PNNL-14730

Pacific Northwest National Laboratory

Operated by Battelle for the U.S. Department of Energy

KE Basin Sludge Flocculant Testing

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June 2004

Prepared for Fluor Hanford and the
the U.S. Department of Energy
under Contract DE-AC06-76RL01830

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Richland, Washington 99352

Summary and Conclusions

In the revised path forward and schedule for the K Basins Sludge Retrieval and Disposal Project, the sludge in K East (KE) Basin will be moved from the floor and pits and transferred to large, free-standing containers located in the pits (so as to isolate the sludge from the basin). When the sludge is pumped into the containers, it must settle fast enough and clarify sufficiently that the overflow water returned to the basin pool will not cloud the water or significantly increase the radiological dose rate to the operations staff as a result of increased suspended radioactive material. The approach being evaluated to enhance sludge settling and speed the rate of clarification is to add a flocculant to the sludge while it is being transferred to the containers. [Flocculation is the process of forming larger particles of a solid phase dispersed in solution by gathering together smaller particles.]

In February 2004, seven commercial flocculants were tested with a specific K Basin sludge simulant to identify those agents that demonstrated good performance over a broad range of slurry solids concentrations. From this testing, a cationic polymer flocculant, Nalco Optimer 7194 Plus (7194+), was shown to exhibit superior performance. Related prior testing with K Basin sludge and simulant in 1994/1996 had also identified this agent as promising. In March 2004, four series of jar tests were conducted with 7194+ and actual KE Basin sludge (prepared by combining selected archived KE sludge samples).

For the flocculant evaluations, the test procedures were similar for both the sludge simulant and the actual KE Basin sludge: 500-ml test slurries were prepared by adding measured quantities of simulant with water or KE Basin sludge with K Basin decant water into 3-in.-diameter, 600-ml vessels (beakers). For each test, two to six vessels were tested simultaneously. The slurries were mixed with a Phipps & Bird jar test apparatus (i.e., gang stirrer with paddle blade impellers made for this type testing) to break up particle agglomerates and obtain a homogeneous mixture. Neat flocculant (as supplied by the vendor) was diluted, with de-ionized water, to a 0.5 wt% working solution, based on the vendor recommendation. While the slurries were mixing at ~125 rpm, selected quantities (doses) of flocculant were added to each vessel. The slurries were mixed again at ~125 rpm for ~10 to 90 s, and slowly mixed (~45 rpm) for an additional 2 min. The mixing was then stopped, and the flocculation, settling, and clarification behavior of slurry in each vessel was monitored and recorded; for the actual sludge, the tests were recorded on videotape.

From the first set of tests, a challenging, representative simulant for the KE Basin sludge was developed, along with protocols, techniques, and equipment for testing with actual sludge in the hot cell. Furthermore, the flocculant dose ranges were established for the testing with actual sludge.

Actual sludge sample material was prepared for the flocculation testing by combining selected archived KE Basin sludge samples (floor, pit, and canister sludges). The resulting KE Basin Flocculation Composite sludge provided a good material for the testing. When quantities of the composite were mixed with sludge decant water to prepare dilute slurries, the solution remained cloudy for extended periods, and self-flocculation did not occur. Even after 30 min of settling, the supernatant did not clarify without flocculant addition.

Several key observations were noted during the testing with actual sludge:

- The results from testing with the actual sludge were generally consistent with the simulant testing results, validating the use of the simulant for flocculant screening.
- At optimal doses, excellent clarification was achieved with 7194+ within as little 30 s from the time mixing was stopped.
- Settling and clarification improved over a wide range of flocculant doses at each slurry concentration tested.
- At high levels of addition (60 mg/L and greater), the flocculant was difficult to distribute when it was rapidly injected above the top surface of the slurry. However, when a different technique was used in which the agent was slowly injected below the surface of the stirred slurry, a good distribution was achieved. This form of addition more closely replicates the process planned for the K Basin—continuous inline injection immediately upstream of a static mixer.
- After the flocculant addition technique was refined, adverse impacts from overdose were not observed until very high concentrations were tested (e.g., 120 mg/L).
- Some improvements in settling/clarification were observed even for most underdose conditions.
- Flocculant addition at 60 mg/L provided significant settling and clarification improvements across the range of slurry concentrations tested (0.23 wt% to 8.2 wt% solids).

As summarized in the table below, the results from these tests demonstrate that 7194+ greatly improves settling of K Basin sludge slurries and clarification of the supernatant.

Summary of Results from Flocculation Testing with KE Basin Sludge

Solids Concentration,[(a)] wt% dry solids	0.23 to 0.27	0.98 to 1.0	4.2	7.8 to 8.2
Concentration Range of 7194+ Tested, mg/L	0 to 60	15 to 60	60 and 120	30 to 150
Optimal[(b)] 7194+ Concentration, mg/L	15	45	60	90
Overdose[(c)] 7194+ Concentration, mg/L	> 60	> 60	~120	150

(a) Weight percent sludge (dry weight basis) in 500 ml of slurry.
(b) Optimal = minimum concentration of 7194+ resulting in rapid settling and thorough clarification of resulting supernatant.
(c) Overdose = concentration at which excess 7194+ remained suspended in solution, evidenced by persistent milky suspension and floating particle agglomerates.

Ultimately, the K Basin sludge will be recovered from the containers and treated and packaged for disposal to the Waste Isolation Pilot Plant (WIPP). One treatment option being considered is solidification of the sludge into a grout matrix. Therefore, related simulant testing was also conducted in March 2004 to determine if 7194+ will have an adverse effect on grout. This testing showed that the presence of 7194+ at 390 ppm in the grout matrix (i.e., resulting from tests with 3.7 wt% simulant slurry with144 mg/L of 7194+) had no perceptible effect on grout set-up or free water release.

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1.0 Introduction

Two water-filled concrete pools [K East (KE) and K West (KW) Basins] in the 100K Area of the Hanford Site contained over 2100 metric tons of N Reactor fuel elements stored in aluminum or stainless steel canisters. The fuel is currently being cleaned and removed from the K Basins. During the time the fuel has been stored (mid 1970s to present), approximately 52 m^3 of heterogeneous solid material (sludge) has accumulated in the canisters, as well as on the floor and in the associated pits.

This sludge consists of various proportions of fuel particulate (oxidized and metallic), canister corrosion products (i.e., various iron and aluminum oxy-hydrates), sand filter backwash, windblown material, and miscellaneous constituents such as ion exchange material (both organic and inorganic) and paint chips (Makenas et al. 1996-99). By definition, material less than 0.25-in. in any two dimensions is considered "sludge." Greater than 25% of the sludge volume is made up of particles smaller than 10 μm (Schmidt 2004).

Under the current sludge management plan, the KE sludge will be moved from the floor and pits and transferred to large, free-standing containers located in the pits (so as to isolate the sludge from the basin). When the sludge is pumped into the containers, it must settle fast enough and clarify sufficiently that the overflow water returned to the basin pool will not cloud the water or significantly increase the radiological dose rate to the operations staff as a result of increased suspended radioactive material. The approach being evaluated to enhance sludge settling and speed the rate of clarification is to add a flocculant to the sludge while it is being transferred to the containers.

Flocculants were previously evaluated for K Basin sludge applications. In 1994, tests were performed on KE Basin sludge slurry simulant (1.5 wt% Class F Flyash in water)[a] to evaluate three flocculants: Nalco Optimer 7128, Optimer 7194 Plus (7194+), and Optimer 7196 Plus (7196+). Of the three flocculants, 7194+ was found to be the most effective agent. The optimal 7194+ dose was ~20 mg/L, and overdose conditions were observed at 60 mg/L and greater.

Based on the promising results of the 1994 testing and the potential applications in the K Basins, a study was conducted to examine the compatibility of flocculants (7194+ and 7196+) with the K Basins Sludge Retrieval and Disposal Project operations (Graves 1995). Graves (1995) provides a general overview of flocculants and the chemistry and physical properties of 7194+ and 7196+, and concludes that the flocculants are compatible with operations, equipment, and materials used in the K Basins.

Further testing was conducted in 1996[b] to determine if flocculant addition could reduce the alpha content in KE Basin water. This testing was conducted with particulate-containing water samples collected from KE Basin. In this testing, the addition of 7194+ resulted in a significant reduction of turbidity, but only minimal reduction in total alpha content. With the KE Basin water tested, it was found that filtration appeared to have a much greater effect on the alpha content reduction.

(a) Internal Memo 8E110-PCD95-037 to SA Brisbin, May 3, 1995. "Informal Test Plan – Evaluation of Polymer Flocculants for Particle Removal from 105-KE Basin Water," Westinghouse Hanford Company, Richland, WA.

(b) Internal Memo 76754-PCS96-059 to SA Brisbin, June 13, 1996. "Results from Flocculant and Filtration Testing on 105-KE Basin Water," Westinghouse Hanford Company, Richland, WA.

In February 2004, seven commercial flocculants, including those evaluated in 1994, were tested with a specific K Basin simulant to identify those agents that demonstrated good performance over a broad range of solids concentrations. From this testing, the 7194+ was shown to exhibit superior performance. In March 2004, four series of jar tests were conducted, in which 7194+ was added to actual KE Basin sludge (prepared by combining archived KE sludge samples).

In this report, Section 2.0 describes the method and test materials used for the 2004 flocculation testing. Section 3.0 summarizes the tests with simulant and describes the results from the tests with KE Basin sludge. Appendix A further describes the flocculation testing in 2004 with the simulant and also includes the 1994/1996 test results. Appendix B provides the results of related testing with simulant, also conducted in 2004, to determine the effects of flocculant on grout set-up and free water release. [Note: the simulant discussed in Appendix B contains 5 wt% FeOOH, while the simulant discussed in Appendix A contains 2 wt% $Fe(OH)_3$.]

2.0 Methods and Materials

This section discusses the materials, protocol, and equipment used for testing with the simulant and with the actual sludge ("Flocculation Composite").

2.1 Test Equipment

For the testing with simulant, a Phipps & Bird Stirrer Model 7790-400 (gang stirrer with paddle blade impellers) was configured to stir six 600-ml vessels (beakers) simultaneously. The Phipps & Bird stirrer includes an integrated controller with digital readout of the mixing speed.

The testing with the actual sludge was conducted in the High Level Radiochemistry Facility (HLRF) located in PNNL's Radiochemical Processing Laboratory (325 Building). A second Phipps & Bird Stirrer Model 7790-400 was modified to accommodate size limitations and to facilitate remote operations. Figure 2.1 shows the modified stirrer, which was configured to stir four vessels simultaneously.

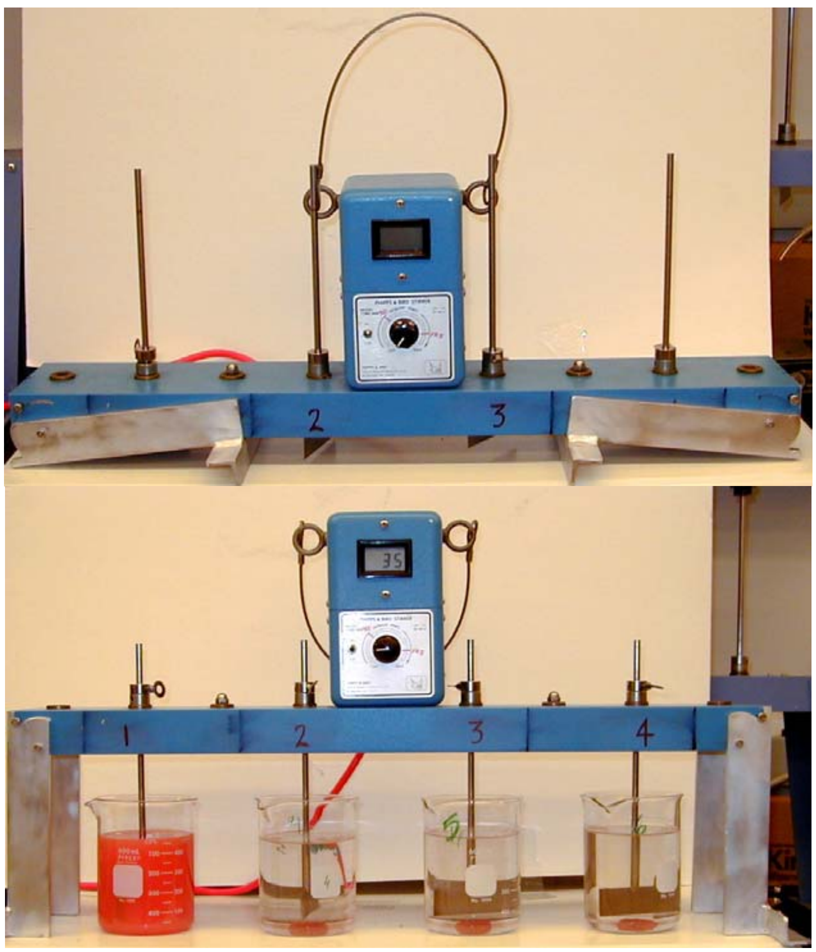

Figure 2.1. Phipps & Bird Stirrer Model 7790-400 (Gang Stirrer), Modified for Remote Operation in Hot Cell

2.2 Flocculants

Seven flocculants, obtained from Nalco Chemical Company, were evaluated: Optimer 7194 Plus, Nalcolyte 8105, Optimer 7196 Plus, 71301, Cat-Floc 8108 Plus, 71307, and NalClear 7763. These flocculants were selected by Fluor Federal Services and provided to PNNL for the testing. Based on vendor recommendation, the neat flocculants were diluted with de-ionized water to prepare 0.5 wt% working solutions. Aliquots of working solution were added to the test slurries in the flocculation testing. Based on vendor recommendation, fresh working solution was prepared daily for the testing with the actual sludge. The neat flocculants had a density close to 1 g/cm^3 (e.g., density of 7194+ = 1.06 g/cm^3); therefore, the density of the working solutions (99.5 wt% de-ionized water) was also approximately 1.0 g/cm^3.

