

**Bench-Scale Enhanced Sludge
Washing and Gravity Settling of
Hanford Tank C-106 Sludge**

K. P. Brooks
R. L. Myers
K. G. Rappe

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Executive Summary

This report summarizes the results of a bench-scale sludge pretreatment demonstration of the Hanford baseline flowsheet using liter-quantities of sludge from Hanford Site single-shell tank 241-C-106 (tank C-106). The leached and washed sludge from these tests provided Envelope D material for the contractors supporting Tank Waste Remediation System (TWRS) Privatization. Pretreatment of the sludge included enhanced sludge washing and gravity settling tests and providing scale-up data for both these unit operations.

Enhanced sludge washing removes caustic-soluble components from the sludge by leaching the sludge twice with 3M NaOH at elevated temperatures (~100°C). The water-soluble components as well as the added sodium are then removed by three washes with "corrosion inhibited" water (0.01 M NaOH/0.01 M NaNO₂) at ambient temperatures. During each stage of the enhanced sludge washing process, some type of solid/ liquid separations are required to remove the leach and wash solutions. Gravity settle/decant is the approach taken for treating tank C-106 sludge.

Approximately 3 kg of wet, as-received tank C-106 sludge was processed in this work. The tests were performed remotely in the 324 Building C-cell using a stainless steel chemical leaching tank (10 liters) and a transparent plastic settling column (10-cm-diameter and 1-m-high). The settling rate (initial rate of decrease of the sediment height) and sludge compaction (solids fraction in the final compacted sediment) data were obtained during each step of the enhanced sludge washing process. Initial and final solids as well as decanted supernatants from each step of the process were analyzed chemically and radiochemically.

The results of this work were compared to those of Lumetta et al. (1996a) who performed a similar experiment with 15 grams of C-106 sludge. A summary of the results are shown in Table S.1. In both experiments, the leaching efficiencies of aluminum and phosphorous were less than the TWRS planning assumptions in Orme (1996). The leaching efficiencies of sodium and chromium exceeded the TWRS planning assumptions. The measured fraction of analytes (aluminum, phosphorous, chromium, and sodium) removed during the enhanced wash steps differed more than expected between the screening and bench-scale tests. These differences may be attributed to differences in equipment and experimental conditions and sample inhomogeneity. One of the primary differences was that the bench-scale work was operated at a higher solids loading than the screening test work resulting the bench-scale sludge sample being washed with less inhibited water. This difference in solids loading is believed to have produced the higher sodium concentration in the washed bench-scale sludge. The differences in removal efficiency could also be the result of the screening test sample not being representative of the bench-scale material. The aluminum concentration in the original sludge, for example, was 30% higher in the screening test sample than in the bench-scale test while the phosphorus was 70% higher in the bench-scale test than the screening test.

Oxalate ions accounted for >20% of the original C-106 sludge. These oxalate ions were (or became) tied up in the sludge as sparingly soluble sodium oxalate, which required multiple water washings to be removed.

For each step of the enhanced sludge washing process, the sludge settling was complete within 48 hours. Both the settling rate and the solids concentration in the final compacted sediment increased

Table S.1. Comparison of Bench and Screening (Lumetta 1996a) Test Experimental Conditions and Component Distributions

	Caustic Leach 1	Caustic Leach 2	Inhibited Water Washes	Residue
[Na ⁺] (M)	4.7/3.2 ^(a)	3.7/3.1	0.9/0.3	4.9/3.9 ^(b)
Free [OH ⁻] (M)	2.7/2.6	3.2/3.0	0.4/nd ^(c)	nd
Solids Concentration (wt%) ^(d)	6.4/3.3	6.5/3.9	~7/~2.9	--
Al ^(e)	30/39	0.7/6	0.5/1	69/53
Cr ^(e)	39/24	8/7	2/<1	51/68
P ^(e)	27/59	3/6	5/3	65/32
¹³⁷ Cs ^(e)	32/50	16/9	0.6/1	51/40

- (a) Displayed as bench-scale result/screening test result.
 (b) Sodium in sludge residue is measured in molality (moles/kg dry material) rather than molarity, as in the case of all other sodium measurements.
 (c) nd = not determined.
 (d) Solids concentrations are estimated based on the caustic-insoluble solids concentration in the final sludge samples.
 (e) Distribution percentages are measured based on the ratio of mass of the component removed in each step and the total mass of component in the sludge sample.

from the caustic to the water wash steps. Similar trends existed for the Lumetta et al. (1996a) screening test data (See Table S.2). In spite of the higher solids loading used on the bench-scale test, the settling rate of the bench-scale work was similar or higher than that of the laboratory work. This result is probably due to wall effects impeding settling in the small container used for the laboratory work. The settling rate exceeded the TWRS planning assumptions of 1-2 cm/hr in all cases.

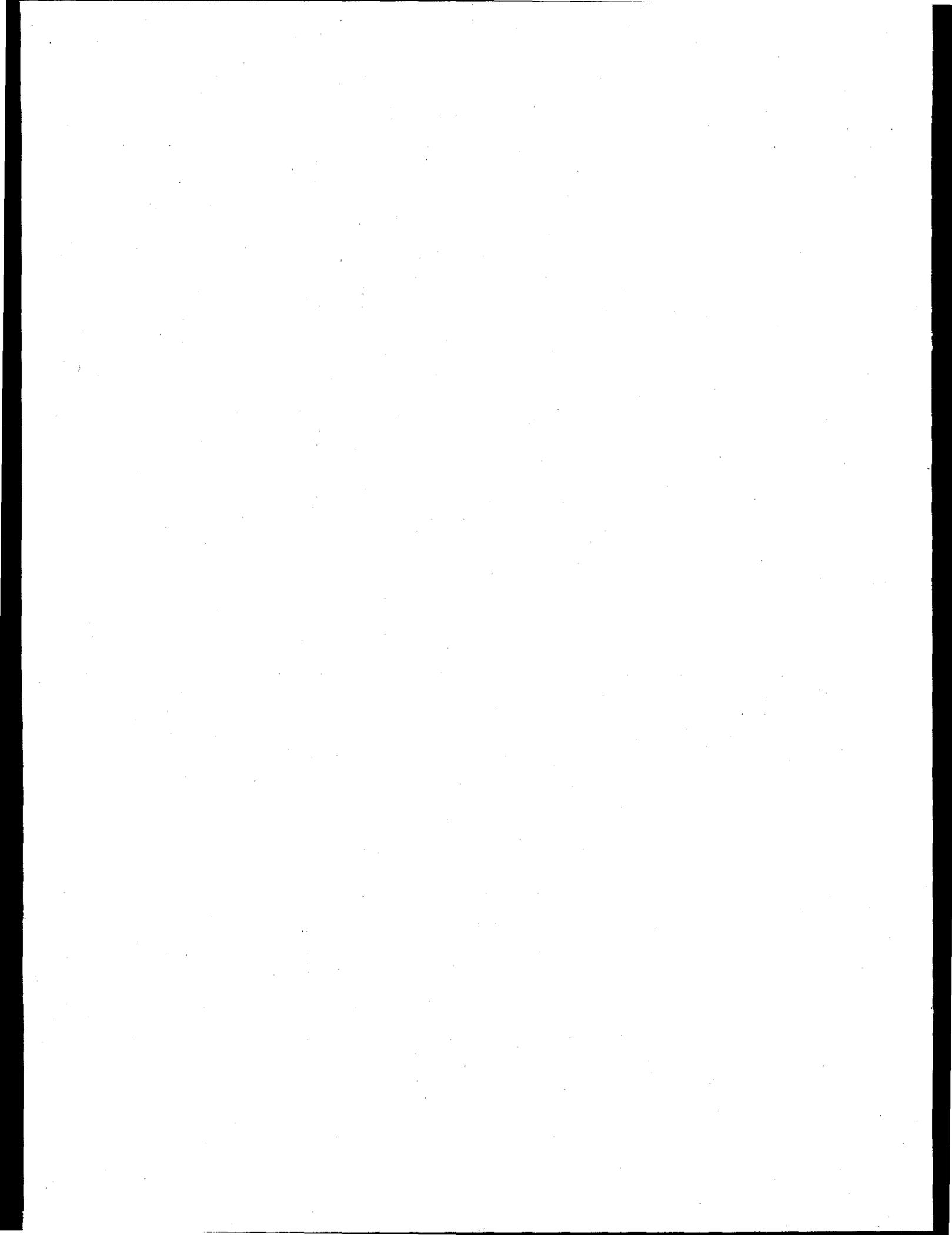
The settle/decant process obtained relatively high separation decontamination factors (DFs) for both Transuranics (TRU) and ⁹⁰Sr (as measured by the ratio of total alpha and ⁹⁰Sr in the solids to that in the solution). The DFs for TRU ranged from 180 to >770 while the DF for ⁹⁰Sr ranged from 539 to 11,000. These values correspond to a low-level waste glass that contains less than NRC Class C in TRU elements and less than NRC Class B in ⁹⁰Sr.

The bench-scale test contained a higher weight percent compacted solids than the screening test. The taller sludge layer associated with the bench-scale test (10-30 cm) allows further compaction due to the increased weight on the lower layers of sludge over the screening test (1 cm). Although the solids concentration in the final compacted sludge did not exceed the TWRS planning assumption of 20 wt% for the two caustic leaches, the sludge should compact even more on the full scale as the result of its much taller sludge layer (~1-3 m).

