocculant Clarifloc N3300-P. The sludge sample characteristics and parameters that PNNL personnel are monitoring:

- Volume / settled density
- Shear strength
- Particle size distribution and particle density
- pH of headspace water
- Visual appearance / observations
- Storage temperature

To date sludge samples have been monitored over a period of approximately 5 years with samples being destructively examined at intervals after being placed into the long-term storage. The availability of sludge samples limits the duration of the long-term monitoring tests. Particle size distribution and particle density measurements are planned to be obtained only if agglomerates are observed in the archived sludge samples. Table 1 summarizes the shear strength measurements performed through February 2015 for archived sludge samples placed into the long-term monitoring program. For some samples, the shear strength was measured at multiple depths using different vanes tools. The highest shear strength value measured for each sample with the most accurate vane tool are reported in Table 1.

Sludge samples examined after 2 to ~53 months of long-term storage exhibit an increase in shear strength as a result of settling and compaction. Hard agglomerated sludge has not been observed to date in the archived sludge samples placed into the long-term monitoring program. The FLOC-1 sample exhibited the highest shear strength of ~84,000 Pa after 42 months of settling. Sludge sample FLOC-1 is a mixture of sludge from engineered container KW220 and KW250 that was treated with Clarifloc N-3300P flocculant. The STP does not plan to mix sludge from engineered container SCS-CON-220 and SCS-CON-250, therefore, the shear strength measurements for this sample are provided for information only and are not representative of sludge that will be loaded into an STSC. Excluding the FLOC-1 sample, sludge samples treated with Clarifloc N-3300-P flocculant and examined after approximately 2 to 34 months of long-term storage exhibit an increase in shear strength to a maximum of approximately 76,000 Pa for sample KW250 A4 Settling Study (Floc 3) after 33.8 months of settling. For archived sludge samples that were not treated with Clarifloc N-3300P flocculant, the highest measured shear strength was approximately 63,000 Pa for sample TI027-KW220B4 after 52.7 months of settling.

4.2 Shear Strength Results for Archived KE Basin Sludge Samples

PNNL personnel used a pocket penetrometer to measure the unconfined compressive strength for archived KE Basin sludge samples that had been maintained wet and settled for 30 to 146 months (PNNL-20977). PNNL personnel correlated the unconfined compressive strength measured for sludge simulants with shear strength measurements obtained using laboratory rheometers. The resulting shear strength values for the archived KE Basin sludge samples are provided in Table 2 (PNNL-20977, Table 3.3). The highest shear strength measured was 143 ± 59 kPa for the KC-4 P250 sludge sample that had settled for 146 months (12 years and 2 months). The KC-4 P250 sample is the greater than 250-μm sieved fraction of sludge obtained from the KE Basin floor between open fuel canisters with high damaged fuel.

The KE Basin sludge samples that were measured represent composites of distinct sludge types collected prior to consolidation of the KE Basin sludge into underwater Engineered Containers SCS-CON-240, -250, and -260 in the KW Basin. Consolidation of these KE Basin sludge types into engineered containers has resulted in the mixing of the KE Basin floor, pit, and some canister sludge. Thus the shear strength measurements for these KE Basin sludge samples may not be representative of sludge stored in Engineered Containers SCS-CON-240, -250, and -260.