2.3 Flocculation Test Protocol

For all of the testing, 500-ml slurries were prepared by adding measured quantities of simulant with water or sludge with K Basin decant water into 600-ml vessels. For each test, two to six vessels were tested simultaneously. Before flocculant addition, the slurries were mixed at ~125 rpm for a minimum of 5 min with the Phipps & Bird stirrer to break up particle agglomerates and obtain a homogeneous mixture. While the slurries were mixing at ~125 rpm, aliquots (doses) of flocculant were added to each vessel using pipettes or syringes. For most of the testing, the flocculant was quickly added above the slurry-air interface. This addition technique resulted in poor dispersion when higher doses were added. As a result, for the final series of testing, flocculant was slowly injected below the slurry surface while mixing at ~125 rpm.

Following flocculant addition, the slurries were mixed again at ~125 rpm for ~10 to 90 s, and then slowly mixed (~45 rpm) for an additional 2 min. The mixing was stopped, and the flocculation, settling, and clarification behavior of slurry in each vessel was monitored and recorded.

The testing with the sludge was conducted in accordance with the approved test instruction: "KE Basin Sludge Flocculation Testing," TI 46498-TI-02, March 1, 2004, and the Sampling and Analysis Plan (Baker et al. 2000). All flocculation tests with actual sludge were videotaped.

2.4 Simulant

The simulant used for most of the testing consisted of a mixture of the K Basin Settling Simulant (Schmidt and Elmore 2002) and $Fe(OH)_3$ (provided as a 13 wt% slurry from NOAH Technologies Corp.). The simulant is described in more detail in Appendix A.

2.5 KE Basin Sludge Composite for Flocculation Testing

The Flocculation Composite was prepared by combining archived KE sludge samples in accordance with the approved test instruction "Preparation of K Basin Sludge Composite for Flocculation Testing," TI 46498-TI-01, February 17, 2004). The sample material was originally collected from the KE Basin floor, pits, or fuel canisters in two sampling campaigns, consolidated sampling and single pull sampling, in FY 1999. The consolidated sampling campaign employed a technique for collecting large quantities of sludge from several locations to form "consolidated samples." In the single pull campaign, isolated cores of sludge were suctioned into bottles. Detailed descriptions of the sampling equipment and the sampling campaigns are given in Pitner (1999). The samples used for the Flocculation Composite are identified in

Table 2.1. Also listed is the individual sample history, including age, heating, and dehydration/reconstitution—factors that could impact particle agglomeration and settling behavior.

Table 2.1. Sludge Samples Used to Prepare the Flocculation Composite

Sludge Sample	Sample Description	Quantity (Settled Sludge) Used for Flocculation Composite		Sample History		
		Mass, g	Wt%	Year Collected	Heated	Dried Out
KE Basin Floor Sludge Samples						
KC-4 M250	KC-4, minus 250-μm fraction	290.1	50.6	1999	No	No
KC-5, whole	Floor sludge, away from canisters	169.4	29.6	1999	No	No
FE-5, whole	Weasel Pit	111.4	19.4	1999	No	No
KE Basin Canister Sludge Samples						
KC Can Comp	Canister sludge composite	~2	0.35	1999	No	Yes
Flocculation Composite		572.9	100	--	--	--

The Flocculation Composite was made up of two consolidated sludge samples [KC-4, floor sludge collected from between slotted fuel canisters containing highly damaged fuel (combined material from three sampling locations)] and KC-5, floor sludge collected away from fuel canisters and away from areas known to contain high concentrations of organic ion exchange resin (combined material from three sampling locations); one single pull sample [Weasel Pit sludge (FE-5), which was prepared by combining two core samples]; and KC Canister Composite (KC Can Comp), prepared from combined canister sludge samples (also from the consolidated sampling campaign) as described in Silvers et al. (2000). Because only a very small quantity of the KC Can Comp was used in the Flocculation Composite, this material is not discussed further in this report.

An existing size-fractionated sludge subsample of KC-4 was used for the Flocculation Composite. For the fractionation, portions of KC-4 were wet-sieved through a Tyler 60-mesh screen (250-μm openings) to separate particles greater than, or "plus," 250 μm (P250) from particles less than, or "minus," 250 μm (M250). Table 2.2 shows how the samples were distributed based on particle size. Most of the material in the KC-4 sample is composed of particles less than 250 μm. On a wet basis, the majority of the particles in KC-5 are also less than 250 μm; however, on a dry basis, the larger particles contribute most to the sample mass.

Available chemical composition data for key species in the settled sludge samples are shown in Table 2.3. Separate chemical analyses were not performed on the P250 and M250 fractions of the KC-4 sample. The samples contained between 2 and 6 wt% (settled sludge basis) total uranium. The Weasel Pit sample (FE-5) contained significantly more iron than the other samples. The KC-5 floor sludge sample contained more aluminum than the other samples. Based on the sample collection locations, the silica values reported in Table 2.3 are probably significantly less than the true values.

Table 2.2. Particle Size Distribution of Sludge Samples

Sludge Sample	Particle Distribution; Wet Basis, wt%		Particle Distribution; Dry Basis, wt%	
	P250, 250 to 6350 μm	M250, <250 μm	P250, 250 to 6350 μm	M250, <250 μm
KC-4[a, b]	10	90	16	84
KC-5[a]	36	64	64	36
FE-5[c]	28	72	30	70

(a) Data from Bredt et al. (1999).
(b) Only the M250 fraction of KC-4 was included in the Flocculation Composite.
(c) Data from Bredt et al. (2000).

Table 2.3. Chemical Compositions of Sludge Materials (Wet Basis)

Analyte, wt%	**KC-4[a]**	**KC-5[b]**	**FE-5[c]**
Al	2.20	5.43	1.75
Ca	0.333	0.171	0.79
Fe	7.80	5.71	20.1
Mg	0.106	0.063	0.096
Na	0.116	0.133	NM
Si	1.58	1.94	0.217
U, ICP	5.74	2.30	4.18
U, phos.	5.37	2.26	3.49
Analyte, μCi/g			
^{60}Co	0.349	0.390	0.574
^{137}Cs	539	468	112
^{154}Eu	0.835	0.394	0.646
^{241}Am	9.42	4.65	6.85
^{238}Pu	1.58	0.706	1.35
$^{239,240}Pu$	12.6	4.65	8.58

NM – not measured or no valid data.
(a) Data from Elmore et al. (2000); values displayed are the average of KC-4 and KC-4 dup.
(b) Data from Elmore et al. (2000).
(c) Data from R. B. Baker and T. L. Welsh, May 10, 2001, Letter Report, 01-SNF/RBB-004, "Summary of Initial Laboratory Data From Consolidated and Single Pull Core Sludge Sampling Campaigns," to K. L. Pearce, Fluor Hanford, Richland, WA.

Settled density and water fraction data are important parameters that were used to determine the quantity of sludge used in each series of testing with flocculant. Table 2.4 presents the settled density, wt% water, and void fraction (calculated from density and wt% water) measurements for the Flocculation Composite. These parameters were measured before the tests were conducted. After material was removed in the first two series of tests, the wt% water in the settled sludge was measured again. Table 2.4 also provides previous data on settled density and water fraction [based on measurements performed in 2001 and 2002 (Poloski et al. 2002)] for the sludge samples used in the Flocculation Composite.

Table 2.4. Settled Sludge Density, Wt% Water, and Void Fraction

Sludge Sample	Settled Sludge Density, g/cm^3	Wt% Water	Void Fraction
Flocculation Composite[(a)] (Tests 1 and 2)	1.25	60	0.76
Flocculation Composite[(b)] (Tests 3 and 4)	NM	67	NM
Data on Subsamples from 2001 and 2002[(c)]			
KC-4 M250	1.53	68	0.82
KC-5	1.28	65	0.84
FE-5	1.43 to 1.5	44	0.65

NM = not measured
(a) Measurements performed on Flocculation Composite, before Flocculant Tests 1 and 2.
(b) Measurement performed on remaining Flocculation Composite after conducting Tests 1 and 2.
(c) Poloski et al. (2002).

3.0 Test Results

This section discusses testing with actual K Basin sludge. The testing with simulant is briefly summarized here and further detailed in Appendix A.

3.1 Flocculant Testing with Simulant

The tests with sludge simulant were conducted to identify the most promising flocculant to use in the testing with actual sludge and to examine the relationship between simulant solids concentration and flocculant dose. The effect of pH on flocculant performance was also examined. Additional testing was performed to evaluate the settling rate of the simulant, with and without flocculant addition, and several mixing techniques for dispersing the flocculant were investigated.

After several screening tests, three flocculants, 7194+, 7196+, and 71307, were identified as superior performers, and Nalcolyte 8105, Cat-Floc 8108+, NalClear 7763, and 71301 were eliminated from further testing. Side-by-side comparisons of 7194+, 7196+, and 71307 were conducted to examine their relative performance as a function of dose, solids concentration, and pH. Optimer 7194+ (one of the two best performers from the 1994 testing) exhibited good performance over the broadest range of conditions. Optimal doses for 7194+ were 5 mg/L, 5 mg/L, and 20 mg/L at slurry concentrations of 0.25 wt%, 1 wt%, and 10 wt%, respectively.

Most of the tests with simulant were conducted without pH adjustment. Without adjustment, the pH of the 1 wt% and 10 wt% simulant slurries was about 9.8 and 10.4, respectively. In a test conducted with 1 wt% simulant slurry, the pH was adjusted to about 7 in four of the six beakers. At a pH of 7 (i.e., approximate pH of the K Basin pool water), better performance was observed with respect to the clarity of the resulting supernatant. The improved performance of 7194+ at neutral pH is consistent with the vendor's experience.

Settling rate testing was performed with 1 wt% simulant slurry in a 2-L graduated cylinder. Without flocculant addition, the settling rate with ~1550 ml of slurry was about 15 ml per minute (as measured by monitoring the volume of settled slurry with time). With flocculant addition (5 mg/L) followed by rapid nitrogen sparging for 30 s, the settling rate was ~64 ml/min. A lower settling rate (21 ml/min) was measured when flocculant addition was followed by moderate nitrogen sparging. When a mechanical mixer was used, with either a turbo-prop or a paddle blade impeller, rapid settling rates were observed (> 500 ml/min, settling rates were too fast for accurate measurement). Flocculated slurry would rapidly resettle after being resuspended by aggressive mechanical mixing.

In this testing, 7194+ was the most effective flocculant. The optimal flocculant dose at low solids slurry concentrations (0.25 and 1 wt%) was 5 mg/L. At 10 wt% solids, the optimal dose was 10 mg/L. In the pH adjustment testing, the flocculants performed better when the pH was adjusted to 7. From the mixing/settling tests, it was concluded that the flocculation testing with actual sludge should be performed with mechanical mixing rather than gas sparging. It was also found that flocculated particles generally remained flocculated even after being mobilized and resuspended.

3.2 Flocculant Tests with KE Basin Composite Sludge

Four series of tests were conducted with the Flocculation Composite. The results from testing with the actual sludge were generally consistent with the simulant testing results, validating the use of the simulant for flocculant screening. This section describes the results and conclusions from each testing series.

3.2.1 Series 1 Flocculant Tests

Series 1 tests were conducted on March 2, 2004, at a target solids concentration of ~0.25 wt% (ranged from 0.23 to 0.27 wt% solids) in 500 ml of KE Basin water (KE North Loadout Pit Decant). The target and actual test conditions, and test results, are summarized in Table 3.1. Before flocculant was added, the four test slurries (Vessels 1-4) were mixed at ~125 rpm for 5 min with a modified Phipps & Bird stirrer, and settling behavior was observed (Figure 3.1). All samples exhibited similar settling behavior: a significant fraction of solids rapidly settled, and the supernatant remained very cloudy for over 20 min and showed poor clarification without any added flocculant.