Table S.2. Comparison of Bench and Screening (Lumetta 1996a) Settling Data

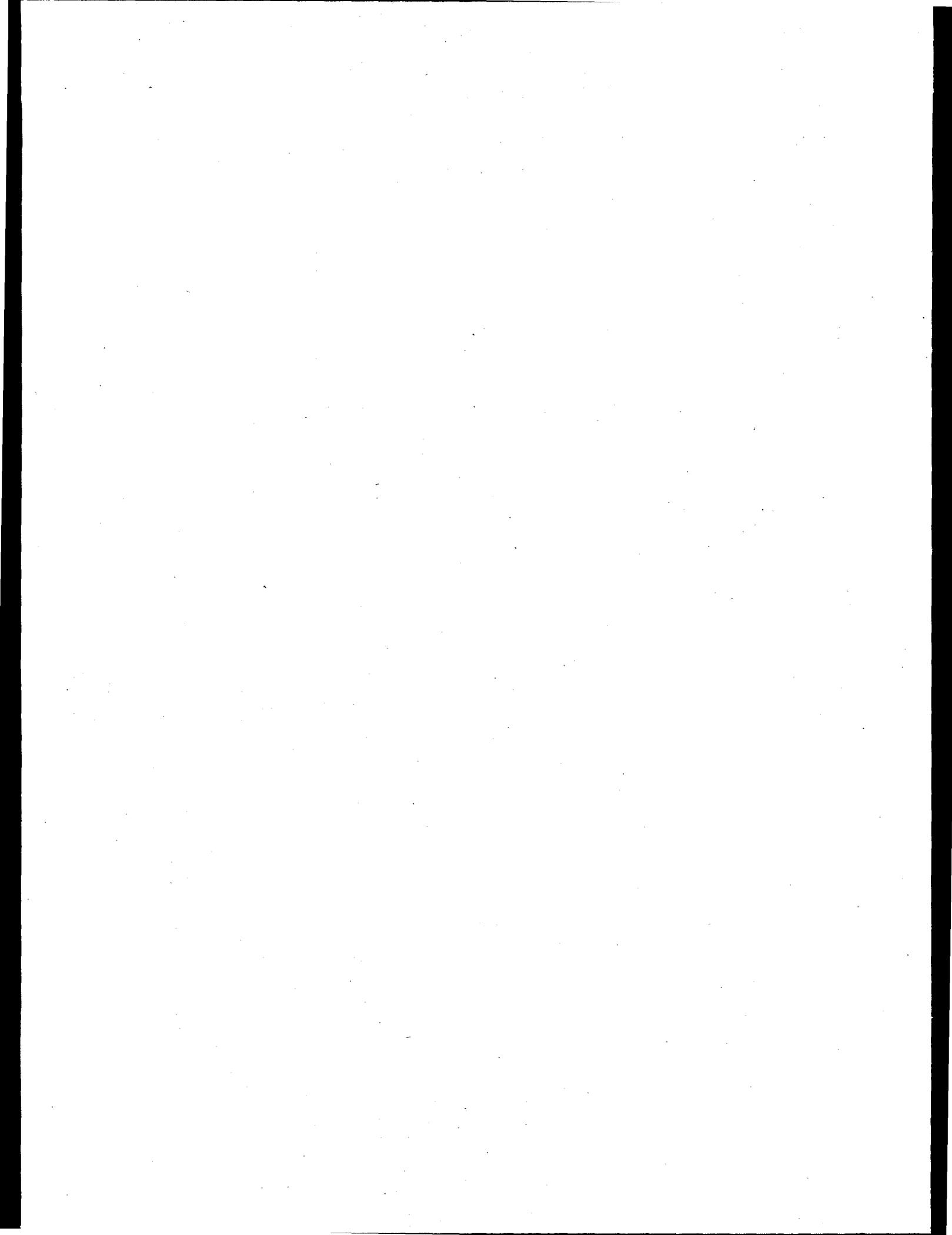
Enhanced Sludge Wash Step	Maximum Settling Rate (cm/hr)	Wt% Solids in Final Compact Sediment ^(a)
Caustic Leach 1	3.4/4.1	14/13
Caustic Leach 2	5.5/2.7	16/12
Water Wash 1	4.4/20	22/13
Water Wash 2	35/14	28/13
Water Wash 3	100/25	32/16

(a) Solids concentrations are estimated based on the caustic-insoluble solids concentration in the final solids samples.



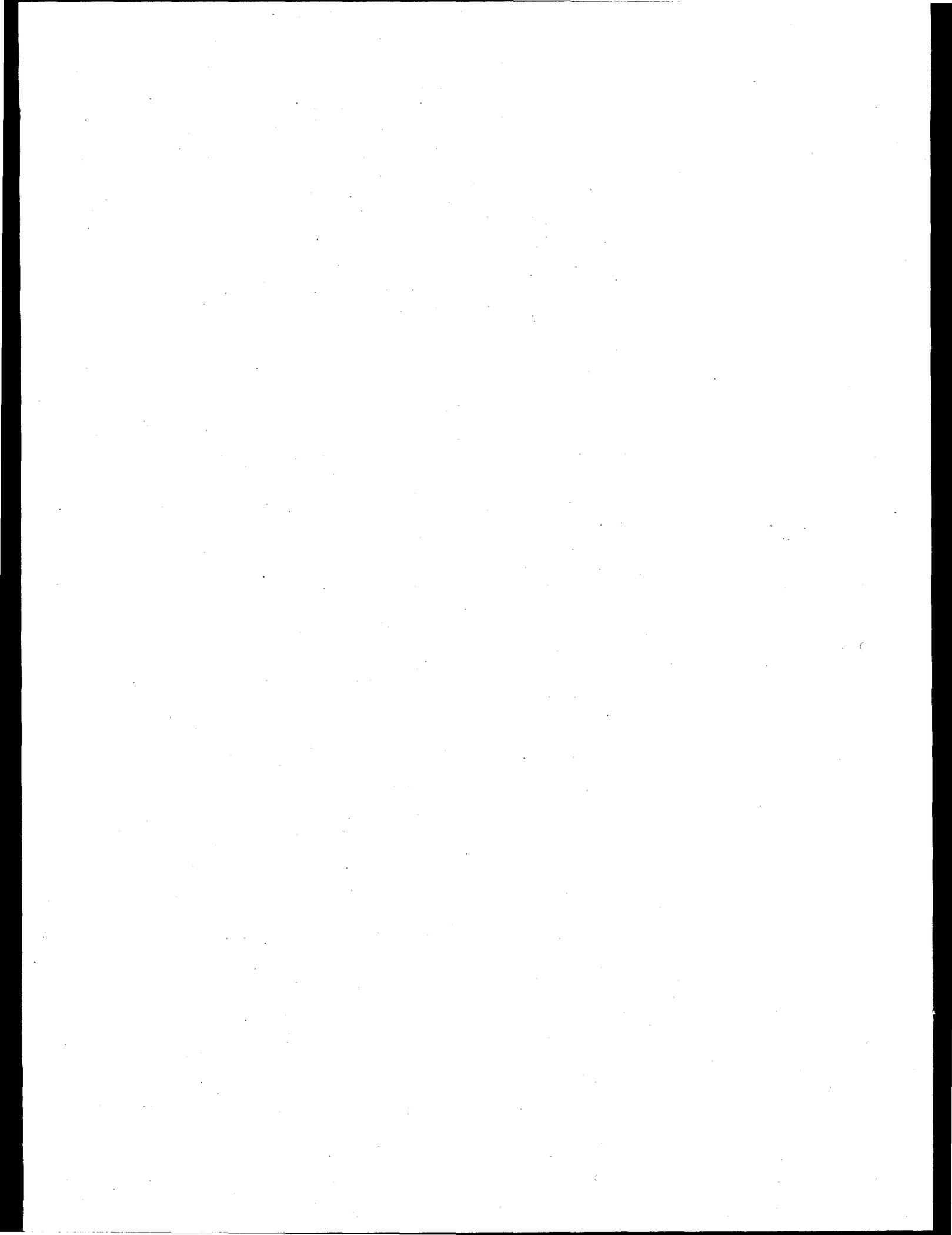
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1.0 Introduction

The U.S. Department of Energy's (DOE's) Hanford Site has 177 underground storage tanks that contain wastes from past nuclear fuel reprocessing and waste management operations and require remediation. The Tank Waste Remediation System (TWRS) is responsible for this remediation effort. The contents of these tanks will be disposed of either as high-level waste (HLW) in a deep geologic repository or as low-level waste (LLW) onsite in near surface burial grounds. Because the cost to dispose of the HLW fraction is expected to be high, the waste may be pretreated before being immobilized to minimize the quantities of HLW generated.

Hanford's tanks contain a mixture of supernate, water-soluble salt cake, and water-insoluble sludge. The salt cake and supernate will be processed to remove cesium, and possibly technetium, and then immobilized as LLW. The tank sludges, on the other hand, contain the bulk of the radionuclides and will be disposed of as HLW. To minimize their impact on the final waste volume, these sludges may be pretreated by enhanced sludge washing.

The enhanced sludge washing process first leaches the sludge with hot caustic (3 M NaOH). This step solubilizes sludge components such as aluminum, phosphorus, and chromium. The sludge is then washed with inhibited water (0.01 M NaOH/0.01 M NaNO₂) to remove the added sodium as well as other water-soluble ions. The TWRS process flowsheet assumes caustic leach factors (fraction of water insoluble component removed by enhanced sludge washing) of 0.6, 0.1, and 0.7 for aluminum, phosphorus, and chromium, respectively (Orme 1996). These components are removed to decrease the volume of HLW generated and improve the quality of the final waste form produced. The transuranic elements (primary alpha emitters) and ⁹⁰Sr (primary beta emitter) are not solubilized during enhanced sludge washing and should remain with the leached solids and be incorporated into the HLW.

During each step in the enhanced sludge washing process, solid/liquid separation techniques will be required. A leading candidate being considered for these separations is gravity settling. To be considered a viable separation technique, gravity settling must provide a high degree of supernate clarification and sludge compaction in an acceptable period of time. The TWRS in-tank pretreatment planning case assumes that sludges settle in a double-shell tank in 1 month (rates between 1-2 cm/hr), and the final compacted solids contain 20 wt% solids (Orme 1996). In addition, gravity settling should be capable of separating the transuranic (TRU) radionuclides from the liquid phase to assure that the LLW generated from these liquids is below the NRC Class C limit of 100 nCi/g (10 CFR 61).