Table 1. Summary of Shear Strength Measurements for Long Term Monitoring of Archived Sludge Samples						
Sample ID	**Engineered Container**	**Sludge Type**	**Rheometer Probe Immersion Depth, mm**	**Settling Time, months**	**Shear Strength, Pa**	**References**
Engineered Containers SCS-CON-210 Samples						
KW210-CC-A	KW210	Less than 600-µm sieved fraction of container composite sample (SCC)	6	2.5	281	4
KW210B1	KW210	Core B1 Archive-1	16	2.6	301	4, 5
KW210B1	KW210	Core B1 Archive-2	6	2.8	301	4, 5
KW210B1	KW210	Core B1 Archive-1	26	10	676	3, 4
KW210B1	KW210	Core B1 Archive-1	16	22.8	592	6
KW210B3	KW210	Core B3 Archive-1	6	2.5	416	4, 5
KW210B3	KW210	Core B3 Archive-2	6	2.8	315	4, 5
KW210B3	KW210	Core B3 Archive-1	12	9.9	456	3, 4
KW210B3-Archive-1	KW210	Core B3 Archive-1	30	33.8	12,570	7
Engineered Containers SCS-CON-220 Samples						
KW220A1	KW220	Core A1 subsample	16	2.2	3,785	1, 4
KW220A1	KW220	Core A1 subsample	16	7.7	7,605	2, 4
KW220A1	KW220	Core A1 subsample	6	33.8	3,544	6
KW220B3	KW220	Core B3 subsample	16	2.2	8,361	1, 4
KW220B3	KW220	Core B3 subsample	6	42	4,550 to 28,360	6
KW220B4	KW220	Core B4 subsample	16	2.2	3,060	1, 4
TI027-KW220B4	KW220	Core B4 subsample	18	52.7	63,040[(b)]	7
Engineered Containers SCS-CON-230 Samples						
TI025-B-Rh	KW230	Less than 600-µm sieved fraction of container composite sample (SCC)	12	0.5	661	4
TI025-B-S4	KW230	Less than 600-µm sieved fraction of container composite sample (SCC)	6	0.5	466	4
TI025-B-S5	KW230	Less than 600-µm sieved fraction of container composite sample (SCC)	6	0.5	362	4
TI025-B-Rh	KW230	Less than 600-µm sieved fraction of container composite sample (SCC)	16	2.9	1,087	2, 4
KW230 Comp Settling Study	KW230	Less than 600-µm sieved fraction of container composite sample (SCC)	~6	5.3	2,762[(a)]	3, 4
52578-TI027-KW230-5	KW230	Less than 600-µm sieved fraction of container composite sample (SCC)	6	6.9	9,606	3, 4
TI025-B-Rh	KW230	Less than 600-µm sieved fraction of container composite sample (SCC)	6	10	2,541	4, 5
TI025-B-Rh Repackaged to TI051-230-B4-2	KW230	Less than 600-µm sieved fraction of container composite sample (SCC)	6	16.6	1,761	6

Table 1. Summary of Shear Strength Measurements for Long Term Monitoring of Archived Sludge Samples						
Sample ID	**Engineered Container**	**Sludge Type**	**Rheometer Probe Immersion Depth, mm**	**Settling Time, months**	**Shear Strength, Pa**	**References**
52578-TI027-KW230-2	KW230	Less than 600-µm sieved fraction of container composite sample (SCC)	16	32.6	6,824	6
52578-TI027-KW230-4	KW230	Less than 600-µm sieved fraction of container composite sample (SCC)	36	45.4	37,530	7
Engineered Containers SCS-CON-240, -250, or -260 Samples						
TI012-SO	KW260	Less than 500-µm sieved fraction of container composite sample (SCC)	16	2.7	302	1, 4
TI011-SO	KW250	Less than 500-µm sieved fraction of container composite sample (SCC)	16	3.6	380	1, 4
TI010-SO	KW240	Less than 500-µm sieved fraction of container composite sample (SCC)	16	4.3	374	1, 4
TI010-SO	KW240	Less than 500-µm sieved fraction of container composite sample (SCC)	6	10.1	12,170	1, 4
TI051-240SCC-1	KW240	Less than 500-micron fraction of container composite sample (SCC)	18	27.6	26,310	7
TI011-SO	KW250	Less than 500-µm sieved fraction of container composite sample (SCC)	6	10.1	5,269	1, 4
TI012-SO	KW260	Less than 500-µm sieved fraction of container composite sample (SCC)	6	10.1	818	1, 4
KECOMP-1	KW240, -250, and -260	Combined sludge from KW240, KW250, and KW260 subsamples; less than 500-micron fraction	16	2.2	5,183[(a)]	1, 4
KECOMP-1	KW240, -250, and -260	Combined sludge from KW240, KW250, and KW260 subsamples; less than 500-micron fraction	6	18	8,031	4, 5
KECOMP-1	KW240, -250, and -260	Combined sludge from KW240, KW250, and KW260 subsamples; less than 500-micron fraction	6	22.8	7,716	6
KECOMP-2	KW240, -250, and -260	Combined sludge from KW240, KW250, and KW260 subsamples; less than 500-micron fraction	16	2.2	3,581[(a)]	1, 4
KECOMP-2	KW240, -250, and -260	Combined sludge from KW240, KW250, and KW260 subsamples	6	7.7	3,781	2, 4
KECOMP-2	KW240, -250, and -260	Combined sludge from KW240, KW250, and KW260 subsamples	6	33.8	9,423 to 18,760	6
KECOMP-3	KW240, -250, and -260	Combined sludge from KW240, KW250, and KW260 subsamples; less than 500-micron fraction	8	2.2	3,542[(a)]	1, 4