Table 3.1. Series 1 Flocculation Test Matrix and Results

Parameters	Position Number/Beaker No.				
	1[(a)]	2[(a)]	3[(a)]	4[(a)]	1B[(b)]
Target Wt% Solids	0.25	0.25	0.25	0.25	0.25
Target Settled Sludge Mass, g	3.1	3.1	3.1	3.1	3.1
Target 7194+ Concentration, mg/L	0	5	10	15	30
Target 7194+ Working Soln. Vol, ml	0	0.5	1.0	1.5	3.0
Actual Wt% Solids	0.23	0.27	0.25	0.24	0.23
Actual 7194+ Working Soln. Vol, ml	0	0.5	1.0	1.5	3.0
pH before 7194+ addition	7.5	--	--	--	7.5
pH after 7194+ addition	NA	7.6	7.6	7.6	7.8
Flocculation Results	Control; very cloudy	Some improvement	Slow; reasonable clarity	**Optimum**; excellent; high clarity	Excellent; high clarity

(a) Test 1A, with Vessel 1 as a control.
(b) In the second part of the test, Test 1B, flocculant was added to Vessel 1.

For Test 1A, the 7194+ flocculant doses in mg/L (neat agent basis) were: Vessel 1 = 0, Vessel 2 = 5, Vessel 3 = 10, and Vessel 4 = 15. Flocculant was added with rapid stirring (~125 rpm) for approximately 25 s followed by 2 min of slow mixing (~40 rpm). During the slow mixing, marbling (rapid and distinct onset of sludge floc formation with zones of clarified supernatant clearly visible) was noted in Vessel 4 and, to a lesser extent, in Vessel 3. The supernatant in Vessel 4 was essentially completely clarified during the slow mixing. One minute after the slow mixing was stopped, no trace or residual cloudiness was observed in Vessel 4 (Figure 3.2). Most of the sludge particulate in Vessel 3 settled quickly (within 1 min); however, the resulting supernatant showed a slight cloudiness that persisted for more than 10 min. Even after 30 min of settling, the supernatant in Vessel 3 had not reached the high level of clarity obtained in Vessel 4. Vessel 2 only showed moderate flocculation and improvement in clarification over the control Vessel 1; i.e., after 10 min of settling, the mixing paddle was clearly visible at the bottom of Vessel 2, but still obscured in Vessel 1 (control).

In the simulant flocculation tests, flocculant doses above the optimum were found to slow clarification at low solids loadings. Test 1B was conducted by adding 30 mg/L of 7194+ to examine settling and clarification behavior of actual sludge slurry in the presence of excess flocculant. The slurry in Vessel 1 flocculated rapidly and completely clarified during the slow mixing, similar to the results obtained in Test 1A with the 15 mg/L dose in Vessel 4. Figure 3.3 shows the flocculated sludge in Vessel 1 after 4 min of settling. The higher dose, 30 mg/L, provided excellent clarification, comparable to 15 mg/L. No adverse effects from an overdose of flocculant were observed. During the remixing, the flocculated sludge agglomerates in Vessels 2 through 4 broke up to some extent. However, within about a minute, the supernatant in Vessel 4 was again clear.

Figure 3.1. Series 1, 0.25 wt% KE Sludge Composite, While Mixing, Before Flocculant Addition

Figure 3.2. Series 1A, 0.25 wt%, 7194+ Dose: 15 mg/L, After Settling for 84 s

Figure 3.3. Series 1B, 0.25 wt%, 7194+ Dose: 30 mg/L, After Settling for 4 min

Series 1 Conclusions: The KE Basin composite sludge provided a good challenge solution for flocculation testing. The solution remained cloudy for extended periods of time, and self-flocculation did not occur at the low solids loading. Even after 30 min of settling, clarification of the supernatant was not achieved without flocculant addition.

Low flocculant doses, 5 to 10 mg/L, were not effective for complete clarification of the slurries. However, dose ranges from 15 to 30 mg/L provided rapid and complete clarification of the slurry. Sludge flocculated at 15 mg/L was remixed and observed. Remixing had only a minor effect on the sludge flocs, and the solution reclarified rapidly.

3.2.2 Series 2 Flocculant Tests

The Series 2 tests were conducted on March 4, 2004, at a target solids concentration of ~1.0 wt% (12.5 to 12.6 g of settled sludge composite) in 500 ml of KE Basin water (KE North Loadout Pit Decant). The target and actual test conditions, and test results, for the Series 2 testing are summarized in Table 3.2. A procedure similar to that used in the Series 1 tests was followed; four samples were prepared, mixed at ~125 rpm with a modified Phipps & Bird stirrer (four-jar test stand) without added flocculant, and settling behavior observed. All samples exhibited similar settling behavior; a significant fraction of solids settled rapidly, and the supernatant remained somewhat cloudy for over 50 min. Without flocculant addition, the Series 2 samples clarified faster and to a greater extent than those in the Series 1 tests (conducted at a lower solids loading, 0.25 wt%).

The Series 2 tests were conducted at the following 7194+ doses in mg/L (neat agent basis):
Vessel 1 = 30, Vessel 2 = 15, Vessel 3 = 45, and Vessel 4 = 60. Vessels 1 and 2 were tested simultaneously (Test 2A). In Test 2A, Vessel 1 (30 mg/L) showed clear marbling during mixing, but this was not observed for Vessel 2 (15 mg/L). With continued mixing, some of the marbling in Vessel 1 was no longer visible (i.e., the slurry may have been over-mixed). When the mixing was stopped, Vessel 1 clarified quite rapidly (complete clarification achieved in 1 to 2 min). Figure 3.4 shows Vessels 1 through 3 after about 3 min of settling. Vessel 2 remained slightly cloudy even after 30 min of settling.

Table 3.2. Series 2 Flocculation Test Matrix and Results

Parameters	Position Number/Beaker No.			
	1[(a)]	**2**[(a)]	**3**[(b)]	**4**[(c)]
Target Wt% Solids	1.0	1.0	1.0	1.0
Target Settled Sludge Mass, g	12.6	12.6	12.6	12.6
Target 7194+ Concentration, mg/L	30	15	45	60
Target 7194+ Working Soln. Vol, ml	3.0	1.5	4.5	6.0
Actual Wt% Solids	0.99	1.0	0.98	0.98
Actual 7194+ Working Soln. Vol, ml	3.0	1.5	4.5	6.0
pH before 7194+ addition	7.8	7.7	7.7	7.7
pH after 7194+ addition	8.1	8.0	7.9	7.9
Flocculation Results	Excellent; high clarity	Improvement, but residual cloudiness	**Optimum**; excellent;[(d)] high clarity	Excellent;[(d)] high clarity

(a) Series 2 Test 2A.
(b) Series 2 Test 2B.
(c) Series 2 Test 2C.
(d) Additional mixing was required to achieve good results due to initial flocculant distribution problems.

Vessel 3 was treated in the next phase of the Series 2 testing with 45 mg/L of flocculant (Test 2B). No marbling was noted during mixing. After the mixing was stopped, the solution remained cloudy and somewhat milky. Upon close observation of the top surface of the solution, two “globs” of flocculant were seen. From this observation, it was apparent that the rapid mixing phase was not adequate to disperse the flocculant throughout the test solution. Therefore, the rapid-slow mix procedure was repeated a second time, with the rapid mix continued for approximately 30 s. In the earlier testing, the rapid mix was performed for only 20 to 25 s. During this remixing, marbling was noted in Vessel 3. The solution was nearly completely clarified during the slow mix step. After the mixer was turned off, the solids settled immediately, leaving a clear solution (Figure 3.5). The solution in Vessel 1 reclarified in about 2 min, with flocculation performance only slightly degraded from that observed in Test 2A.

Vessel 4 was treated in the final phase of the Series 2 testing with 60 mg/L of flocculant (Test 2C). The rapid mix was continued for approximately 40 s, followed by a slow mix for 70 s. Marbling was noted during mixing. After the mixing was stopped, the solids settled rapidly, but the solution remained milky/cloudy (Figure 3.6). Upon close observation with the camera to the top surface of the beaker, the milky white color appeared to indicate an excess flocculant material in the clear (solids-free) solution (i.e., overdose). As a result, the rapid-slow mix procedure was repeated a second time (30-s rapid mix) as was done for Vessel 3. Marbling was noted during this remixing. The solution clarified during the slow mix step. Once the mixer was turned off, the solution was clear, with no milky color. The supernatant in Vessels 1 and 3 also achieved a high degree of clarification after the final mixing sequence (i.e., the sludge flocs were not destroyed after repeated mixings.)

Figure 3.4. Test 2A, Vessel 1, 15 mg/L; Vessel 2, 30 mg/L; Vessel 3, 0 mg/L, After Settling for 2 min 47 s

Figure 3.5. Test 2B, Vessel 1, 15 mg/L; Vessel 2, 30 mg/L; Vessel 3, 45 mg/L; Vessel 4, 0 mg/L, After Settling for 6 min 40 s

Figure 3.6. Test 2C, 60 mg/L, 1 min Settling
Note milky color to supernatant.

Series 2 Conclusions: A dose range from 30 to 60 mg/L provided complete clarification of the 1 wt% solution, after achieving complete mixing and dispersion of the flocculant. The higher doses tested, 45 and 60 mg/L, were found to require significant mixing to thoroughly distribute the agent. It is believed that 60 mg/L was close to the maximum dose that could be used for a 1 wt% solids slurry. Incomplete clarification was achieved with 15 mg/L of 7194+ at 1 wt% solids loading. At 1 wt% solids, and 30 to 60 mg/L 7194+, a high level of flocculation efficacy was retained even after multiple mixing cycles.

3.2.3 Series 3 Flocculant Tests

Series 3 tests were conducted on March 11, 2004, with a solids content of about 8 wt% (~125 g of wet sludge composite plus KE Basin water added to bring test solution volume to ~500 ml). Because of the large amount of sludge required for these tests, only two samples were tested. In parallel with Series 3, the weight percent solids of the Flocculation Composite was remeasured by drying two sample aliquots. The target and actual test conditions, and test results, for the Series 3 testing are summarized in Table 3.3.

Before flocculant addition, Vessels 1 and 2 were mixed for 5 min and then allowed to settle. Unlike the Series 1 and 2 testing, with the high solids concentration, hindered settling was observed almost immediately. After 15 min of settling, about half the solution in each vessel was clarified. After 30 min, reasonable clarification was achieved for 330 ml in Vessel 1 and 300 ml in Vessel 2. After 47 min of settling, the settled sludge had consolidated to 150 ml in Vessel 1 and 175 ml in Vessel 2 (Figure 3.7). For Series 3, Test 1A, Vessels 1 and 2 were tested simultaneously at 7194+ doses of 30 mg/L (Vessel 1) and 60 mg/L (Vessel 2). After flocculant addition, the solution was rapidly mixed for 45 s, and then mixed slowly for 2 min. Marbling was not observed in either vessel during or following mixing, and neither sample clarified to the extent noted in earlier tests. After the mixer was shut off, hindered settling was observed at a rate greater than that observed before flocculant addition. After about 5 min of settling, about half the solution in each vessel was clarified; however, cloudiness/milkiness persisted in the clarified supernatant, indicating poor flocculant dispersion. Vessels 1 and 2 were remixed (60-s high

Table 3.3. Series 3 Flocculation Test Matrix and Results

Parameters	Position Number/Beaker No.			
	1[(a)]	**2[(a)]**	**1[(b)]**	**2[(c)]**
Target Wt% Solids	10	10	10	10
Target Settled Sludge Mass, g	125	125	125	125
Target 7194+ Concentration, mg/L	30	60	30+60	60+90
Target 7194+ Working Soln. Vol, ml	3.0	6.0	9.0	15.0
Actual Wt% Solids	7.8	8.2	7.8	8.2
Actual 7194+ Working Soln. Vol, ml	3.0	6.0	9.0	15.0
pH before 7194+ addition	7.6	7.6	7.6	7.6
pH after 7194+ addition	--	--	7.5	7.7
Flocculation Results	Some improvement; slow settling	Moderate improvement; residual cloudiness	**Best;** [(a)] reasonable clarity achieved	Good; overdose,[(a)] residual milkiness

(a) Test 3A.
(b) Additional flocculating agent was added to Vessel 1 for this test (Test 3B).
(c) Additional flocculating agent was added to Vessel 2 for this test (Test 3C).

Figure 3.7. Test 3, Vessels 1 and 2 with No Flocculant Added, After 47 min of Settling

Figure 3.8. Test 3A, Vessel 1, 30 mg/L; Vessel 2, 60 mg/L, 2 min of Settling, After Remixing. Note polymer hang-up on stir shaft of Vessel 2.

speed/60-s low speed) to ensure better flocculant dispersion. The clarity of the supernatant improved in Vessel 2, but little change was observed in Vessel 1 after remixing. Figure 3.8 shows Vessels 1 and 2 at 2 min of settling after the remixing. Polymer hang-up on the stir shaft of Vessel 2 can also be seen. After 9 min of settling, about half the solution in each vessel was clarified (a marginal improvement in the settling rate compared to the settling test with no flocculant addition).

An additional 60 mg/L (total of 90 mg/L = 60 +30) of flocculant was added to Vessel 1 for Series 3 Test 3B. Some evidence of marbling was observed, but it was not significant. After 30 s of settling, approximately 150 ml of solution clarified, and within 2 min, about half the solution was clarified. Figure 3.9 shows Vessel 1 after 4 min of settling. Some polymer hang-up on the stir shaft occurred, and some floating agglomerates were also visible in Vessel 1 (Figure 3.10).