Recently, DOE elected to privatize several aspects of the TWRS efforts. This privatization has been divided into two phases. Phase 1 will be a Proof-of-Concept/Commercial Demonstration Phase and will involve the pretreatment and LLW vitrification of approximately 6-13 percent of the total waste using a pilot-scale system. Phase 1 also allows for immobilization of a fraction of the HLW sludges if the privatization contractor elects to do so. Phase 2 will be the Full-Scale Production Phase. Facilities will be sized so all of the remaining waste from the 177 tanks can be processed and immobilized by the year 2018.

In the TWRS Privatization Request for Proposal, the DOE specified a concentration range envelope in which the Phase 1 sludge for HLW immobilization should fall (Envelope D). At the commencement of Phase 1 of privatization, the contractors also were to be provided with samples of actual sludge that would be within this envelope. Under the current technical baseline, the sludge from single-shell tank C-106 would be processed as part of HLW sludges of Phase 1 of Privatization, if the contractors elect to do so. Sludge from tank C-106 was selected as the source material to be shipped to the contractors as representative of the HLW envelope.

This report describes the preparation of approximately 3 kg of tank C-106 contractor material. To define the sludge processing requirements, a screening test was performed with a 15-gram sample of C-106 before the processing of the 3 kg of the contractor material. Both a simple water wash with dilute sodium hydroxide (0.02 M Na⁺) and enhanced sludge washing (as described above) were performed on the sludge sample. Based on the results of this screening test, DOE-Richland Operations Office (RL) elected to perform enhanced sludge washing on the contractor C-106 sample. In both the screening and bench-scale testing, settle/decant was used as the means of solid/liquid separations during each stage of the enhanced sludge washing process.

This report will compare the results of the screening and bench-scale testing. The quantities of both nonradioactive elements and radioactive isotopes removed during the various stages of the enhanced sludge wash will be presented. The settling rates and final compaction of the sludge as well as the TRU and ⁹⁰Sr separation efficiencies are also described. This report will not attempt to compare the final sludge product to the Envelope D specification or describe the entire life cycle of the C-106 sludge from sampling to shipment to the privatization contractors as this has been provided elsewhere.^(a) Furthermore, DOE-RL and the Project Hanford Management Contractors have not yet made a decision on what pretreatment will be implemented before the HLW sludge is transferred to the private contractors. Thus, these data may not be applicable to operations scale-up.

(a) Urie, M. W., *Tank Waste Remediation System (TWRS) Privatization Contractor Samples, Waste Envelope D Material, 241-C-106, Analytical Summary Report*, PNNL-draft, November 1996.

2.0 Experimental Methods

The bench-scale enhanced sludge washing and settle/decant for the contractor samples of the C-106 material was performed using the Sludge Pretreatment Demonstration (SPD) apparatus. A brief description of the equipment and the testing performed are described in the sections below.

2.1 Equipment Description

The SPD apparatus consists of two processing tanks and three chemical holding tanks connected by stainless steel tubing with valves and pumps to facilitate transfer of test materials. This equipment was in the 324 Building C-cell with supporting equipment in the C-cell operating gallery. The test equipment design is shown in Figure 2.1, the process flow diagram for the sludge pretreatment for the TWRS privatization contractor samples.

2.1.1 Tanks

The first processing tank is the sludge receipt tank, C-202, which was used for retrieval and sludge washing and leaching functions. This 8-liter tank was equipped with an agitator, a heater, thermocouples for temperature monitoring, and inlet and outlet lines. A port on the top of the tank is used to transfer the sludge into the equipment. A funnel was used to assist the transfer of the tank waste sludge sample into the sludge receipt tank. The temperature of the tank contents can be controlled to between 25°C and 110°C during chemical processing of the sludge. To reduce the effects of evaporation, vapors from this tank and the sludge settler are passed through a condenser and demister. The collected liquid is then allowed to drain back into the tanks.

The second processing tank is the sludge settler, C-201, which is approximately 10 cm in diameter and 1 m tall. The sludge settler is constructed of polysulfone, a transparent polymer resistant to boiling caustic and radiation. A ruler, visible from the cell window, was attached to the column so that 0 inches was near the top of the column and 36 inches (91 cm) was at the bottom. The ruler was used for observation of the solids/slurry and slurry/liquid interface levels and for the determination of volume in the sludge settler. The tank's temperature is controlled to between 25°C and 85°C by circulating water from a hot water bath through a cylindrical annulus surrounding the sludge settler. Penetrations through the top flange allow the insertion of the sample tube and the transfer of materials. The sample tube is mounted on a linear motion apparatus that enabled the end of the tube to be placed at accurate axial locations within the sludge settler. Axial supernatant location samples were then obtained at these locations. This same sample tube is also used to pump supernatant out of the top of the column and into the bottom of the column enabling the sludge to be refluidized following a settling test. Once it is refluidized, it can then be transferred back into the sludge receipt tank for continued chemical processing.

The dimensions of the settling column were based on an understanding of the effects of geometry on the sludge settling characteristics. Small settling systems can provide an accurate measure of free and

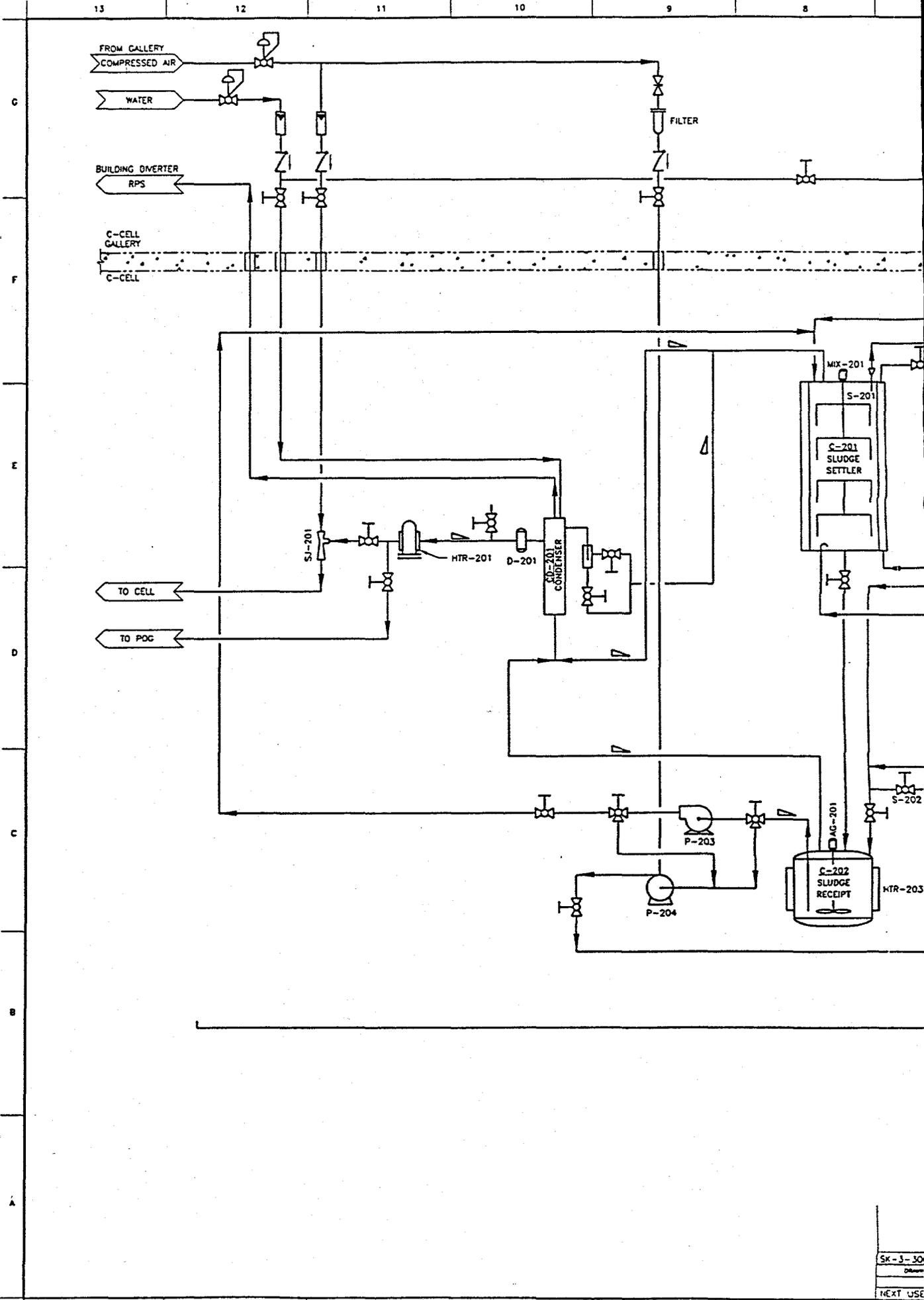
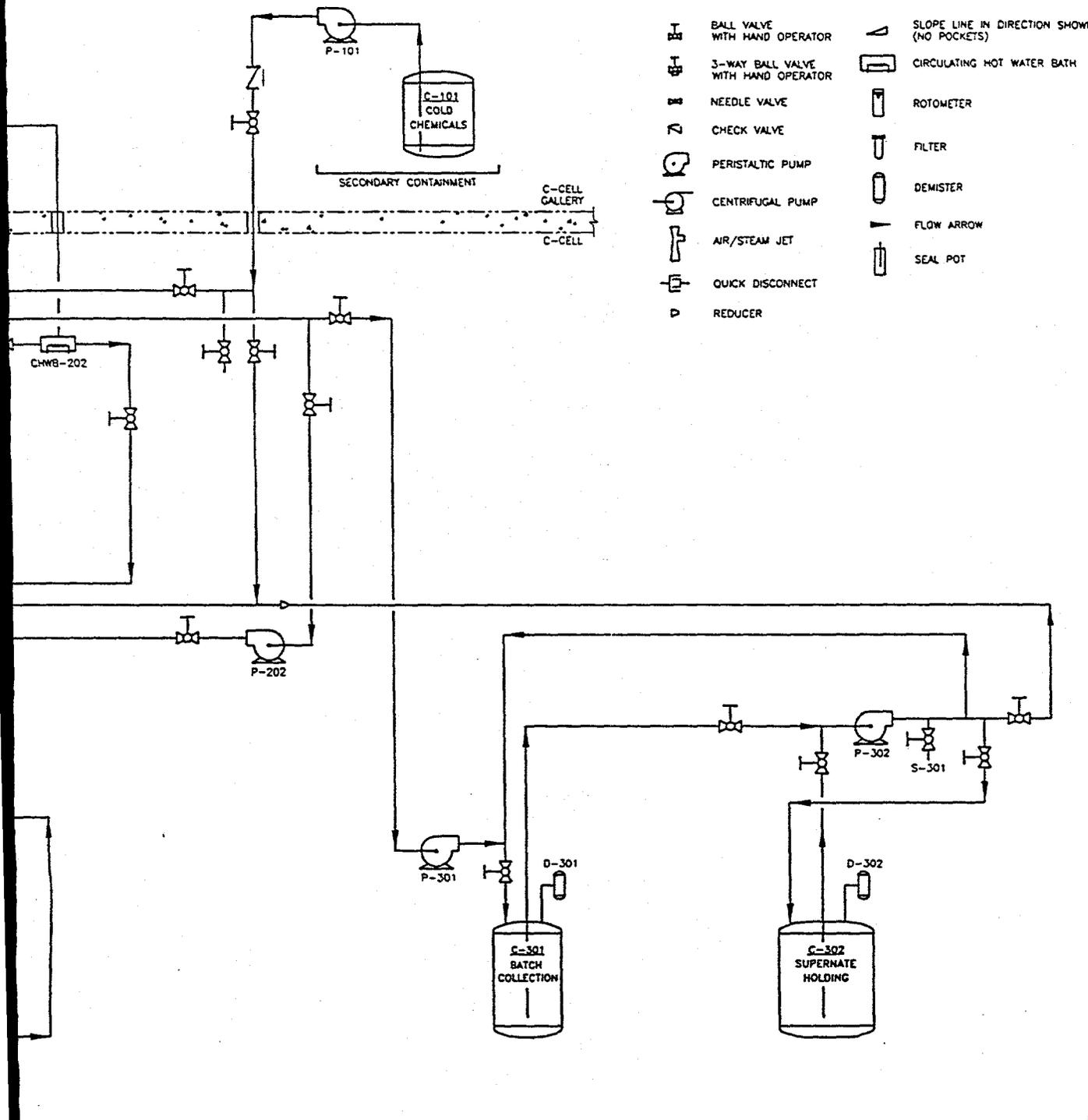