Table 1. Summary of Shear Strength Measurements for Long Term Monitoring of Archived Sludge Samples						
Sample ID	**Engineered Container**	**Sludge Type**	**Rheometer Probe Immersion Depth, mm**	**Settling Time, months**	**Shear Strength, Pa**	**References**
KECOMP-3	KW240, -250, and -260	Combined sludge from KW240, KW250, and KW260 subsamples; less than 500-micron fraction	6	42	15,360	6
KECOMP-4	KW240, -250, and -260	Combined sludge from KW240, KW250, and KW260 subsamples; less than 500-micron fraction	16	2.2	4,979[a]	1, 4
KECOMP-4	KW240, -250, and -260	Combined sludge from KW240, KW250, and KW260 subsamples; less than 500-micron fraction	24	52.7	52,000	7
KECOMP-5	KW240, -250, and -260	Combined sludge from KW240, KW250, and KW260 subsamples; less than 500-micron fraction	8	2.2	2,952[a]	1, 4
KECOMP-6	KW240, -250, and -260	Combined sludge from KW240, KW250, and KW260 subsamples; less than 500-micron fraction	16	2.2	4,341[a]	1, 4
Clarifloc N-3300P Treated Samples						
FLOC-1	KW250 / KW220	Mixture of Clarifloc N-3300P flocculant treated SCC sludge from KW250 core A4 subsample and KW220 core B4 subsample	16	2.1	2878[a]	1, 4
FLOC-1	KW250 / KW220	Mixture of Clarifloc N-3300P flocculant treated SCC sludge from KW250 core A4 subsample and KW220 core B4 subsample	~6	42	32,000 to 84,000[b]	6
KW250 A4 Settling Study (Floc 3)	KW250	Clarifloc N-3300P flocculant treated SCC sludge from KW250 core A4 subsample	6	2.8	686	4, 5
KW250 A4 Settling Study (Floc 3)	KW250	Clarifloc N-3300P flocculant treated SCC sludge from KW250 core A4 subsample	~12	6.5	1,390	3, 4
KW250 A4 Settling Study (Floc 3)	KW250	Clarifloc N-3300P flocculant treated SCC sludge from KW250 core A4 subsample	12	33.8	75,480[b]	7
KW220B4 Settling Study (Floc 3)	KW220	Clarifloc N-3300P flocculant treated core B4 subsample	6	2.8	1,797	4, 5
KW220B4 Settling Study (Floc 3)	KW220	Clarifloc N-3300P flocculant treated core B4 subsample	~12	7.3	1,514	3, 4
KW220B4 Settling Study (Floc 3)	KW220	Clarifloc N-3300P flocculant treated core B4 subsample	6	22.8	24,060	6

Table 1. Summary of Shear Strength Measurements for Long Term Monitoring of Archived Sludge Samples

Sample ID	Engineered Container	Sludge Type	Rheometer Probe Immersion Depth, mm	Settling Time, months	Shear Strength, Pa	References
KW210-CC-A Settling Study (Floc 3)	KW210	Clarifloc N-3300P flocculant treated SCC sludge from KW210 container composite subsample	20	2.8	3,191	4, 5
KW210-CC-A Settling Study (Floc 3)	KW210	Clarifloc N-3300P flocculant treated SCC sludge from KW210 container composite subsample	~15	5.2	195	3, 4
TI047-KW230-CC-Floc Study (Floc 3)	KW230	Clarifloc N-3300P flocculant treated KW230 container composite subsample	16	2.1	563	4, 5

[a] Data suspect. Vane immersed to desired depth but distance from the bottom of the jar is not consistent with the rheology measurement procedure due to insufficient settler solids or insufficient sample to fully immerse vane

[b] Rheometer head rose up during shear strength measurement

References:

1. PNNL Memorandum 5278-2011-M01
2. PNNL Memorandum 5278-2012-L03
3. PNNL Memorandum 52758-2012-L06
4. PNNL Memorandum 52578-2013-L05
5. PNNL Memorandum 52578-2013-L03
6. PNNL Memorandum 52578-2014-L07
7. PNNL Memorandum 52578-2015-L02