Vessel 2 was then treated with an additional 90 mg/L of flocculant (150 mg/L total) in Test 3C. After flocculant addition, a 90-s high-speed mix was followed by a 90-s low-speed mix. Within 3 min, half the solution was clarified (Figure 3.11). Some residual cloudiness/milkiness persisted in the clarified supernatant. Also, some solids were observed stuck to the mixer shaft, and agglomerates were observed floating on the top of the liquid surface (Figure 3.11).

Series 3 Conclusions: For the 8 wt% solids samples, 90 mg/L appeared to provide the best clarification; however, the solution did not clarify as quickly or as thoroughly relative to the Series 1 and 2 tests. Incomplete sludge flocculation and clarification was noted for all dose levels, because good flocculant distribution was not achieved. Some solids were clumped on the rod of the stir paddle, and some floating agglomerates remained at the interface of slurry-air at the wall.

Figure 3.9. Test 3B, Vessel 1, 90 mg/L (30 + 60); Vessel 2, 60 mg/L, After 4 min of Settling.
Supernatant in Vessel 1 is much clearer than Vessel 2.

Figure 3.10. Test 3B, Vessel 1, 90 mg/L (30 + 60), After 10 min of Settling.
Note polymer hang-up on stir shaft of Vessel 1, and floating sludge floc agglomerates.

Figure 3.11. Test 3C, Vessel 1, 90 mg/L (from Test 3B); Vessel 2, 150 mg/L (60 + 90), After 3 min of Settling. Note polymer hang-up on stir shaft of Vessel 2, and floating sludge floc agglomerates.

The starting volume of the settled sludge, ~100 ml (8 wt% solids mixture, 20 vol% settled sludge), increased to about 150 ml after flocculation, and after settling overnight. However, the volume of the flocculated solids appeared to decrease when the solids were transferred to another jar.

Simulant tests were conducted immediately after the Series 3 tests to evaluate an alternative addition method that could better disperse the flocculant. For the standard approach, flocculant was rapidly injected above the top surface of the slurry. For the alternative approach, flocculant was added by slowly injecting it below the surface of the stirred slurry. With 50 and 150 ml of settled sludge simulant at a total volume of 500 ml and mixing at ~125 rpm, 9 ml (equivalent to 90 mg/L) of agent was injected over a period of 60 to 90 s at a level mid-way in the solution. With this method, marbling was noted for both samples after approximately 4.5 ml were added in about 30 s (Figure 3.12). After the remaining flocculant was added, the samples were then slowly mixed and allowed to clarify. The solids settled rapidly in both tests. The test vessel at low solids, ~50 ml settled sludge, appeared to be milky, apparently resulting from excess flocculant in the supernatant. At the high solids, 150 ml settled sludge, the supernatant was clear after flocculant addition.

3.2.4 Series 4 Flocculant Tests

Series 4 tests were conducted on March 16, 2004, with two test vessels: one at 0.25 wt% solids, and the other at 4.2 wt% solids. Each test was conducted with a slurry volume of approximately 500 ml. The target and actual test conditions, and test results, for the Series 4 testing are summarized in Table 3.4. Before flocculant addition, Vessels 3 and 4 were mixed for 5 min (~125 rpm) and then allowed to settle. Because of the higher solids concentration, hindered settling started almost immediately in Vessel 4, while Vessel 3 remained cloudy (Figure 3.13). After 6 min of settling, about half the solution in Vessel 4 was clarified. After 20 min, the supernatant in Vessel 3 was hazy, while more than 400 ml of solution in Vessel 4 was clarified.

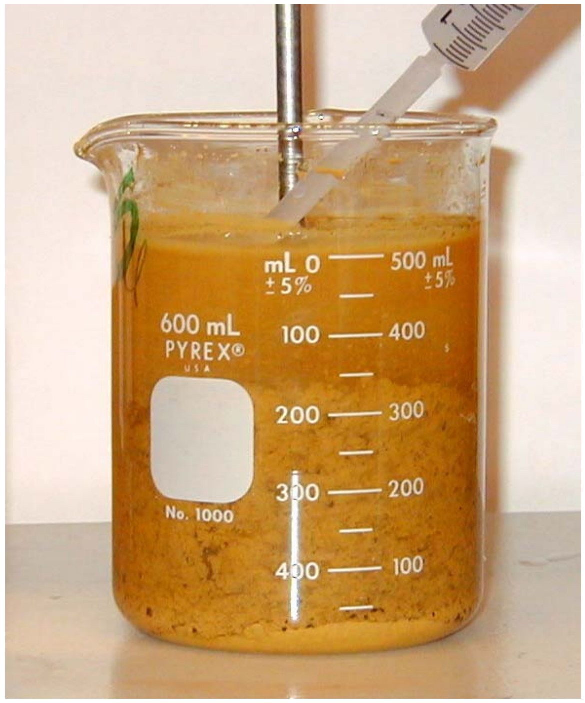

Figure 3.12. High Solids Simulant Marbling During Flocculant Addition (Rapid Mixing). The flocculant was injected below the surface of the slurry, near the 250-ml level in the beaker.

For Series 4, Test 4A, 60 mg/L of 7194+ was slowly added (60 s) to Vessel 4 under the surface of the slurry while mixing rapidly. [For Test 4A, no flocculant was added to Vessel 3.] Very good flocculant distribution was observed, along with marbling of the solids, in Vessel 4. Approximately 400 ml of the slurry was clarified within 1 min (Figure 3.14), and after several minutes, the supernatant was clear.

For Test 4B, to test the effect of a high flocculant dose on a low solids content slurry, 60 mg/L of 7194+ was slowly added (60 s) to Vessel 3 (0.25 wt%) under the surface of the slurry while mixing rapidly. [For Test 4B, no additional flocculant was added to Vessel 4.] The flocculation was very successful, with most of the solids settled and supernatant well clarified after 40 s of settling (Figure 3.15). No evidence of excess flocculant (e.g., milkiness) was observed in the supernatant. As shown in Figures 3.15 and 3.16, the slurry in Vessel 4, which was flocculated in Test 4A with 60 mg/L, did not clarify as rapidly after remixing. Some cloudiness remained in the supernatant in Vessel 4 even after 15 min of settling.

In Test 4C, Vessels 3 and 4 were remixed, and an additional 60 mg/L of flocculant was added to Vessel 4 (flocculant slowly injected under the slurry surface while mixing rapidly). No additional flocculant was added to Vessel 3. Vessel 3 resettled and clarified rapidly. The slurry in Vessel 4 marbled during flocculant addition and settled and clarified at a reasonable rate (Figures 3.17 and 3.18); much better than in Test 4B, but not as well as in Test 4A. Some excess flocculant was observed on the stir shaft; the second addition likely resulted in an overdose concentration in Vessel 4. The initial settled sludge volume in Vessel 4 was approximately 60 ml, and appeared to be about 100 ml after Test 4C.

Series 4 Conclusions: The 60 mg/L 7194+ dose results in good flocculation performance over a wide range of solids concentration, 0.25 to 4.2 wt% solids. The low solids slurry did not show signs of "overdosing." The clarified solution was clear, and no residual excess flocculant was noted. The 60 mg/L dose appears to be near optimum for 4.2 wt% solids. Doubling the dose provided good results, but the flocculant distribution was not as good and some excess agent adhered to the stir shaft.

Table 3.4. Series 4 Flocculation Test Matrix and Results

Parameters	Position Number/Beaker No.		
	Positions 1[a] Beaker 3	**Position 2[b] Beaker 4**	**Position 2[c] Beaker 4**
Target Wt% Solids	0.25	5	5
Target Settled Sludge Mass, g	3.1	63	63
Target 7194+ Concentration, mg/L	60	60	60+60
Target 7194+ Working Soln. Vol, ml	6.0	6.0	6.0 + 6.0
Actual Wt% Solids	0.25	4.2	4.2
Actual 7194+ Working Soln. Vol, ml	6.0	6.0	12.0
pH before 7194+ addition	7.5	7.2	7.2
pH after 7194+ addition	7.4	--	7.4
Flocculation Results	Excellent; high clarity	Excellent; high clarity	Very Good; minor haze

(a) Test 4B.
(b) Test 4A.
(c) Additional flocculant was added to Vessel 2 (Test 4C).

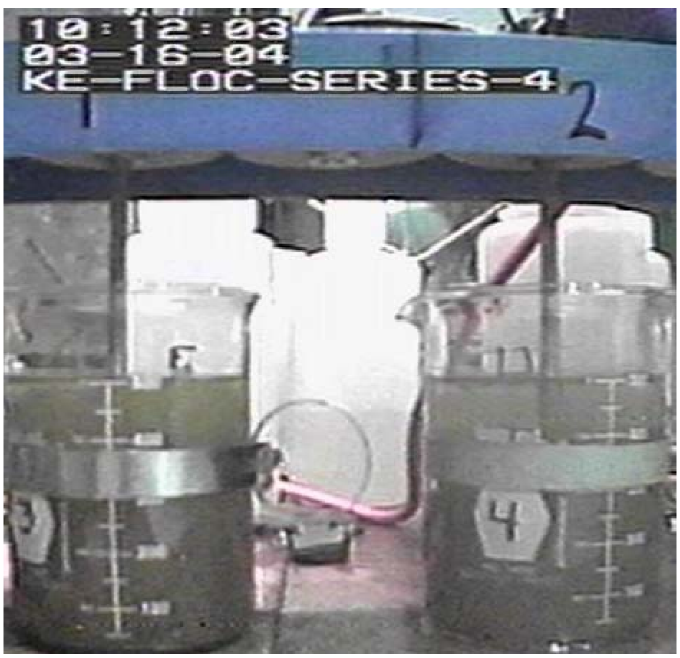

Figure 3.13. Test 4, Vessel 3, 0.25 wt% Solids, and Vessel 2, 4.2 wt% Solids, with No Flocculant Added, After 5 min of Settling

Figure 3.14. Test 4A, Vessel 4, 60 mg/L, After 1 min of Settling

Figure 3.15. Test 4B, Vessel 3, 0.25 wt% Solids, 60 mg/L; Vessel 4, 4.2 wt% Solids (60 mg/L Added During Test 4A), After 40 s of Settling

Figure 3.16. Test 4B, Vessel 3, 0.25 wt% Solids, 60 mg/L; Vessel 4, 4.2 wt% Solids (60 mg/L Added During Test 4B), After 3 min 40 s of Settling

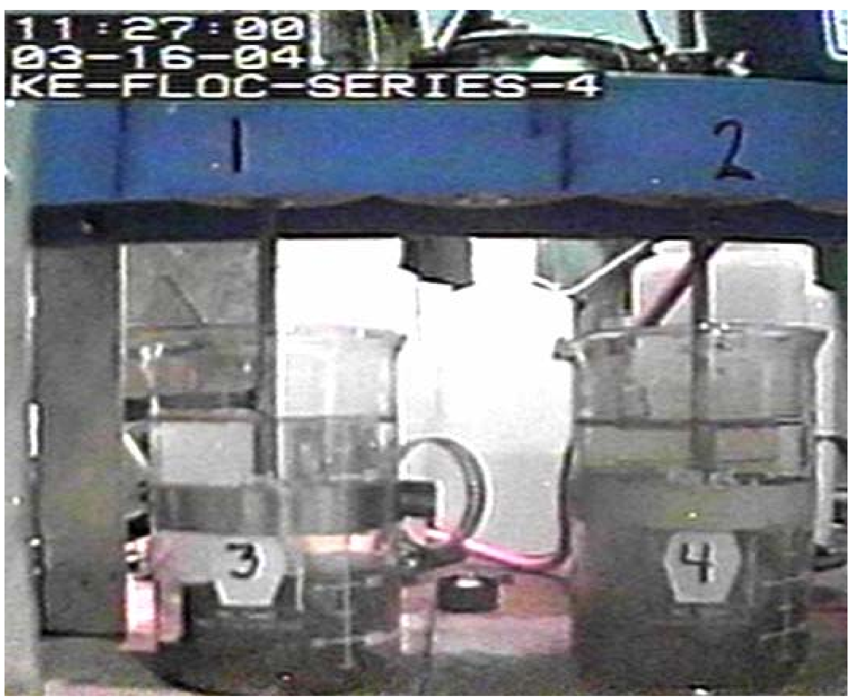

Figure 3.17. Test 4C, Vessel 3, 0.25 wt% Solids (60 mg/L Added During Test 4B); Vessel 4, 4.2 wt% Solids (120 mg/L Added During Test 4A and 4C), After 30 s of Settling

Figure 3.18. Test 4C, Vessel 3, 0.25 wt% Solids (60 mg/L Added During Test 4B); Vessel 4, 4.2 wt% Solids (120 mg/L Added During Test 4A and 4C), After 2 min 30 s of Settling

The slower, subsurface injection of flocculant provided much better results than those observed in the Series 3 tests. Using this technique, good flocculant distribution was noted for a relatively high dose with a low solids slurry. The resulting flocculated sludge (high dose/low solids) was also quite stable, and the sludge flocs were not broken up after an additional high-speed mixing. In comparison, at the higher solids loading (4.2 wt%) with 60 mg/L, the resulting sludge flocs were partially broken up during high-speed remixing.