Figure 2.1. Test Equipment Design

SK-3-30
 DIM
 NEXT USE

LEGEND

- ⊘ BALL VALVE WITH HAND OPERATOR
- ⊘ 3-WAY BALL VALVE WITH HAND OPERATOR
- ⊘ NEEDLE VALVE
- ⊘ CHECK VALVE
- ⊘ PERISTALTIC PUMP
- ⊘ CENTRIFUGAL PUMP
- ⊘ AIR/STEAM JET
- ⊘ QUICK DISCONNECT
- ⊘ REDUCER
- ▲ SLOPE LINE IN DIRECTION SHOWN (NO POCKETS)
- ◻ CIRCULATING HOT WATER BATH
- ⊘ ROTOMETER
- ⊘ FILTER
- ⊘ DEMISTER
- ⊘ FLOW ARROW
- ⊘ SEAL POT



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hindered settling that can be applied directly to larger systems if the sides of the settling column do not influence the settling rate. The column diameter needed to be large enough to prevent these wall effects. The column height also needed to be tall enough to allow accurate measurement of the sludge settling rates. Because large quantities of sludge are not readily available, the height and diameter must be balanced. Standard sludge settling methods for scale-up have used a 10-cm-diameter, 1-m-tall column (Greenberg 1992). Furthermore, rules of thumb indicate that if the flocs are less than 1 mm, wall effects will not exist for this particular geometry (Osborne 1990). Floc sizes are thought to be significantly smaller than 1 mm for tank sludges (see particle size distribution data in, for example, Lumetta et al. 1996b).

To assure that wall effects were indeed negligible for the sized column, a physical simulant (kaolin clay) and a chemical simulant (C-106 simulant) were studied at Washington State University with 10 and 30-cm-diameter columns, both 1 m tall. Results showed no statistical difference between these two sizes of columns. The final report of this study is found in Appendix A.

The cold chemical tank, C-101, was used to store caustic (10 M NaOH) or inhibited water (0.01 M NaOH and 0.01 M NaNO₂), which was used for the retrieval, solids resuspension, wash, and leach steps. This tank is in the operating gallery and is used with a metering pump for accurate measurement of the caustic and water added to the in-cell tanks.

The batch collection tank, C-301, and the supernate holding tank, C-302, were both used to store liquid separated from the solids by gravity settling.

2.1.2 Pumps

The pumps used to move slurry and liquid between processing stations were peristaltic pumps of various sizes. These pumps had a head that rotated against a flexible tube, thereby generating the pumping action. The pumps could be operated at any speed setting (within its range), in either forward or reverse direction, and in one of several modes. They can be set to pump at a given speed, flow rate, or to pump a set volume and shut off. The sludge was generally pumped at greater than 3.8 liter/min to prevent its settling during transfers. The supernatant, in contrast, was decanted from the settled sludge at 200 mL/min to prevent its refluidizing.

2.1.3 Valves and Tubing

The tanks and pumps described above are connected to each other through a network of stainless steel tubing mounted on a steel framework attached to a table. The table sits in a secondary containment pan on the floor in the 324 Building C-cell. Outlets from each tank come from a dip tube at the bottom of the tank while the inlets are in the top of the tank. Valves in the tubing allow each tank and pump to be connected/disconnected from each other so the contents of the tanks can be transferred to other tanks, sampled, additions made, etc. All of the tubing fittings are stainless steel Swagelok fittings. All in-cell equipment has been designed or modified for operation with master slave manipulators.

2.1.4 Instrumentation and Data Acquisition System

Liquid level and density were measured on the in-cell tanks using dip legs connected to differential pressure transducers. Temperature was measured using calibrated thermocouples. This instrumentation was connected to a data acquisition system in the C-cell operating gallery. Results were monitored and saved throughout the test. Unfortunately, the dip legs in the sludge receipt tank became plugged during testing, and the density and liquid level could not be measured.

2.1.5 Photographic Data Recording

A video camera was mounted on a Master Slave Manipulator in C-cell during all of the settling tests. The camera was turned on before the start and turned off just after the end of the settling test. All of the settling data were thus recorded on videotape using time-lapse photography. This system also provided a means of checking what was seen through the cell window by looking at a monitor. This was helpful for distinguishing color and parallax error.

2.2 Sludge Washing and Gravity Settling Test

This section of the report summarizes the actual step-by-step activities conducted during the TWRS Privatization Contractor Sample enhanced sludge washing and gravity settling Test with C-106 waste. The sludge preparation, two caustic leaches, and three inhibited water washes were performed with the grab sample in the 324 Building radiochemical engineering cell. The workplace copy of the operating procedures, including noted observations, and the laboratory record book (BNW 55983) contain the detailed description of the actual test activities. An overview of the processing steps and target conditions are shown in Table 2.1.

Table 2.1. Summary of Target Processing Conditions for Tank C-106 Bench-Scale Sample

Condition	Caustic Leaches	Water Washes
Total Performed	2	3
Initial Solids Concentration	5 wt%	5 wt%
Chemical Additions	3M NaOH	Corrosion Inhibited Water
Processing Temperature	100°C	Ambient
Processing Time	5 hours	30 minutes
Settling Temperature	85°C	Ambient

2.2.1 Waste Sample Preparation

The first procedure performed in the 324 Building C-cell, after transfer of the tank C-106 waste sludge sample into the cell, is the Retrieval Wash and Settling Test, Procedure number D7F64/F-27. Only the parts of this procedure that are used to transfer the tank waste sample into the sludge receipt tank and prepare it for the next wash were performed. The retrieval wash settling test was not performed as determined by DOE-RL. The procedure was started on July 29, 1996, and completed on August 1, 1996. Figure 2.2 shows an overview of the retrieval sludge sample preparation. A detailed step-by-step description of the activities is given in Appendix B.

The tank C-106 sludge sample was obtained using the grab method, obtaining only the upper layers of the sludge in the tank. The 20 bottles were transferred to PNNL 325 Building and combined to make a single composite. The sample for the screening test (Lumetta et al. 1996a) and for the processing was taken from this composite. The tank C-106 waste sample received from the 325 Building was transferred