Table 2. Summary of Shear Strength Measurements for Archived KE Basin Sludge Samples			
Sample ID	**Sludge Type**	**Settling Time, months**	**Shear Strength, kPa**
KC-2/3 Composite	Sludge sample obtained from multiple fuel canisters with highly and moderately damaged fuel	30	12 ± 10
96-05	Sludge sample obtained from a single closed bottom fuel canister with high damaged fuel	52	11 ± 3
96-13 KE Composite A	Composite of sludge obtained from single fuel canisters with good to poor fuel	52	14 ± 8
KE NLOP #2	Composite sludge from top to bottom of KE North Load-Out Pit (NLOP)	30	16 ± 6
KC-4-2	Sludge sample obtained from KE Basin floor between open fuel canisters with high damaged fuel	52	21 ± 4
FE-Composite-1	Composite of sludge obtained from KE Basin Weasel Pit and South Load-Out Pit	42	12 ± 0
KE Flocculant Composite	Composite of sludge samples obtained from KE Basin floor and canister sludge that had been treated with Nalco Optimer 7194 Plus flocculant	30	13 ± 1
KC-4 Whole	Sludge sample obtained from KE Basin floor between open fuel canisters with high damaged fuel	30	19 ± 4
KE Pit (1995)	Composite of sludge obtained from KE Basin Weasel Pit	52	110 ± 27
KE NLOP #1	Composite of sludge from top to bottom of KE North Load-Out Pit (NLOP)	52	12 ± 0
KE NLOP #3	Composite of sludge from top to bottom of KE North Load-Out Pit (NLOP)	90	12 ± _
KC-4 P250	Greater than 250-µm sieved fraction of the KC-4 Whole sample.	146	143 ± 59

5.0 Conclusions

The sludge stored in the six Engineered Containers SCS-CON-210, -220, -230, -240, -250, and -260 contain on average less than 50 wt. % dry total uranium, which is primarily uraninite. This sludge likely will be unable to produce continuous metaschoepite layers that inhibit further oxidation or which self-cement to form high strength agglomerates. Instead, the metaschoepite may act to coagulate non-uranium sludge solids and produce settled solids that are more tightly packed and have a lower settled-solids volume and a lower volume fraction of void water. The effect of decreased water-void volume may be to increase the settled-sludge strength. However, the long-range binding of sludge solids through metaschoepite recrystallization with itself will not be possible because of insufficient metaschoepite.

The shear strength increases noticeably for the archived Engineered Containers SCS-CON-210, -220, -230, -240, -250, and -260 sludge samples placed into long-term monitoring. Sludge samples examined after 2 to 53 months of long-term storage exhibit an increase in shear strength from several hundred Pa to a maximum of approximately 86,000 Pa as a result of settling and compaction. Sludge samples treated with Clarifloc N-3300-P flocculant and examined after approximately 2 to 34 months of long-term storage exhibit an increase in shear strength to a maximum of approximately 74,000 Pa. Hard agglomerated sludge has not been observed to date in the archived sludge samples placed into the long-term monitoring program. The shear strength of the archived Engineered Containers SCS-CON-210, -220, -230, -240, -250, and -260 sludge samples is significantly lower than the maximum 170 kPa shear strength measured for agglomerated sludge samples from hydrothermal testing (PNNL-16496).

PNNL personnel also measured the shear strength of archived sludge samples obtained from the KE Basin floor, pits, and some canisters. These KE Basin sludge samples had been maintained wet and settled for 30 to 146 months under hot cell conditions. The highest shear strength measured was 143 ± 59 kPa for the KC-4 P250 sludge sample that had settled for 146 months (12 years and 2 months). The KC-4 P250 sample is the greater than 250-μm sieved fraction of sludge obtained from the KE Basin floor between open fuel canisters with high damaged fuel. Consolidation of the KE Basin sludge types into engineered containers has resulted in the mixing of the KE Basin floor, pit, and some canister sludge. Thus the shear strength measurements for these KE Basin sludge samples may not be representative of sludge stored in Engineered Containers SCS-CON-240, -250, and -260.

PNNL personnel have developed high shear strength, homogeneous simulants based on plaster of Paris™ water mixtures to mimic the properties of the agglomerated K Basin sludge samples (PNNL-20048). The highest shear strength of the homogeneous simulants is 170 kPa, which exceeds the shear strength measured for hydrothermal treated and archived sludge samples stored under hot cell conditions. The STP has subsequently used this high shear strength simulant to demonstrate retrieval of potentially agglomerated sludge from a STSC (PRC-STP-TR-00482). The shear strength measured for this simulant was >210 kPa (limit of the measuring tool) after loading into the STSC mockup used to demonstrate retrieval of potentially agglomerated sludge (PRC-STP-TR-00482 page 4).

6.0 References

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