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Appendix A

Previous Flocculant Testing: 1994 – 1996 and February 2004

Appendix A

Previous Flocculant Testing: 1994 – 1996 and February 2004

Earlier testing (1994-1996) with K Basin simulant and actual sludge is summarized here, and the testing with simulant conducted in February 2004 is described.

A.1 Flocculant Testing in 1994-1996 with K Basin Simulant and Sludge

Flocculants were previously evaluated for K Basin sludge applications as a means to increase settling rates or aid in filtration. In 1994, a series of tests were performed using a simple KE Basin sludge slurry simulant (1.5 wt% Class F Flyash in water) [Internal Memo 8E110-DCD95-037 to SA Brisbin, May 3, 1995. "Informal Test Plan – Evaluation of Polymer Flocculants for Particle Removal from 105-KE Basin Water," Westinghouse Hanford Company, Richland, WA]. Three flocculants, Nalco Optimer-7128, Optimer 7194 Plus (7194+), and Optimer 7196 Plus (7196+), were evaluated. Consistent with vendor recommendation, the neat flocculants were diluted, with de-ionized water, to 0.5 wt% working solutions. For each test, 250 ml of the 1.5 wt% simulant slurry was mixed in a 400-ml beaker with a magnetic stirrer. Flocculant was added while mixing, and mixing was stopped when marbling (floc body formation) was observed. After mixing was stopped, the flocculation behavior of the slurry was observed and recorded. The results of this testing are summarized in Table A.1.

Table A.1. 1994 Flocculant Test Results with 1.5 wt% Flyash Slurry

Run	Polymer	Dose[(a)]	Results
1	7128	11 ml (220 ppm)	Good floc and settling, water still cloudy. Supernatant very clear after 2 min.
2	7128	20 ml (400 ppm)	Good floc and settling. After 1 min supernatant still cloudy, appears to be unused floc; i.e., floc was overdosed.
3	7196+	10 ml (200 ppm)	Good floc and excellent settling, water remains cloudy.
4	7196+	3 ml (60 ppm)	Good floc and settling, water remains cloudy, indications of continual overdoses.
5	7196+	1 ml (20 ppm)	Good floc, though not as large as before, excellent settling. Supernatant becomes clear enough to read the numbers on the beaker through the water.
6	7194+	1 ml (20 ppm)	Good floc and excellent settling, excellent water clarity.
7	7128	3ml (60 ppm)	Repeated test using 7128 due to indications of overdose, water remained cloudy.
8	7194+	1 ml (20 ppm)	Good floc, after agitation stopped the following noted: Plus 15 s: the supernatant becomes clear enough to read the numbers on the beaker through the water. Plus 60 s: supernatant is very clear.

(a) An error in the calculation and reported values of ppm's was discovered in the original report (Internal Memo, J.G. Wagner to S. A. Brisbin, November 28, 1994, "Surrogate Sludge Floc Testing," Westinghouse Hanford Company, Richland, WA). The ppm values provided in Table A.1 are the correct values and are based on the final concentration of neat flocculant in the sample (250 ml) and neglecting the volume of added flocculant.

From this testing, it was concluded that of the three flocculants, the 7194+ was the most effective. The best 7194+ dose was ~20 mg/L; however, lower doses were not tested. Overdose conditions were observed at 60 mg/L and greater.

Based on the promising results of the 1994 testing and the potential applications in the K Basins, a study was conducted to examine the compatibility of flocculants (7194+ and 7196+) with the K Basins Sludge Retrieval and Disposal Project operations (Graves 1995). Graves (1995) provides a general overview of flocculants and the chemistry and physical properties of 7194+ and 7196+, and concludes that the flocculants are compatible with operations, equipment, and materials used in the K Basins.

Further testing was conducted in 1996 to determine if flocculant addition could reduce the alpha content in KE Basin water. Based on the 1994 test results, 7194+ was used. For the first series of testing (Table A.2), 20 water samples from the KE Basin pool, collected a few minutes after gently agitating the sludge, were used (samples collected in July 1995). The water samples were distributed to create five samples for flocculant testing, including a control. Each of the samples contained a different amount of particles; therefore, the analytical results given in Table A.2 for Trials 1 through 4 can only be roughly compared to that of the control (Trial 5). In Trials 1 through 4, the clarity of the samples improved significantly within 2 to 3 min of flocculant addition. While a narrow range of flocculant doses were used (13 to 22 ppm), alpha reduction ranged from 32 to 77% relative to the control. The alpha reduction did not trend consistently with flocculant dose and was probably influenced more by sample inhomogeneity.

Table A.2. 1996 Flocculant Testing with KE Basin Water – Series I Tests

Trial	Sample Volume (ml)	Flocculant Addition	Total Alpha (µCi/ ml)	Total Alpha Reduction
1	160	0.7 ml (22 ppm)	7.75E-04	77%
2	160	0.4 ml (13 ppm)	8.86E-04	66%
3	150	0.6 ml (20 ppm)	1.07E-03	59%
4	130	0.5 ml (19 ppm)	1.79E-03	32%
5	--	None (control)	2.64E-03	NA

A second series of tests to evaluate alpha reduction were conducted in 1996, using KE Basin water samples collected behind the Weasel Pit screen during sludge pumping (samples collected March 1, 1996). The samples were composited and then divided into 100-ml aliquots. In this series of testing, the effects of flocculant addition and filtration (0.45-µm filter) on turbidity and alpha reduction were investigated. However, the samples contained fewer particles than those in the first series, which made turbidity reduction more difficult to evaluate. After flocculant addition, small flocs formed that settled after 15 to 20 min. The test matrix and alpha analysis results are provided in Table A.3. In general, very little alpha reduction was achieved in the tests with flocculant addition only. Adjustment of the pH (with sodium hydroxide) to 7 or 8 did not have a significant effect. The alpha content was reduced by 2 to 3 orders of magnitude by filtering the slurry through a 0.45-µm filter. In Trials 7 and 8, the un-filtered sample exhibited a high alpha reduction, while the filtered sample exhibited only a small alpha reduction. It is probable that the analytical samples from Trials 7 and 8 were reversed.

Based on the 1994 and 1996 testing, it was concluded that addition of 7194+ results in significant reduction of turbidity, but only minimal reduction in total alpha content. Filtration of K Basin pool water samples had a much greater effect on the alpha content reduction.

Table A.3. 1996 Flocculant and Filtration Testing with KE Basin Water – Series II Tests

Trial	Flocculant Addition	Total Alpha (μCi/ml)	% Reduction Relative to Control (Trial 1)	Comments
1	None	8.23E-03	NA	Feed Solution
2	None	2.10E-05	99.74	Filtered Only
3	2.0 ml (100 ppm)	1.75E-05	99.79	Flocculant & Filter
4	0.8 ml (40 ppm)	1.97E-05	99.76	Flocculant & Filter
5	2.0 ml (100 ppm)	9.00E-03	none	Flocculant Only
6	0.8 ml (40 ppm)	6.80E-03	17	Flocculant Only
7	3.0 ml (150 ppm)	6.81E-03	17	Flocculant & Filter (pH adjusted)
8	5.0 ml (250 ppm)	6.99E-06	99.92	Flocculant Only (pH adjusted)
9	3.0 (150 ppm)	6.06E-06	99.93	Flocculant & Filter (pH adjusted)
10	5.0 ml (250 ppm)	8.22E-03	<1	Flocculant Only (pH adjusted)

A.2 Flocculant Testing in February 2004 with K Basin Simulant

In February 2004, a series of tests were conducted with a K Basin sludge simulant to identify the most promising flocculants to use in the testing with K Basin sludge and to examine the relationship between simulant solids concentration and flocculant dose. The effect of pH on flocculant performance was also examined. Testing was also performed to evaluate the settling rate of the simulant, with and without flocculant addition. Several mixing techniques for dispersing the flocculant were also investigated.

A.2.1 Test Equipment

A Phipps & Bird Stirrer Model 7790-400 (gang stirrer with paddle blade impellers) was configured to stir six 600-ml beakers simultaneously. The Phipps & Bird stirrer includes an integrated controller with digital readout of the mixing speed.

A.2.2 Flocculants

Seven flocculants, obtained from Nalco Chemical Company, were evaluated: Optimer 7194 Plus, Nalcolyte 8105, Optimer 7196 Plus, 71301, Cat-Floc 8108 Plus, 71307, and NalClear 7763. These flocculants were selected by Fluor Federal Services and provided to PNNL for the testing. Based on vendor recommendation, the neat flocculants were diluted with de-ionized water to prepare 0.5 wt% working solutions. Aliquots of working solution were added to the test slurries in the flocculation testing. Based on vendor recommendation, fresh working solution was prepared daily for the testing with the actual sludge. The neat flocculants had a density close to 1 g/cm^3 (e.g., density of 7194+ = 1.06 g/cm^3); therefore, the density of the working solutions (99.5 wt% de-ionized water) was also approximately 1.0 g/cm^3.

A.2.3 Flocculation Test Protocol

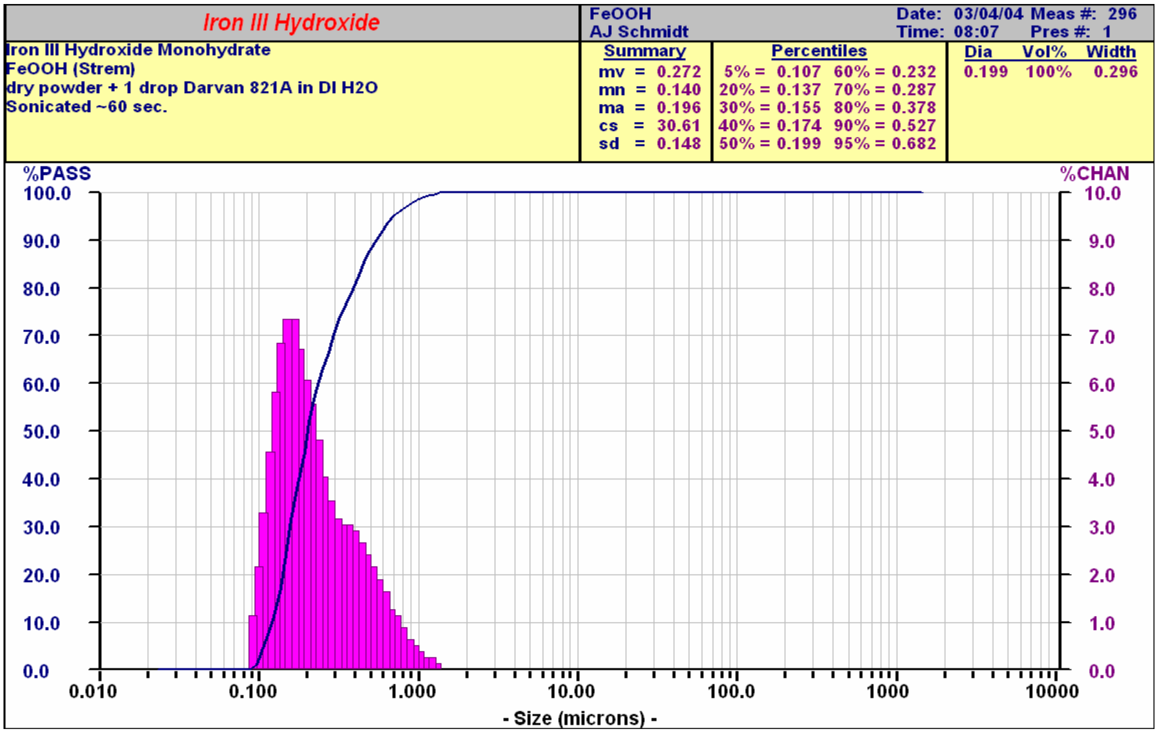
Test slurries (~500 ml) were prepared by adding measured quantities of simulant and water into 600-ml beakers. For each test, six vessels were tested simultaneously. Before flocculant addition, the slurries were mixed at ~125 rpm for a minimum of 2 min with the Phipps & Bird stirrer to break up particle agglomerates and obtain a homogeneous mixture. While the slurries were mixing at ~125 rpm, aliquots (doses) of flocculant were quickly added (above the slurry-air interface) to each beaker, using pipettes. After flocculant addition, the slurries were mixed at ~125 rpm for ~30 s, and then slowly mixed (~45 rpm) for an additional 2 min. The mixing was stopped, and the flocculation, settling, and clarification behavior of slurry in each vessel was monitored and recorded.

A.2.4 Settling Rate Protocol

Settling rate measurements, with and without flocculant addition, were performed with 1 wt% simulant slurry in a 2-L graduated cylinder. Approximately 1500 ml of slurry was added to the graduated cylinder and mixed for at least 5 min. Flocculant was then added, and the slurry was mixed by gas sparging or an overhead mixer to disperse the flocculant. After mixing was stopped, the settling rates were measured by monitoring the volume of settled slurry with time.