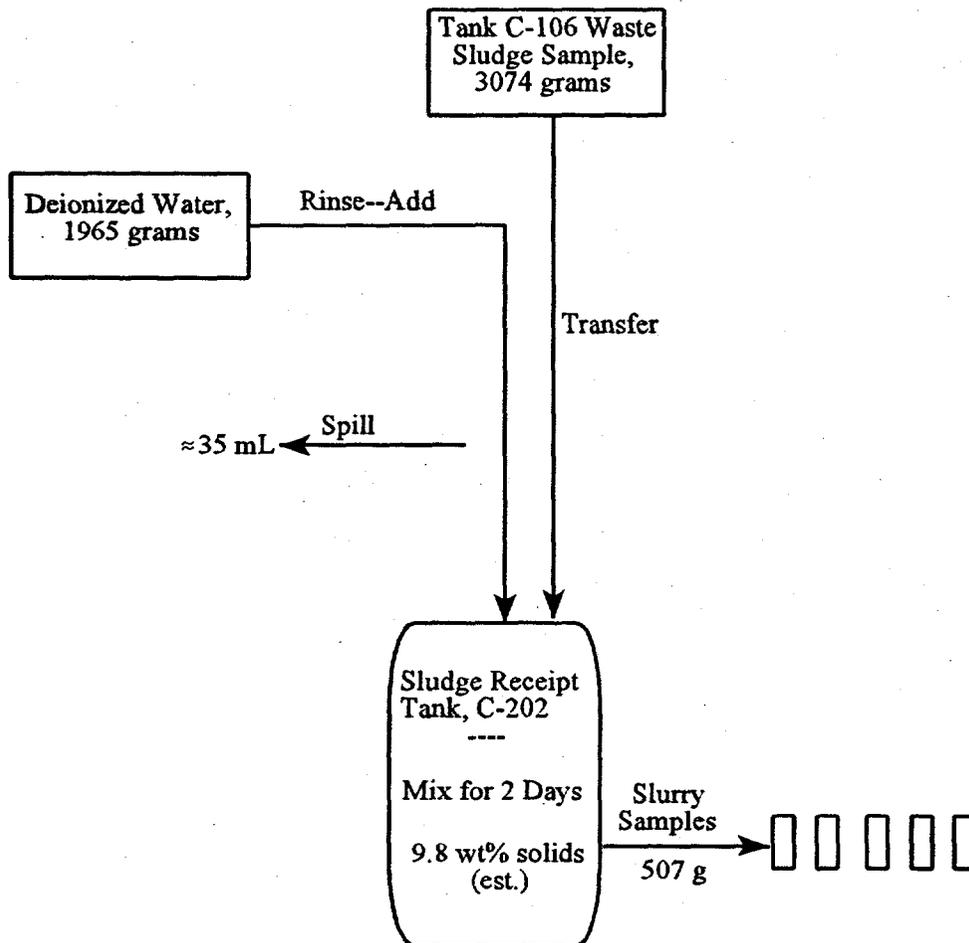


Figure 2.2. Overview of Sample Preparation

into the 324 Building C-cell, weighed, and transferred into the sludge receipt tank. Only 3074 grams of sludge out of a total of 3900 grams from tank C-106 were used in the tests. This amount was limited by the capacity of the sludge settler. When the tank C-106 sludge was transferred to the sludge receipt tank through the funnel, the sludge was so thick that it would not flow through the funnel opening. A steel rod was used to stir it enough to get it to pass through the funnel. The sludge was very thick and sticky (about the consistency and color of chocolate pudding). Deionized water (1780 g) was used to rinse the sludge sample containers and the funnel and was added to the sample in the sludge receipt tank. After the first rinse, small globules of ~0.5-cm-diameter and smaller remained in the bottom of the container. After two more rinses, all material was transferred into the sludge receipt tank. The resulting slurry was estimated to be 10.1 wt% water-insoluble solids. This solids concentration is based on the results of the screening test indicating that 16 wt% of the original sludge was water-insoluble solids. The slurry was then mixed for two days, and five samples of approximately 100 grams each of the slurry were obtained. Of these samples, four were sent for chemical, radiochemical and physical property analysis, and one was archived.

2.2.2 First Caustic Leach and Settling Test

The first caustic leach and settling test, procedure number D7F64/F-38, was performed following the retrieval sample preparation. This procedure started on August 1, 1996, and was completed on August 7, 1996. Figure 2.3 shows an overview of the first caustic leach and settling test. A detailed step-by-step description of the test is given in Appendix B.

Approximately 2340 grams of 10 M caustic (NaOH) was added to the slurry in the sludge receipt tank for the first caustic leach. This amount of caustic was estimated to have produced a 3.4 M NaOH solution (measured to be 2.7 M free hydroxide by titration) at 5.9 wt% caustic-insoluble solids. The slurry was then mixed while heating to 100°C and then mixed at 100°C for 5 hours. It was then transferred to the sludge settler, and the gravity settling test was performed at 85°C.

The solids concentration (in wt%) for the first caustic leach and all subsequent processing steps is based on caustic-insoluble solids. The amount of liquid to be added to the sludge during each processing step is based on the caustic-insoluble solids present in the sludge. However, the mass of these solids is determined only after the test is complete. Therefore, the amount of solids used to determine liquid volumes was estimated from the screening test results. The screening test showed that 13% of the initial sludge was caustic-insoluble solids (the remaining material being either water or caustic soluble solids). Following the bench-scale tests, the caustic-insoluble solids concentration of the sludge used was found to be 14.2% instead of 13%. This difference resulted in the solids concentrations in each enhanced sludge washing step being higher than the targeted value of 5%.

The weight of caustic-insoluble solids for the bench-scale test sludge was determined in the following way. The wt% solids of the final slurry was measured by drying (at 105°C) after all enhanced sludge washing steps (14.8%) were completed. The mass of soluble salts (primarily sodium and oxalate), which remain in its supernatant (3.62%) was subtracted from the total wt% solids. The total weight of insoluble solids was then calculated from the total mass of final slurry to be 392 g (or 14.2 wt% of the initial

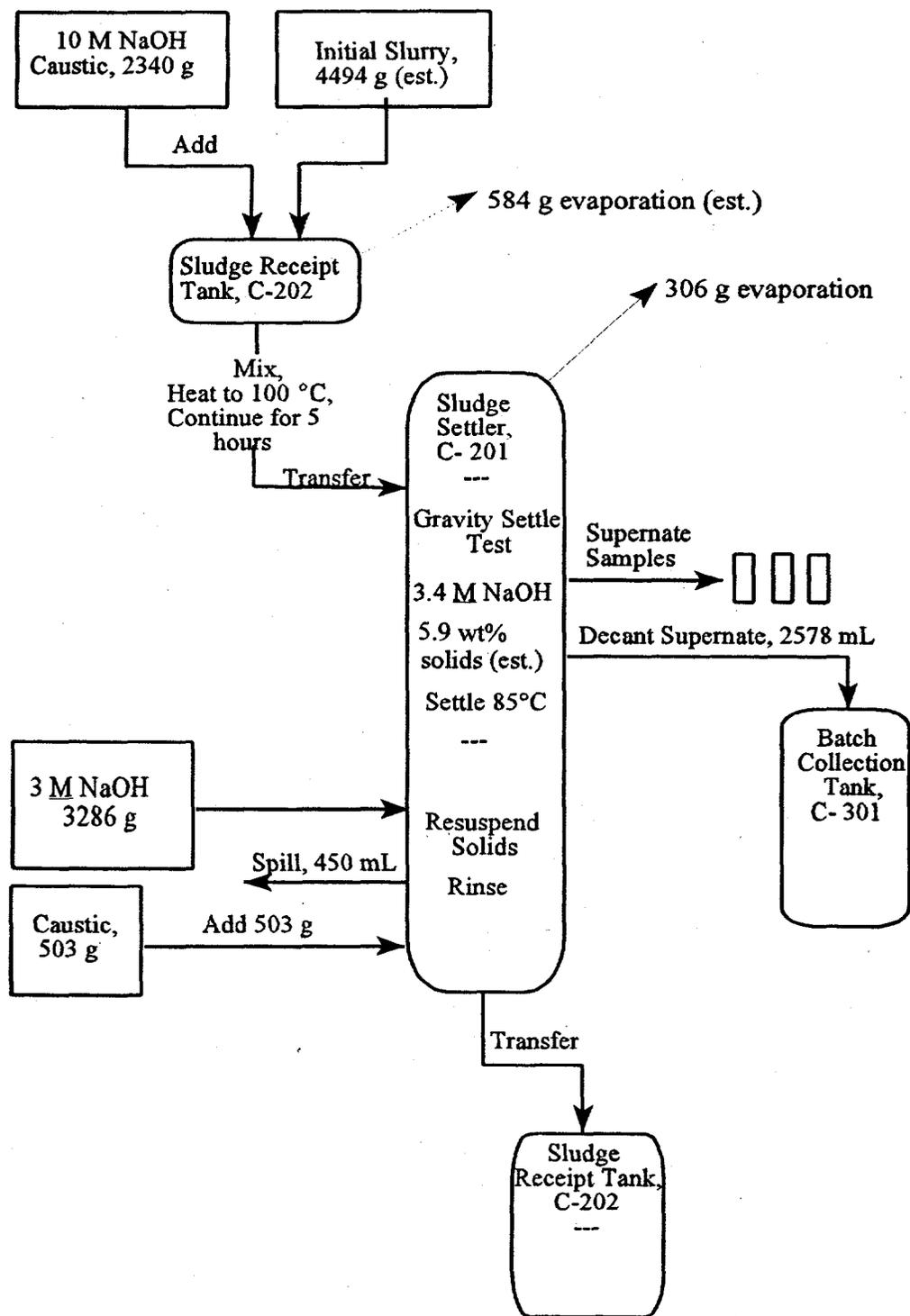


Figure 2.3. Overview of First Caustic Leach and Settling Test

sludge). This approach assumes that no solids were lost during any step in the process, and no soluble salts remained in the sludge after the first caustic leach. Although these assumptions are not entirely correct, it provides a constant basis on which to compare the steps of enhanced sludge washing. The wt% solids at each step was then determined by dividing the caustic-insoluble solids by the estimated total weight of slurry.

Following the gravity settling test, difficulties obtaining the three axial supernate samples were resolved by replacing the flexible hose on the sample tube line. Then three axial supernate samples were obtained. After the samples were obtained, the supernate was decanted into the batch collection tank.

A total of 3286 grams of a 3 M caustic (NaOH) solution was prepared for addition to the solids in the sludge settler. Approximately 500 mL of this caustic was added to the solids in the sludge settler. The solids were resuspended, and the resulting slurry was transferred to the sludge receipt tank. The remaining caustic was added to the sludge settler and recirculated to rinse the settler. During that recirculating rinse, the tubing in pump P-202 split, and about 450 mL of caustic were lost. Little or no solids were lost. After replacing the hose, additional caustic (503 grams) was added. The sludge settler was rinsed, and the caustic was transferred to the sludge receipt tank.

2.2.3 Second Caustic Leach and Settling Test

The second caustic leach and settling test, procedure number D7F64/F-39, was performed following the first caustic leach and settling test. This procedure started on August 7, 1996, and was completed on August 9, 1996. Figure 2.4 shows an overview of the second caustic leach and settling test. A detailed step-by-step description of the test is given in Appendix B.