A.2.5 Flocculant Simulant Composition

The simulant used for the flocculation testing was prepared by adding iron (III) hydroxide to the K Basin Settling Simulant (Schmidt and Elmore 2002). The Settling Simulant was developed to resemble a nominal 40/60 volume percent mixture of KE canister/floor sludge with respect to particle size distribution and particle density [see Schmidt and Elmore (2002) for composition basis]. The Settling Simulant was used to investigate the distribution of uranium metal surrogate (cobalt-cemented tungsten carbide) while loading (and transporting) K Basin sludge in containers. To modify the Settling Simulant for flocculation testing, iron (III) hydroxide was added as a surrogate for the fine uranium/iron/aluminum oxy-hydrate particles in the K Basin sludge. The iron (III) hydroxide used for the Flocculation Simulant was obtained from NOAH Technologies Corporation as a 13 wt% slurry (in water). Consistent with uranium oxide, most of the iron (III) hydroxide particles were less than 1 μm (Figure A.1).



SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN
1408	100.00	0.00	74.00	100.00	0.00	3.889	100.00	0.00	0.204	52.02	6.20
1291	100.00	0.00	67.86	100.00	0.00	3.566	100.00	0.00	0.187	45.82	6.80
1184	100.00	0.00	62.23	100.00	0.00	3.270	100.00	0.00	0.172	39.02	7.43
1086	100.00	0.00	57.06	100.00	0.00	2.999	100.00	0.00	0.158	31.59	7.45
995.6	100.00	0.00	52.33	100.00	0.00	2.750	100.00	0.00	0.145	24.14	6.87
913.0	100.00	0.00	47.98	100.00	0.00	2.522	100.00	0.00	0.133	17.27	5.91
837.2	100.00	0.00	44.00	100.00	0.00	2.312	100.00	0.00	0.122	11.36	4.56
767.7	100.00	0.00	40.35	100.00	0.00	2.121	100.00	0.00	0.111	6.80	3.33
704.0	100.00	0.00	37.00	100.00	0.00	1.945	100.00	0.00	0.102	3.47	2.25
645.6	100.00	0.00	33.93	100.00	0.00	1.783	100.00	0.00	0.094	1.22	1.22
592.0	100.00	0.00	31.11	100.00	0.00	1.635	100.00	0.03	0.086	0.00	0.00
542.9	100.00	0.00	28.53	100.00	0.00	1.499	99.97	0.08	0.079	0.00	0.00
497.8	100.00	0.00	26.16	100.00	0.00	1.375	99.89	0.21	0.072	0.00	0.00
456.5	100.00	0.00	23.99	100.00	0.00	1.261	99.68	0.30	0.066	0.00	0.00
418.6	100.00	0.00	22.00	100.00	0.00	1.156	99.38	0.37	0.061	0.00	0.00
383.9	100.00	0.00	20.17	100.00	0.00	1.060	99.01	0.47	0.056	0.00	0.00
352.0	100.00	0.00	18.50	100.00	0.00	0.972	98.54	0.59	0.051	0.00	0.00
322.8	100.00	0.00	16.96	100.00	0.00	0.892	97.95	0.75	0.047	0.00	0.00
296.0	100.00	0.00	15.56	100.00	0.00	0.818	97.20	0.92	0.043	0.00	0.00
271.4	100.00	0.00	14.27	100.00	0.00	0.750	96.28	1.14	0.039	0.00	0.00
248.9	100.00	0.00	13.08	100.00	0.00	0.688	95.14	1.38	0.036	0.00	0.00
228.2	100.00	0.00	12.00	100.00	0.00	0.630	93.76	1.65	0.033	0.00	0.00
209.3	100.00	0.00	11.00	100.00	0.00	0.578	92.11	1.96	0.030	0.00	0.00
191.9	100.00	0.00	10.09	100.00	0.00	0.530	90.15	2.25	0.028	0.00	0.00
176.0	100.00	0.00	9.250	100.00	0.00	0.486	87.90	2.52	0.026	0.00	0.00
161.4	100.00	0.00	8.482	100.00	0.00	0.446	85.38	2.75	0.023	0.00	0.00
148.0	100.00	0.00	7.778	100.00	0.00	0.409	82.63	2.94			
135.7	100.00	0.00	7.133	100.00	0.00	0.375	79.69	3.06			
124.5	100.00	0.00	6.541	100.00	0.00	0.344	76.63	3.10			
114.1	100.00	0.00	5.998	100.00	0.00	0.315	73.53	3.27			
104.7	100.00	0.00	5.500	100.00	0.00	0.289	70.26	3.57			
95.96	100.00	0.00	5.044	100.00	0.00	0.265	66.69	4.12			
88.00	100.00	0.00	4.625	100.00	0.00	0.243	62.57	4.92			
80.70	100.00	0.00	4.241	100.00	0.00	0.223	57.65	5.63			

Figure A.1. Particle Size Distribution of Iron (III) Hydroxide Used in Flocculant Simulant

The components used for the Flocculation Simulant are described below.

- Cobalt-cemented Tungsten Carbide (referred to as W/Co): = 3.1 wt% (dry simulant basis). KENFCEXP; -2000 µm down (having a composition of 8.00% Co, max; 5.70% C, max; 0.20 wt% Ti, max; balance is W). Particle density of W/Co is ~15.0 g/cm^3, bulk dry density, ~10 g/cm^3).

- Stainless Steel powder: = 31.2 wt% (dry simulant basis). A434-L stainless steel powder in which all particles are less than 125 µm.

- Kleen Blast: 28.4 wt% (dry simulant basis). Kleen Blast is a sand blasting product, sold in a range of size distributions. -16+30 mesh was used to simulate the larger-diameter inert particles. Kleen Blast is composed of approximately 45% silicon, 23 wt% iron oxide, 19% calcium oxide, and 7% aluminum, and its particle density is approximately 2.8 g/cm^3.

- Flyash = 30.8 x 0.5 = 17.6 wt% (dry simulant basis). Class F Flyash, particle density, ~ 2.2 to 2.5 g/cm^3. Particles between 0.5 and 180 µm.

- Min-U-Sil 40 = 30.8 x 0.5 = 17.6 wt% (dry simulant basis). Ground high purity silica, particle density = 2.65 g/cm^3, mean particle diameter 11 µm.

- Iron (III) hydroxide $Fe(OH)_3$ = 2 wt% (dry simulant basis). $Fe(OH)_3$ was added in slurry form. The slurry contained 12.2679 wt% $Fe(OH)_3$ and had a density of 1.0987 g/ml.

Table A.4 summarizes the Flocculant Simulant composition and provides the component particle densities and particle size distributions. Figure A.2 compares the Flocculant Simulant particle size distribution to that of KE Canister and KE Floor sludge.

Table A.4. Simulant Composition and Properties

	W/Co	SS Powder	Kleen Blast	Flyash	Min-U-Sil 40	$Fe(OH)_3$	Flocculant Simulant
Wt Fraction, dry	3.1	31.2	28.4	17.6	17.6	2	99.9
Particle Density, g/cm^3	13.9 – 14.5	7.8	2.6 – 2.8	2.2 – 2.5	2.65	2.4-3.6	
Particle Size Distribution, Percent Less Than							
µm	**W/Co**	**SS Powder**	**Kleen Blast**	**Flyash**	**Min-U-Sil 40**	**$Fe(OH)_3$**	**Flocculant Simulant**
2000	100	100	99.78	100	100	100	99.9
1000	34.33	100	78.94	100	100	100	92.0
500	5.66	100	47.48	100	100	100	82.1
250	1.32	100	15.98	100	100	100	73.1
106	0.23	83.6	1.71	97.8	100	100	63.5
100	0.21	80.7	1.52	97.4	100	100	62.4
53	0.13	39.5	0.1	88	98	100	47.1
30	0.01	17.3	0.1	75	94	100	37.2
20	0	7.8	0	65	83	100	30.5
10	0	1.3	0	45.6	46	100	18.5
5	0	0	0	30	26	100	11.9
1	0	0	0	7.8	7	92.8	4.5

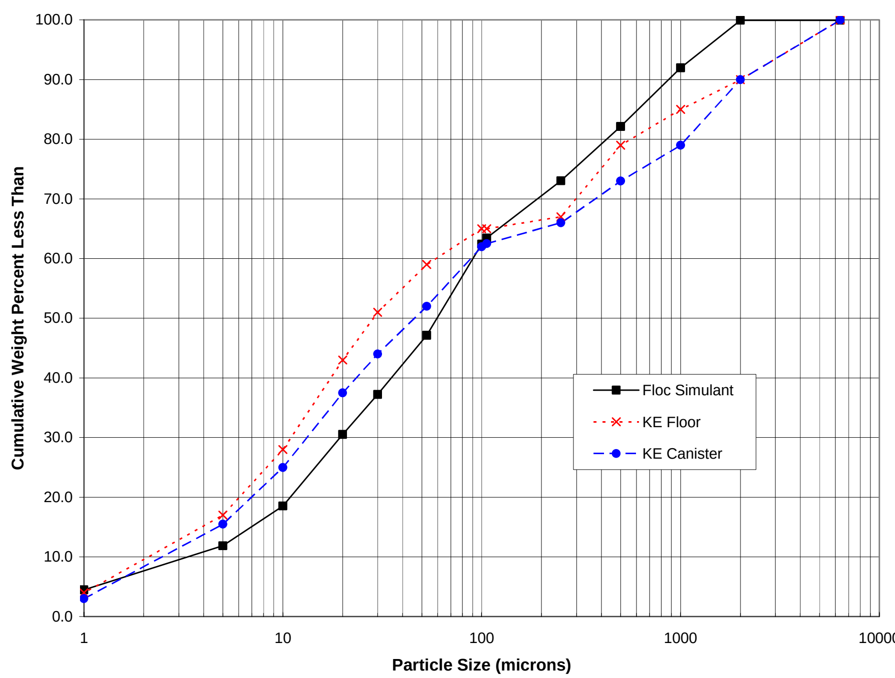


Figure A.2. Particle Size Distribution of Flocculant Simulant, KE Floor Sludge, and KE Canister Sludge

A.2.6 Test Matrix

Table A.5 summarizes the flocculation testing with simulant and provides the objective of each test. Tests 1 and 2 were conducted with 7194+ to refine test protocols and establish appropriate flocculant doses to use for side-by-side comparison of the other six flocculants. In Test 3, the six flocculants were compared at a single solids concentration (1 wt%) and at a single flocculant dose (5 mg/L). In Test 4, the two best-performing flocculants from Test 3 were tested with a 1 wt% slurry at three dose levels to evaluate the effective range of flocculants. In Test 5, the best performer from Test 4, 7196+, was compared with 7194+, with and without pH adjustment. Test 6 was conducted to examine the value of testing flocculants with a 20 wt% slurry. In Test 7, the effect on an overdose flocculant concentration in a low solids slurry (0.25 wt%) was investigated for 7194+ and 7196+.

Table A.5. Test Matrix

Test No.	Test Objective
1	Determine optimal dose of 7194+ at 1 wt% solids
2	Determine optimal dose of 7194+ at 10 wt% solids
3	Evaluate performance of remaining six flocculants at 1 wt% and a dose of 5 mg/L
4	Conduct side-by-side comparison of the two best flocculants from Test No. 3 (evaluate range and overall clarity)
5	Evaluate effect of pH on flocculation and comparison of 7194+ and 7196+
6	Evaluate self-flocculation/settling at 20 wt% solids (no flocculant added)
7	Determine effectiveness of flocculant addition at low solids slurry (0.25 wt% solids)
8	Measure simulant settling rate without flocculant addition.
9	Measure simulant settling rate after flocculant addition and a rapid N_2 sparge.
10	Measure simulant settling rate after flocculant addition and a moderate N_2 sparge.
11	Measure simulant settling rate with flocculant addition and mechanical stirring.
12	Evaluate hardiness of flocculated particles.

In Tests 8 through 11, the settling rates of a 1 wt% slurry, with and without flocculant, were measured. These tests also examined the effect of mixing on flocculant performance. In Test 12, flocculated sludge was poured from beakers into a 2-L graduated cylinder to examine the impact of mobilization/resuspension on existing sludge flocs.

A.2.7 Results

The test results are provided in Tables A.6 through A.18 and Figures A.3 through A.14.

Table A.6. Test No. 1, Dose Range Testing (7194+) with 1 wt% Slurry

Beaker	Wt% Solids	Flocculant	Flocculant Dose (mg/L)	Results	
				10 min	24 hrs
1	1	Optimer 7194 Plus	0	Limited Settling/Poor Clarity	Limited Settling/Poor Clarity
2	1	Optimer 7194 Plus	1	Limited Flocculation	Clear Solution
3	1	Optimer 7194 Plus	2	Fairly Clear	Clear Solution
4	1	Optimer 7194 Plus	5	Clear Solution (Best)	Clear Solution
5	1	Optimer 7194 Plus	10	Clear Solution	Clear Solution
6	1	Optimer 7194 Plus	25	Overdose	Fairly Clear

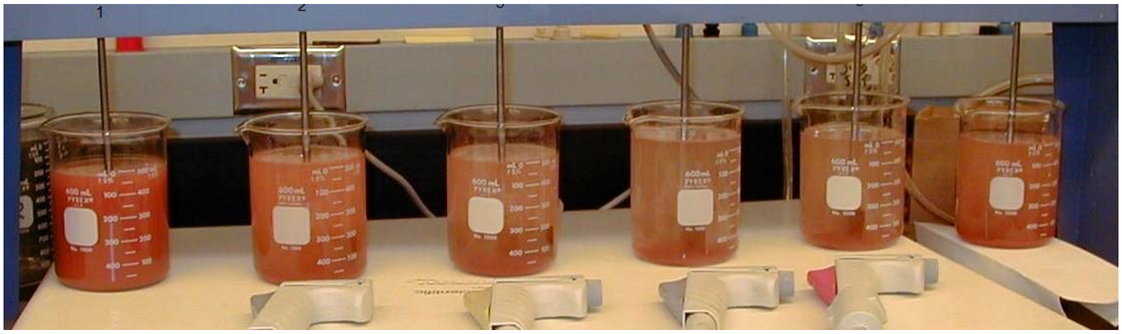


Figure A.3. Test No. 1 After 2 min, Beakers 1-6, Left to Right, 1 wt% Slurry, 7194+ Doses: 1 = 0 mg/L; 2 = 1 mg/L; 3 = 2 mg/L; 4 = 5 mg/L; 5 = 10 mg/L; and 6 = 25 mg/L

Table A.7. Test No. 2, Dose Range Testing (7194+) with 10 wt% Slurry

Beaker	Wt% Solids	Flocculant	Flocculant Dose (mg/L)	Results	
				10 min	24 hrs
1	10	Optimer 7194 Plus	0	Limited Settling/Poor Clarity	Fairly Clear
2	10	Optimer 7194 Plus	2	Limited Flocculation	Clear Solution
3	10	Optimer 7194 Plus	5	Fairly Clear	Clear Solution
4	10	Optimer 7194 Plus	10	Fairly Clear	Fairly Clear
5	10	Optimer 7194 Plus	20	Clear Solution (Best)	Clear Solution
6	10	Optimer 7194 Plus	40	Fairly Clear	Fairly Clear

Figure A.4. Test No. 2 After 2 min, Beakers 1-6, Left to Right, 10 wt% Slurry, 7194+
Doses: 1 = 0 mg/L; 2 = 2 mg/L; 3 = 5 mg/L; 4 = 10 mg/L; 5 = 20 mg/L; 6 = 40 mg/L

Figure A.5. Test No. 2 After 10 min, Beakers 1-6, Left to Right, 10 wt% Slurry, 7194+
Doses: 1 = 0 mg/L; 2 = 2 mg/L; 3 = 5 mg/L; 4 = 10 mg/L; 5 = 20 mg/L; 6 = 40 mg/L

Table A.8. Test No. 3, Flocculant Screening with 1 wt% Slurry at 5 mg/L

Beaker	Wt% Solids	Flocculant	Flocculant Dose (mg/L)	Results	
				10 min	24 hrs
1	1	Nalcolyte 8105	5	Limited Settling/Poor Clarity	Test ended at 1hr due to poor performance
2	1	Cal-Floc 8108 Plus	5	Limited Settling/Poor Clarity	Test ended at 1hr due to poor performance
3	1	Optimer 7196 Plus	5	Clear Solution (Best)	Clear Solution
4	1	71301	5	Fairly Clear	Clear Solution
5	1	71307	5	Clear Solution	Clear Solution
6	1	NalClear7763	5	Limited Settling/Poor Clarity	Test ended at 1hr due to poor performance

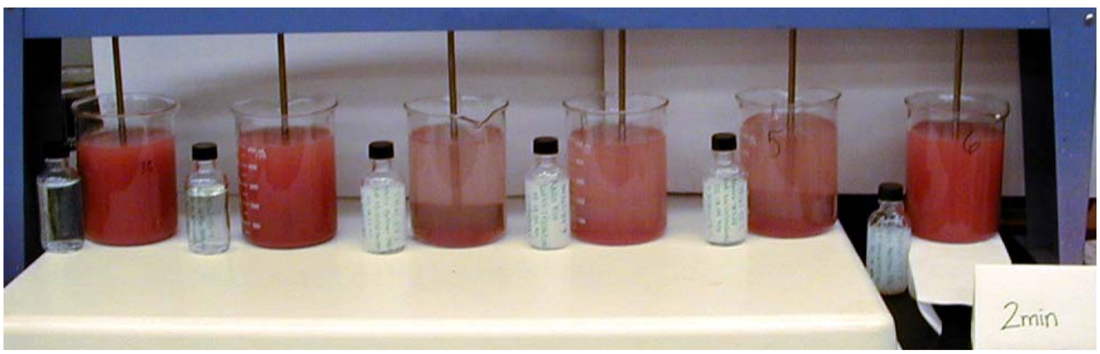


Figure A.6. Test No. 3 After 2 min, Beakers 1-6, Left to Right, 1 wt% Slurry; Various Flocculants at 5 mg/L

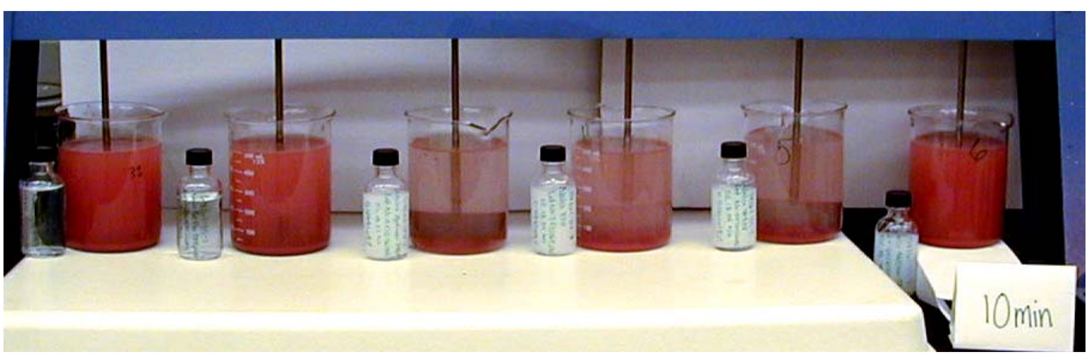


Figure A.7. Test No. 3 After 10 min, Beakers 1-6, Left to Right, 1 wt% Slurry; Various Flocculants at 5 mg/L

Table A.9. Test No. 4, Comparison of 7196+ with 71307

Beaker	Wt% Solids	Flocculant	Flocculant Dose (mg/L)	Results	
				10 min	24 hrs
1	1	Optimer 7196 Plus	2.5	Clear Solution	Clear Solution
2	1	Optimer 7196 Plus	10	Clear Solution (Best)	Clear Solution
3	1	Optimer 7196 Plus	20	Clear Solution	Clear Solution
4	1	71307	2.5	Limited Settling/Poor Clarity	Test ended at 1hr due to poor performance
5	1	71307	10	Fairly Clear	Test ended at 1hr due to poor performance
6	1	71307	20	Limited Settling/Poor Clarity	Test ended at 1hr due to poor performance

Figure A.8. Test No. 4 After 2 min, Beakers 1-6, Left to Right, 7196+ in Beakers 1-3; 71307 in Beakers 4-6

Figure A.9. Test No. 4 After 10 min, Beakers 1-6, Left to Right, 7196+ in Beakers 1-3; 71307 in Beakers 4-6

Table A.10. Test No. 5, Comparison of 7194+ with 7196+ with/without pH Adjustment

Beaker	Wt% Solids	Flocculant	Flocculant Dose (mg/L)	pH adjusted to 7	Results	
					10 min	24 hrs
1	1	Optimer 7194 Plus	5	Yes	Clear Solution	Clear Solution
2	1	Optimer 7194 Plus	5	No	Fairly Clear	Clear Solution
3	1	Optimer 7196 Plus	5	Yes	Clear Solution	Clear Solution
4	1	Optimer 7196 Plus	5	No	Fairly Clear	Clear Solution
5	1	Optimer 7194 Plus	2	Yes	Clear Solution	Clear Solution
6	1	Optimer 7194 Plus	10	Yes	Clear Solution	Clear Solution

Figure A.10. Test No. 5 After 2 min, Beakers 1-6, Left to Right, 7194+ in Beakers 1, 2, 5, and 6; 7196+ in Beakers 3 and 4; pH Adjustments to Beakers 1, 3, 5, and 6

Figure A.11. Test No. 5 After 10 min, Beakers 1-6, Left to Right, 7194+ in Beakers 1, 2, 5, and 6; 7196+ in Beakers 3 and 4; pH Adjustments to Beakers 1, 3, 5, and 6

Table A.11. Test No. 6, Settling/Clarification of 20 wt% Slurry with No Flocculant

Beaker	Wt% Solids	Flocculant	Flocculant Dose (mg/L)	Results	
				10 min	24 hrs
1	20	NA	NA	Settling began immediately, appearance similar to a 1 wt% simulant	Fairly Clear

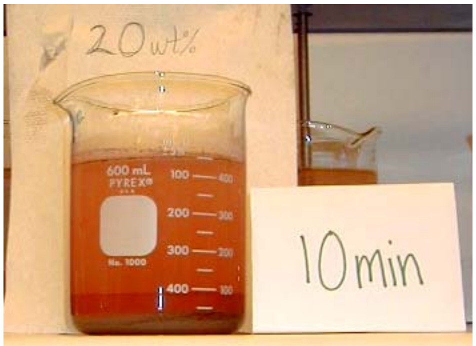


Figure A.12. Test No. 6 After 10 min, 20 wt% Slurry, No Flocculant

Table A.12. Test No. 7, Flocculant Overdose with Dilute (0.25 wt%) Slurry

Beaker	Wt% Solids	Flocculant	Flocculant Dose (mg/L)	Results	
				10 min	24 hrs
1	0.25	Optimer 7194 Plus	5	Clear Solution (Best)	Clear Solution
2	0.25	Optimer 7194 Plus	10	Fairly Clear	Clear Solution
3	0.25	Optimer 7194 Plus	15	Fairly Clear	Clear Solution
4	0.25	Optimer 7196 Plus	5	Clear Solution	Clear Solution
5	0.25	Optimer 7196 Plus	10	Fairly Clear	Clear Solution
6	0.25	Optimer 7196 Plus	15	Fairly Clear	Clear Solution

Figure A.13. Test No. 7 After 2 min, Beakers 1-6, Left to Right, 0.25 wt% Slurry; 07194+ in Beakers 1-3 and 7196+ in Beakers 4-6

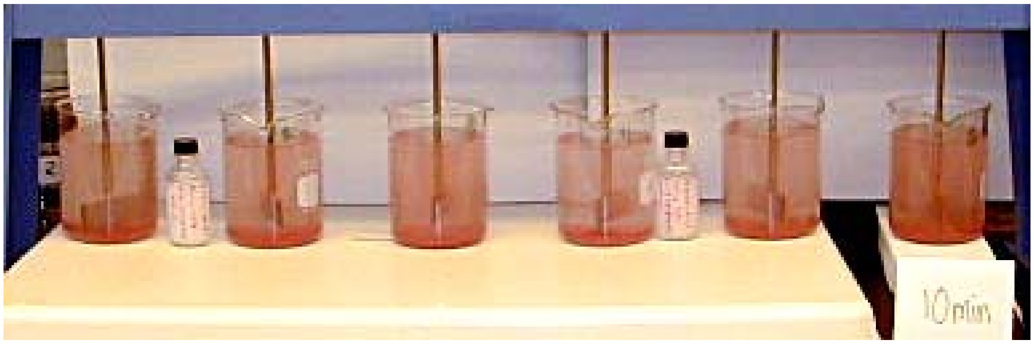


Figure A.14. Test No. 7 After 10 min, Beakers 1-6, Left to Right, 0.25 wt% Slurry; 07194+ in Beakers 1-3 and 7196+ in Beakers 4-6

Table A.13. Test No. 8, Settling Rate of 1 wt% Slurry with no Flocculant Addition

Wt% Solids	Flocculant	Flocculant Dose (mg/L)	Nitrogen Gas Sparge Rate, ml/min	Nitrogen Gas Sparge Duration After Flocculant Addition, min
1	None	NA	710	5
Time (min)	**Mark (ml)**	**Time (min)**	**Mark (ml)**	
0	1545	16	1325	
2	1500	18	1300	
4	1480	20	1280	
6	1460	22	1240	
8	1420	24	1200	
10	1400	26	1160	
12	1380	28	1120	
14	1340	30	1100	
Average Settling Rate (ml/min)		15		

Table A.14. Test No. 9, Settling Rate of 1 wt% Slurry, 7194+ = 5 mg/L, Rapid Gas-Sparge Mixing

Wt% Solids	Flocculant	Flocculant Dose (mg/L)	Nitrogen Gas Sparge Rate, ml/min	Nitrogen Gas Sparge Duration After Flocculant Addition, min
1	Optimer 7194 Plus	5	660	0.5
Time (min)	**Mark (ml)**			
0	1545			
2	1400			
4	1300			
6	1200			
8	1000			
10	880			
12	740			
14	600			
16	520			
Settling Rate (ml/min)	64			
Post-Test Observations: After initial test, flocculated simulant solution was resuspended with a mechanical stirrer (small turbo-prop impeller) at a rate of ~7500 rpm. Subsequent settling was rapid.				