Caustic had been added to the slurry at the end of the first caustic leach and settling test. The slurry contained approximately 6.4 wt% solids (based once again on total caustic-insoluble solids divided by the estimated mass of the slurry) and a NaOH concentration of 3.2 M. The slurry in the sludge receipt tank was mixed while heating to 100°C. The slurry was then mixed at 100°C for 5 hours and transferred to the sludge settler. Immediately after the transfer, the gravity settling test was performed at 85°C.

Following the gravity settling test, three axial supernate samples were obtained, and the supernate was decanted to the batch collection tank.

Part of the 3164 grams of inhibited water (0.01 M NaOH/0.01 M NaNO₂) for the next water wash and gravity settling test was added to the slurry in the sludge settler, and the solids were resuspended. This slurry was then transferred to the sludge receipt tank. Remaining inhibited water in the cold chemical tank was transferred to the sludge settler. The sludge settler was rinsed by recirculated the water. The rinse water was transferred to the sludge receipt tank, and the resulting slurry was mixed with the agitator.

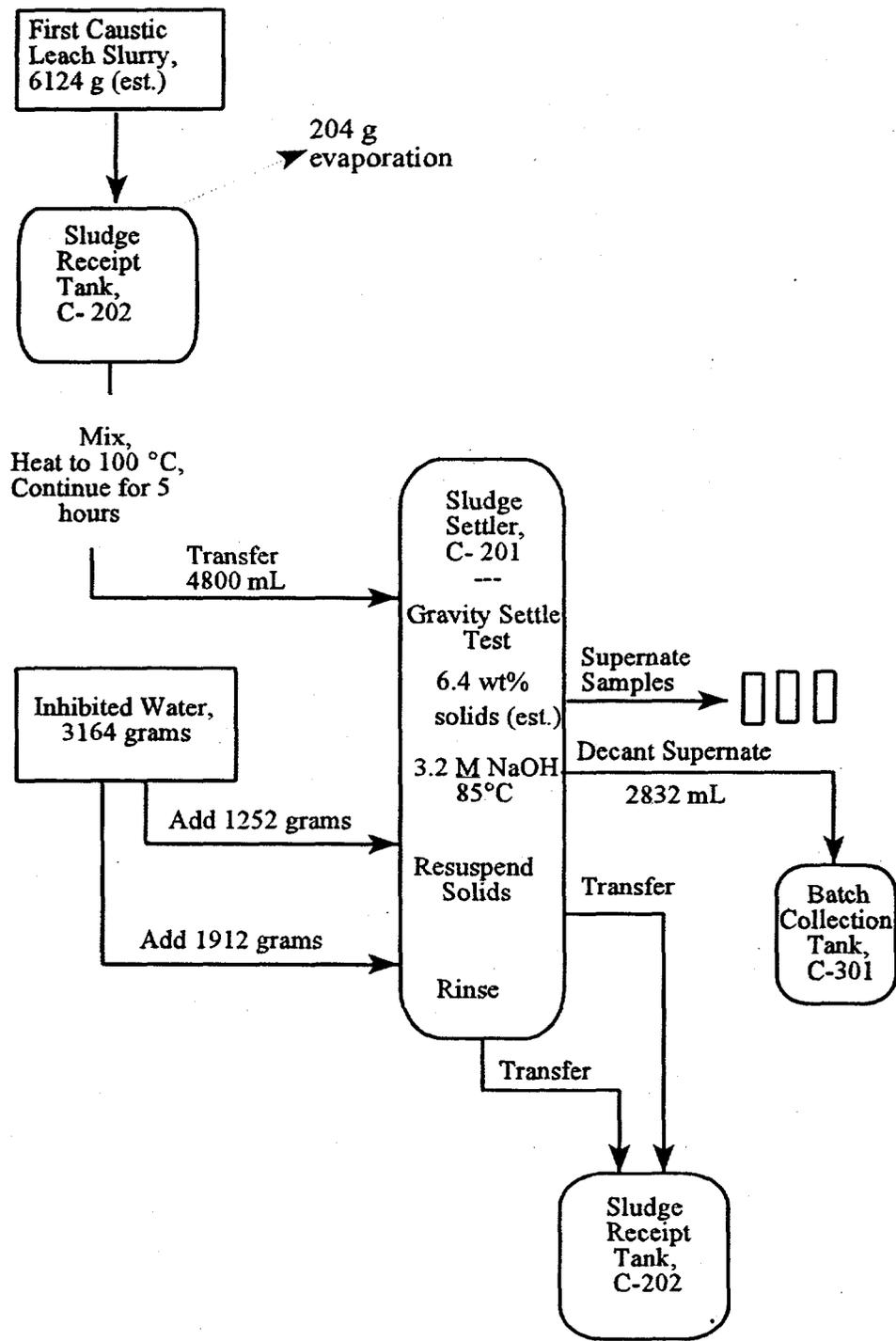


Figure 2.4. Overview of Second Caustic Leach and Settling Test

2.2.4 First Water Wash and Settling Test

The first water wash and settling test, procedure number D7F64/F-40, was performed following the second caustic leach and settling test. One gravity settling test was performed following the first water wash. This procedure started on August 9, 1996, and was completed on August 12, 1996. Figure 2.5 shows an overview of the first water wash and settling test. A detailed step-by-step description of the test is given in Appendix B.

The slurry in the sludge receipt tank was cooled to ambient temperature and then transferred to the sludge settler. The first water wash gravity settling test was then performed at 6.9 wt% solids.

Following the gravity settling test, three axial supernate samples were obtained. The supernate was decanted to the batch collection tank.

Part of the 3700 mL of inhibited water for the second water wash was added to the slurry in the sludge settler, and considerable foaming was observed as the solids were resuspended and the slurry was transferred to the sludge receipt tank. The remaining inhibited water was then added to the sludge settler as a rinse and then transferred to the sludge receipt tank.

2.2.5 Second Water Wash and Settling Test

The second water wash and settling test, a repeat of procedure number D7F64/F-40, was performed following the first water wash and settling test. A gravity settling test was performed at ambient temperature following this second water wash. This procedure started on August 12, 1996, and was completed on August 14, 1996. Figure 2.6 shows an overview of the second water wash and settling test. A detailed step-by-step description of the test is given in Appendix B.

The slurry in the sludge receipt tank was mixed at ambient temperature. The slurry was transferred to the sludge settler, and the gravity settling test was performed at ambient temperatures and an estimated 7.2 wt% solids. Following the gravity settling test, three axial supernate samples were obtained. The supernate was decanted to the batch collection tank.

Inhibited water was prepared for the next water washing step (3824 g) and part of it was added to the solids in the sludge settler, and the solids were resuspended. During this resuspension, some significant foaming was observed. The resulting slurry was transferred to the sludge receipt tank. The remaining inhibited water was transferred to the sludge settler and recirculated to rinse the sludge settler. During this rinse the drive hose on pump P-202 broke and was replaced. The rinse water was added to the slurry in the sludge receipt tank.

2.2.6 Third Water Wash and Settling Test

The third water wash and settling test, procedure number D7F64/F-41, was performed following the second water wash and settling test. A gravity settling test was performed at ambient temperature