Table A.15. Test No. 10, Settling Rate of 1 wt% Slurry, 5 mg/L 7194+, Moderate Gas-Sparge Mixing

Wt% Solids	Flocculant	Flocculant Dose (mg/L)	Nitrogen Gas Sparge	
			Rate, ml/min	Duration After Flocculant Addition, min
1	Optimer 7194 Plus	5	350	0.5

Time (min)	Mark (ml)
0	1520
2	1460
4	1420
6	1400
8	1360
10	1300
12	1260
14	1220
16	1180
Settling Rate (ml/min)	21
Observations: With moderate nitrogen sparge, much of the flocculant remained near the surface.	
Post-Test Observations: After the initial test, flocculated simulant solution was resuspended with a mechanical stirrer (small turbo-prop impeller) at a rate of ~7500 rpm, and subsequent settling rate was similar to Test No. 11. After remixing and adding 5 ml/L of flocculant, the settling rate increased.	

Table A.16. Test No. 11, Settling Rate of 1 wt% Slurry, 5 mg/L 7194+, Paddle-blade Impeller Mixing

Wt% Solids	Flocculant	Flocculant Dose (mg/L)	Stir Speed (rpm)/Duration (min)
1	Optimer 7194 Plus	5	>125 (mechanical stirrer with paddle blade on lowest setting)/0.5

Time (min)	Mark (ml)
0	1400
2	Settling too rapid to quantify
Settling Rate (ml/min)	Too rapid to quantify
Post-Test Observations: After the initial test, the paddle blade was replaced with a turbo-prop impeller, and flocculated simulant solution was resuspended. Flocculated particles did not resuspend completely.	

Table A.17. Test No. 12, Resuspension/Settling of Flocculated Simulant

Test Description: Poured Beakers 1-3 from Test No. 7 into a 2-L graduated cylinder and observed settling.
Observations: Flocculated sludge particles held together. All large agglomerates had settled out by 1 min. Small particles continued to settle for 30 min, after which time the solution was essentially clarified.

Table A.18. Summary of Test Results

Test No.	Results
1	The optimal dose of Optimer 7194 Plus at 1 wt% solids is 5 ml/L.
2	The optimal dose of Optimer 7194 Plus at 10 wt% solids is 20 ml/L, but the sensitivity to dose seems to be less at this solids concentration. The control appeared to clarify by self-flocculation.
3	Optimer 7196 Plus and 71307 performed the best.
4	Optimer 7196 Plus outperformed 71307 in regards to both range and overall clarity.
5	pH adjustment improved performance of Optimer 7194 Plus and 7196 Plus.
6	At 20 wt% solids, with no flocculant addition, settling began immediately, appearance similar to a 1 wt% simulant.
7	Flocculants effective at low solids loading with evidence of overdosing at 15 ml/L.
8	Rate of settling after rapid N_2 sparge in the absence of a flocculant was 14.4 ml/min.
9	Rate of settling after flocculant addition and rapid nitrogen sparge was 65 ml/min.
10	Rate of settling after flocculant addition and moderate nitrogen sparge was 21 ml/min.
11	Rate of settling after flocculant addition and stirring was too rapid to quantify (>500 ml/min).
12	Flocculated sludge particles remained flocculated after being mobilized and resuspended.

A.2.8 Discussion of Results

After several screening tests, three flocculants, 7194+, 7196+, and 71307, were identified as superior performers, and Nalcolyte 8105, Cat-Floc 8108+, NalClear 7763, and 71301 were eliminated from further testing. Side-by-side comparisons of 7194+, 7196+, and 71307 were conducted to examine their relative performance as a function of dose, solids concentration, and pH. Optimer 7194+ (one of the two best performers from the 1994 testing) exhibited good performance over the broadest range of conditions. Optimal doses for 7194+ were 5 mg/L, 5 mg/L, and 20 mg/L at slurry concentrations of 0.25 wt%, 1 wt%, and 10 wt%, respectively.

Most of the tests with simulant were conducted without pH adjustment. Without adjustment, the pH of the 1 wt% and 10 wt% simulant slurries was about 9.8 and 10.4, respectively. In a test conducted with 1 wt% simulant slurry, the pH was adjusted to about 7 in four of the six beakers. At a pH of 7 (i.e., approximate pH of the K Basin pool water), better performance was observed with respect to the clarity of the resulting supernatant. The improved performance of 7194+ at neutral pH is consistent with the vendor's experience.

Settling rate testing was performed with 1 wt% simulant slurry in a 2-L graduated cylinder. Without flocculant addition, the settling rate with ~1550 ml of slurry was about 15 ml per minute (as measured by monitoring the volume of settled slurry with time). With flocculant addition (5 mg/L) followed by rapid nitrogen sparging for 30 s, the settling rate was ~64 ml/min. A lower settling rate (21 ml/min) was measured when performing moderate nitrogen sparging after the flocculant addition. When using a mechanical mixer, with either a turbo-prop or a paddle blade impeller, rapid settling rates were observed

(> 500 ml/min, settling rates were too fast for accurate measurement). It was also found that flocculated slurry would rapidly resettle after being resuspended by aggressive mechanical mixing.

In summary, 7194+ was found to be the most effective flocculant. The optimal flocculant dose at low solids slurry concentrations (0.25 and 1 wt%) was 5 mg/L. At 10 wt% solids, the optimal dose was 10 mg/L. In the pH adjustment testing, the flocculants performed better when the pH was adjusted to 7. From the mixing/settling tests, it was concluded that the flocculation testing with actual sludge should be performed with mechanical mixing rather than gas sparging. It was also found that flocculated particles generally remained flocculated even after being mobilized and resuspended.

A.2.9 Reference

Schmidt AJ, and MR Elmore. 2002. *Settling Test Using Simulants to Evaluate Uranium Metal Distribution in K Basin Sludge*. PNNL-13854, Pacific Northwest National Laboratory, Richland, WA.

Appendix B

Effect of Flocculant on Grout Set-Up/Free Water Release

Appendix B

Effect of Flocculant on Grout Set-Up/Free Water Release

B.1 Purpose of Test

The testing described here was conducted to determine the effect of flocculant on grout set-up and free water release. The selected agent, 7194+, is an acrylamide modified polymer. In general, poly acrylamide sorbents have no adverse effects on grout set-up (although they have the potential to absorb some water). However, since this flocculant includes active functional groups, grout testing with flocculated sludge simulant was performed.

B.2 Results

A high concentration of 7194+ (144 mg/L – neat agent basis) was added to a ~ 3.7 wt% (1.1 vol% solids) K Basin simulant sludge slurry. Assuming all of the flocculant partitioned to the solids, the resulting flocculant concentration, on a total solids basis, was approximately ~3700 ppm. In comparison, for the KE flocculation process, the maximum planned agent addition is 60 mg/L when treating the maximum solids content slurry of 4 vol% solids [personal communication; A. J. Schmidt (PNNL) and G. T. MacLean (Fluor Federal Services), March 29, 2004]. (For lower content solids volume slurries, lower flocculant doses are planned.) Table B.1 compares the flocculation test parameters for simulant to some potential K Basin sludge flocculation operating parameters. Based on Table B.1, the flocculant testing with simulant resulted in a significantly higher flocculant concentration in the resulting solids than that expected in the actual operation.

After completing the flocculation testing, both flocculated and non-flocculated K Basin sludge simulant samples were grouted using the grout formula and solids loading that were used for the KE North Loadout Pit Sludge (Mellinger et al. 2004). With this grout formulation, the flocculant concentration in the resulting grout matrix was 390 ppm (assuming 100% of the flocculant partitioned to the solids). The presence of the flocculant had no perceptible effect on grout set-up or free water release (i.e., no differences were observed in the behavior of the flocculated and non-flocculated grouted simulant samples).

Table B.1. Flocculation Test Parameters Compared to Potential K Basin Flocculation Parameters

	K Basin Simulant Test	**KE Design Basis Floor Sludge**		**KE Safety Basis 40/60 Canister Floor Sludge**	
Weight % Solids	3.7	2.6	4.4	9.8	16.1
Volume % Solids	1.1	1	4	1	4
Flocculant Dose in Solution, mg/L	144	60[(a)]	60	60[(a)]	60
Flocculant in Solids,[(b)] ppm	3700	2300	1300	580	330

(a) For a 1 wt% solids volume slurry, the planned flocculant dose is 30 mg/L; however, a value of 60 mg/L has been used here to provide a conservative estimate of the agent concentration in solids.
(b) Assuming 100% of flocculant partitions to solids (i.e., no residual flocculant in liquid).

B.3 Flocculation Test Description

For the testing described here, a slurry was prepared by adding 20 g of the K Basin uranium segregation sludge simulant (Schmidt and Elmore 2004) to 500 ml of water. The uranium segregation simulant contains 5 wt% FeOOH, while the simulant described in Appendix A contains 2 wt% $Fe(OH)_3$. The slurry was mixed with a Phipps & Bird jar test apparatus for about 90 min to break up agglomerates and to ensure that the simulant components were well hydrated. Neat 7194+ was diluted, with de-ionized water, to a 0.5 wt% working solution, based on the vendor recommendation. While mixing at 125 rpm, 15 ml of 0.5 wt% 7491+ was added by slow injection under the surface of the slurry. Following the 7194+ injection, the slurry was mixed at 125 rpm for 30 s, and then slowly mixed (45 rpm) for an additional 2 min. The flocculated sludge settled rapidly, and the supernatant achieved a high level of clarity. No evidence of excess flocculant was observed. Table B.2 provides the measured and calculated test parameters for the flocculation test. Figure B.1 shows the flocculated sludge (left) and the same quantity of settled sludge simulant without flocculant (right).

Table B.2. Parameters for Flocculation Test

Parameter	Value
Solids (dry basis)	20 g
Weight % Solids	3.7 wt%
Volume % Solids	1.1 vol% (based on simulant particle density of 3.6 g/cm^3)
Neat Flocculant	0.075 g (total)
Neat Flocculant	144 mg/L (concentration)
Flocculant in Solids	3700 ppm (dry solids basis, assuming all agent partitions to solids)

Figure B.1. Settled Flocculated Sludge Simulant (left) and Settled Sludge Simulant with No Flocculant (right). Each beaker contains ~ 20 g dry solids.

B.4 Grouting

Flocculated and non-flocculated K Basin sludge simulant samples were grouted in accordance with the procedure developed for the KE North Loadout Pit sludge, described in Appendix F of Mellinger et al. (2004). The grout formulation is provided in Table B.3.

Table B.3. Grout Formulation for Flocculated and Non-Flocculated Sludge Simulant

Parameter	Value
Dry Solids (Sludge Simulant)	20 g
Total Water (associated with wet sludge and additional free water)	55 g
Portland Type I/II Cement	110 g
Bentonite Powder/Clay	6.6 g

Cement was added to the settled sludge simulant + water at a cement to total water ratio of 2:1, and mixed for approximately 3 min. Next, bentonite clay was slowly added while mixing. To ensure a homogeneous distribution of components, mixing continued for another 3 to 4 min. The mixtures were then transferred to 5-cm-diameter poly containers (Figure B.2), covered with Parafilm (to minimize water evaporation), and allowed to cure.

Figure B.2. Flocculated Sludge Simulant (left) and Non-flocculated Sludge Simulant (right) ~5 min After Being Loaded into 5-cm-diameter Poly Containers

After ~20 min, a small quantity of free water (less than 1 ml) was visible above both grout samples. Within 2 hours both grout samples (with and without flocculant) were warm to the touch (heat of hydration) and were setting up. Within 3 ½ hours the free water was incorporated back into the grout matrix, and the samples were rigid. After 6 hours the samples were removed from the poly containers (Figure B.3), and both samples appeared to be well set and resisted deformation with moderate pressure. After 48 hours, both samples appeared reasonably well cured.

Figure B.3. Grouted Flocculated Sludge Simulant (left) and Non-Flocculated Sludge Simulant (right), After 6 Hours of Curing

B.5 References

Mellinger, GB, CH Delegard, MA Gerber, BN Naft, AJ Schmidt, and TL Walton. 2004. *Disposition Options for Hanford Site K-Basin Spent Nuclear Fuel Sludge*. PNNL-14729, Pacific Northwest National Laboratory, Richland, WA.

Schmidt, AJ, and MR Elmore. 2004. *Interim Report on Uranium Metal Segregation Testing.* PNNL-14731, Pacific Northwest National Laboratory, Richland, WA.