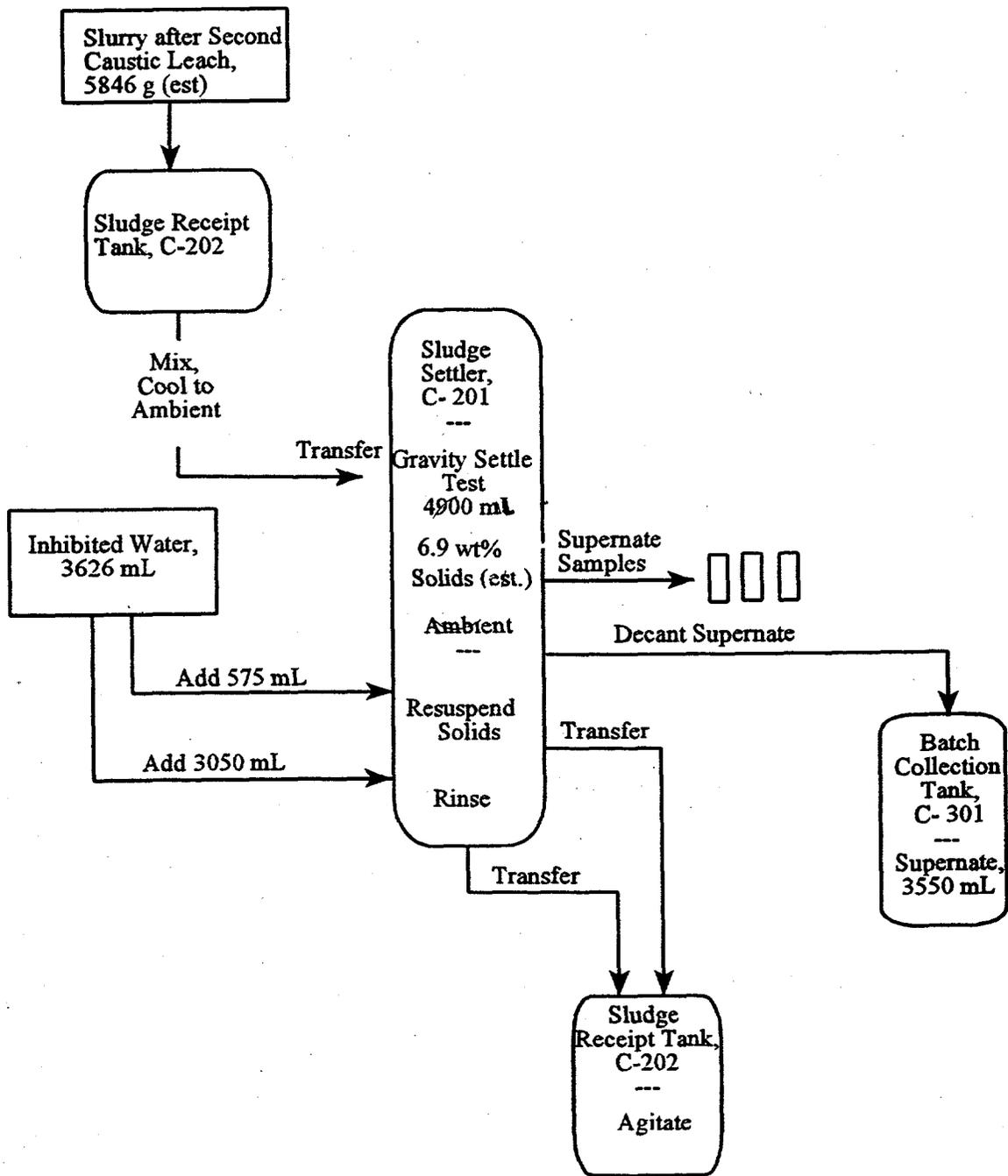


Figure 2.5. Overview of First Water Wash and Settling Test

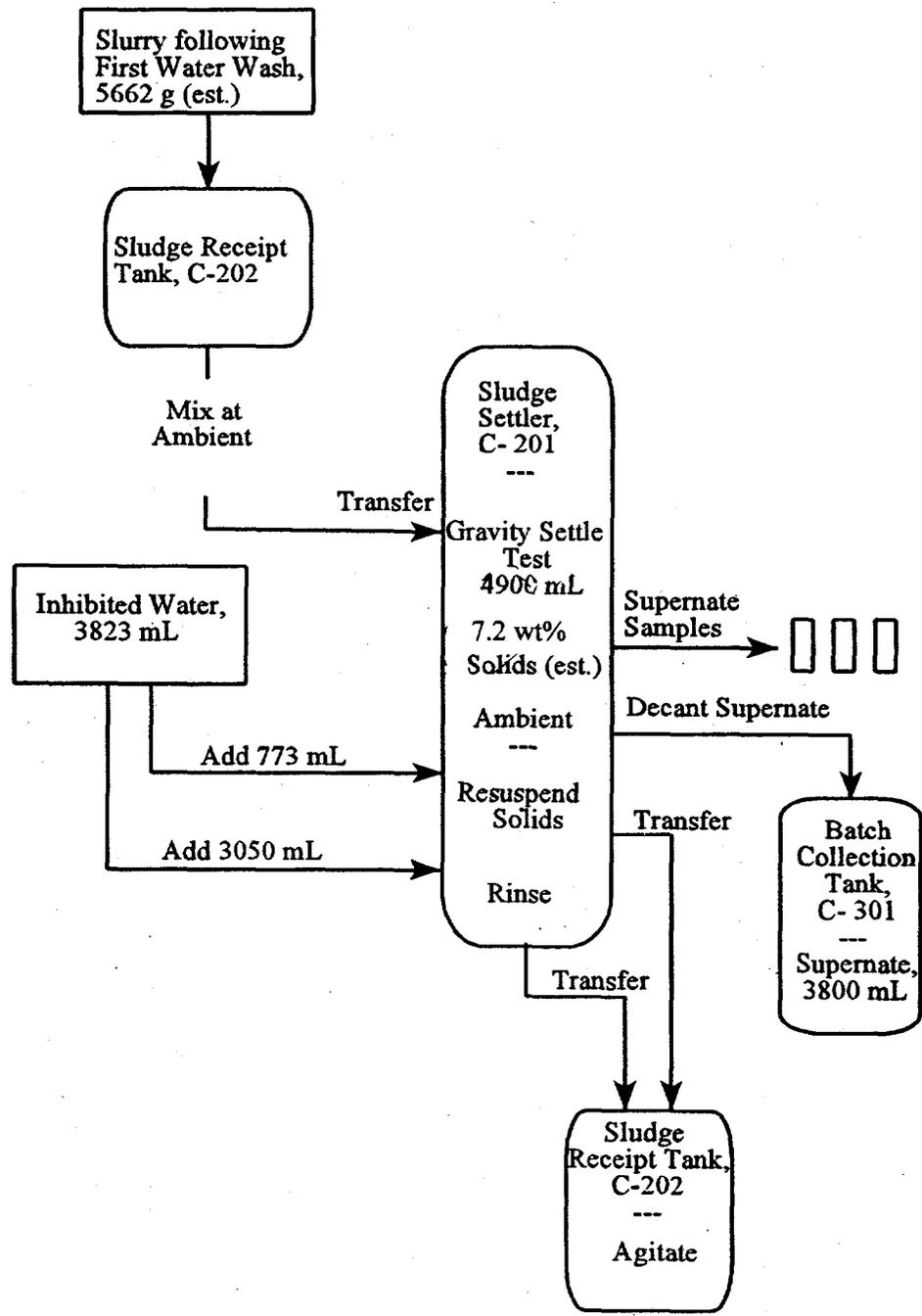


Figure 2.6. Overview of Second Water Wash and Settling Test

following this third water wash. This procedure started on August 14, 1996, and was completed on August 22, 1996, except for the final disposition of liquid in the supernate holding tank, C-302. Figure 2.7 shows an overview of the third water wash and settling test. A detailed step-by-step description of the test is given in Appendix B.

The slurry in the sludge receipt tank was mixed at ambient temperature and transferred to the sludge settler and the settling test was performed at an estimated 7.5 wt% solids. A layer of foam was present on the slurry at the beginning of the settling test, but it dissipated during the settling test. Following the gravity settling test, three axial supernate samples were obtained. The supernate was decanted to the batch collection tank.

2.2.7 Sludge Removal and Disposition

2225 grams of deionized water, used in place of inhibited water, was prepared and added to the solids in the sludge settler. The total volume in the sludge settler was 3135 mL, determined by adding the amount of sludge in the sludge settler with the amount of water added. Solids in the sludge settler were then resuspended and transferred to the sludge receipt tank. Five slurry samples were obtained with a total slurry weight of 364 grams. Four of the five samples were analyzed for chemical, radiochemical and physical property analysis. One sample was saved for archive. The remaining slurry was transferred into two 2-L bottles. The material in these 2-L bottles was transferred to the 325 Building in preparation for its being sent to the privatization contractors. The weight of this material was 3147 grams and contained 14.8 wt% solids upon drying.

2.3 Analyses Performed

Five samples of tank C-106 sludge were taken both before and after the enhanced sludge wash. The initial sludge samples were taken after the sludge was slurried with water and placed in the SPD equipment (see Figure 2.2). The final sludge samples were taken after the third water wash had been decanted and the settled solids were slurried with deionized water (see Figure 2.7). Comprehensive chemical and radiochemical analysis were performed on three of the five samples. Physical analyses along with analyses of the decanted supernatant were performed on the fourth samples. The fifth samples were the archive. A complete description of the analyses performed and the results are provided in Urie (1996).^(a) A fraction of the analyses performed are of interest here and are shown in Table 2.2.

The initial and final slurry analyses were performed on a dried solids basis. The weight percent solids of the initial and final sludge were determined by drying the sample to a constant weight at 105°C per PNNL standard operating procedure PNL-ALO-501. The initial slurry wt% solids used an average of

(a) Urie, M. W., *Tank Waste Remediation System (TWRS) Privatization Contractor Samples, Waste Envelope D Material, 241-C-106, Analytical Summary Report*, PNNL-draft, November 1996.

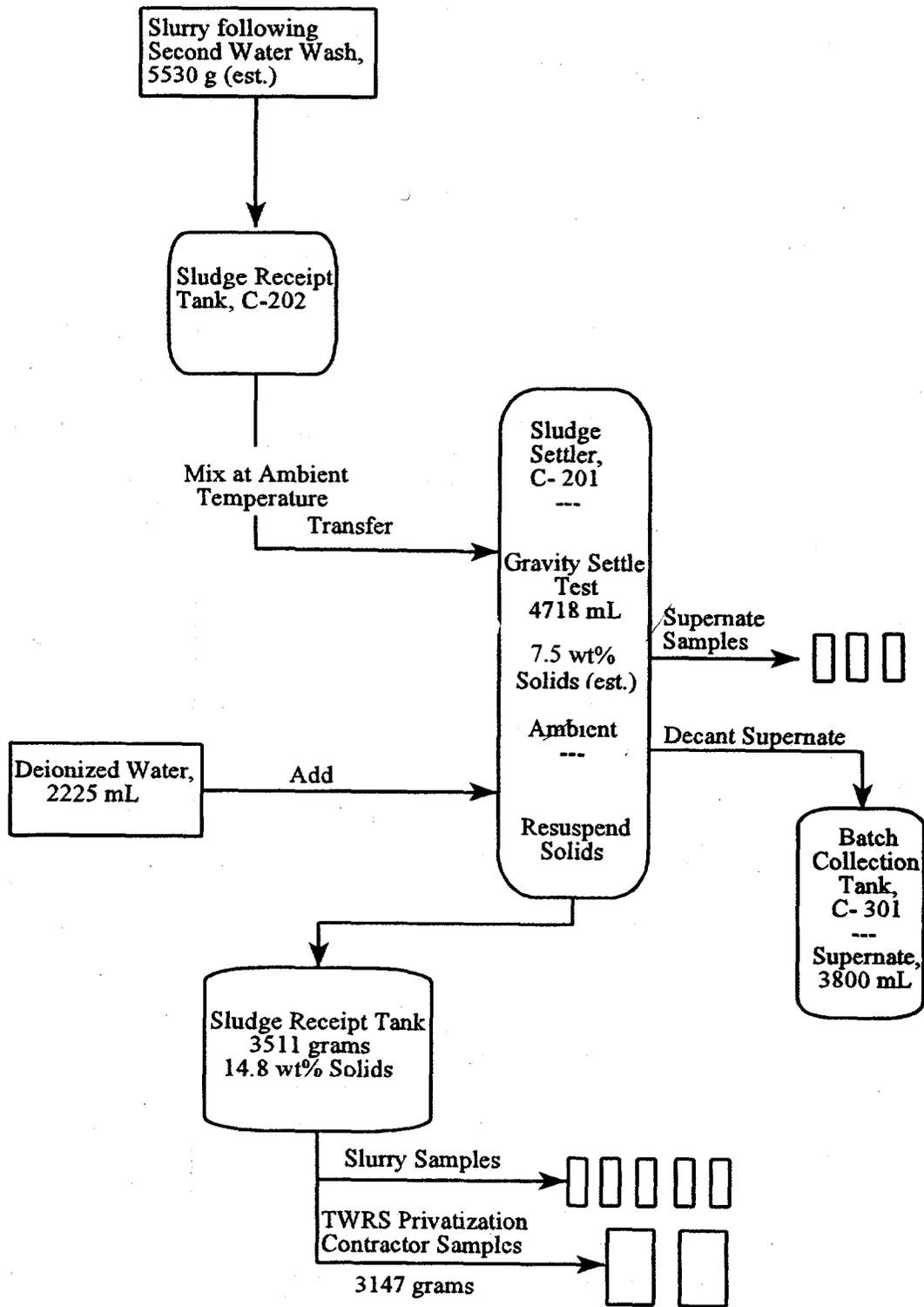


Figure 2.7. Overview of Third Water Wash and Settling Test

Table 2.2. Analyses Performed on Sludges and Supernatants

Supernatant Samples		
Sample ID Number	Sample Taken After Settling of:	Analyses Performed
SPD1-C106-010	Caustic Leach 1	ICP-AES IC Free Hydroxide Total Alpha Total Beta GEA AEA ⁹⁰ Sr Analysis ⁹⁹ Tc Analysis
SPD1-C106-015	Caustic Leach 2	
SPD1-C106-020	Water Wash 1	
SPD1-C106-024	Water Wash 2	
SPD1-C106-029	Water Wash 3	
Slurry Samples		
Sample ID Number	When Sample Taken	Analyses Performed
SPD1-C106-003 SPD1-C106-004 SPD1-C106-005	Initial Sludge after Slurrying with Deionized Water and Mixing	Chemical and Radiochemical Analyses: ICP-AES IC TOC Total Alpha Total Beta AEA GEA ⁹⁰ Sr Analysis ⁹⁹ Tc Analysis
SPD1-C106-002		Physical Analyses: Weight Percent Solids Slurry Density
		Decanted Supernatant: ICP-AES & IC
SPD1-C106-047 SPD1-C106-048 SPD1-C106-049	Final Product after Enhanced Sludge Washing Process	Chemical and Radiochemical Analyses (as above)
SPD1-C106-046		Physical Analyses (as above)
		Decanted Supernatant: ICP-AES & IC

the screening test and bench-scale analytical results. The final slurry wt% solids used only the bench-scale analytical results because the bench-scale and screen test samples were processed slightly differently. Slurry densities were measured for the initial and final samples using this same procedure. The decanted supernatant densities were estimated from the sample compositions.

Supernatant samples were also taken during each stage of the enhanced sludge washing process. These samples were taken from the sludge settling column after the sludge was allowed to settle. The samples analyzed were taken within an inch of the middle of the supernatant. Analyses performed on these samples are also provided in Table 2.2.

The major metallic elements were determined by inductively coupled plasma/atomic emission spectroscopy (ICP-AES). This method provides sufficient information to quantify the effects for each step of the enhanced sludge washing process on such elements as aluminum, phosphorus, chromium, iron, silicon, and sodium.

Major soluble anions were determined by ion chromatography (IC), including anions such as chloride, fluoride, nitrate, nitrite, sulfate, phosphate, and oxalate. The sludge samples were water leached to provide samples for IC analyses. Free hydroxide concentration was measured on the supernatant samples. This provided a means of comparing the quantities of caustic added during the leaching process and the caustic removed during the washing steps. Total carbon and total organic carbon (TOC) were also provided for the sludge samples.

Radionuclide analysis included total alpha and alpha spectroscopy (AEA) for measuring TRU elements, total beta, ^{99}Tc , and ^{90}Sr to measure the beta emitting isotopes, and gamma energy analysis (GEA) to measure the gamma emitting isotopes. Established PNNL Analytical Chemistry Laboratory procedures were used for all analyses performed, with the exception of oxalate IC analysis.

Physical property analysis of interest performed on the final and initial sludges include density measurements and wt% solids, both essential components to complete the mass balance. A portion of the physical property samples (both initial and final tank C-106 slurry material) were centrifuged, and the supernate was decanted. The supernate was then analyzed for metals and anions using ICP-AES and ion chromatography, providing a means of measuring the water soluble portion of the slurry.

3.0 Results and Discussion

The results of the bench-scale washing and settling tests are discussed below in Sections 3.1 and 3.2, respectively.

3.1 Results of Enhanced Sludge Washing

Results of the caustic leaching and washing experiments performed on a composite sample of single-shell Tank C-106 sludge are presented in the following sections. A summary of the aluminum, chromium, phosphorus, and sodium removal results is presented in Table 3.1. Tables 3.2, 3.3, 3.5, and 3.7 present the partitioning/leach and wash efficiency measured for the enhanced sludge wash bench-scale test on the non-radioactive components of the sludge. Tables 3.4, 3.6, and 3.8 provide the analogous results on the sludge radionuclides. Table 3.9 provides a comparison between the laboratory-scale enhanced sludge washing screening test in Lumetta et al. (1996a) and these bench-scale results.

Tables 3.2 through 3.4 provide the concentrations of the nonradioactive and radioactive analytes in each of the process streams. These were determined by laboratory analysis. The mass of analyte dissolved in each process step is also presented in these tables. These masses have been corrected for interstitial liquid carried over from previous steps. Tables 3.5 and 3.6 display how the analytes are distributed between the process streams. The percentages shown are the mass of analyte found in each stream divided by the sum of the masses of the analyte for all streams. Finally, Tables 3.7 and 3.8 show the mass recoveries, which can be represented as follows:

$$\text{Recovery} = \frac{\text{Analyte}_{\text{Initial Sludge}}}{\sum \text{Analyte}_{\text{Leached}} + \text{Analyte}_{\text{Residue}}} * 100$$

The mass recovery is the mass of analyte present in the initial sludge compared to the mass of analyte present based on the sum of the mass of analyte leached and the mass remaining in the sludge residue.

3.1.1 First and Second Caustic Leaches

The leach efficiency for the first and second caustic leaches are summarized from Table 3.5 in Table 3.1. Aluminum, chromium, phosphorus, and sodium are the four most significant nonradioactive analytes present in the sludge that are removed by the enhanced sludge washing process. These will be discussed in detail. The remaining analytes are provided for completeness but will not be discussed. Three primary observations were made. The first observation is that the larger fraction of aluminum, chromium, and phosphorus was removed during the first caustic leaching. For example, while there was 30% removal of aluminum in the first caustic leach, there was no measurable aluminum leached during the second. Thus, a second caustic leach appears to provide little benefit to aluminum removal. The second observation is that very little aluminum and chromium were solubilized with the initial water addition,

Table 3.1. Comparison of C-106 Aluminum, Chromium, Phosphorus, and Sodium Removal Efficiencies During the First and Second Caustic Leach Steps

Percentage of Total Analyte in Sludge:	Aluminum	Chromium	Phosphorus	Sodium
Removed during Caustic Leach 1	30	39	27	32
Removed during Caustic Leach 2	<0.1	8	3	N/A
Removed during Initial Water Addition ^(a)	<0.1	0.5	10	22
Percentage of "Water Insoluble" Analyte:	Aluminum	Chromium	Phosphorus	Sodium
Removed during Caustic Leaches	30	47	33	49 ^(b)
Removed per TWRS Flowsheet Assumptions	60	10	70	45

- (a) This is a single water addition and decant rather than a series of water washes, thus these result can only loosely be defined as the "water insoluble" fraction of each component present in the sludge.
- (b) This percentage of "water insoluble" sodium is for all steps of the Enhanced Sludge Washing Process since sodium was significantly removed in the water wash steps as well.

indicating that a high fraction of these analytes are water insoluble. For phosphorus, on the other hand, one-third of the material removed in the first caustic leach can be considered water soluble phosphorus. Similarly, half of the sodium was solubilized in the first water addition indicating that a considerable quantity is water soluble. The third observation is that the leach efficiencies for aluminum and phosphorus were half of the TWRS planning assumptions (Orme 1996). Only sodium and chromium leaching efficiency exceeded the TWRS planning assumptions. Possible explanations for the aluminum and phosphorus include the presence of an insoluble aluminosilicate as suggested by the nearly stoichiometric ratio of silicon/aluminum in the sludge and the presence of caustic insoluble calcium phosphates as suggested by the presence of relatively high quantities of calcium. Aluminosilicate was observed when the samples were evaluated with TEM during the screening test (Lumetta 1996a). Chromium met the TWRS planning assumptions only because the fraction expected to dissolve decreased from 60% to 10% from the 1995 to the 1996 version of the TWRS flowsheet.

The concentration of analytes in the process streams are shown in Table 3.3. Because the insoluble forms of these anions can not be measured, it is not appropriate to discuss the percent removed as can be done with the metals and radionuclide analyses shown in Tables 3.5 and 3.6. Some general trends with regard to the anion data are as follows. There is no detectable chloride in the supernate throughout the enhanced washing steps. Nearly 98% of the nitrite that could be washed from the sludge was removed in the first caustic leach step. The nitrite seen in the water wash steps was added as part of the inhibited water ($0.01 \text{ M NaNO}_2 = 460 \text{ ppm NO}_2^-$). A similar trend exists for sulfate, where 95% of the sulfate that could be washed from the sludge was removed in the first caustic leach step. These results are reasonably consistent with the solubility studies of Barney (1976), except in the case of nitrate, which should have leached from the sludge only during the first caustic leach. By comparing the phosphate measured from IC and the

Table 3.2. Concentration of Nonradioactive Tank C-106 Components in Various Process Streams

Analyte	First Caustic Leach		Second Caustic Leach		First Water Wash		Second Water Wash		Third Water Wash		Leached Solids	
	Conc., $\mu\text{g/ml}$	Mass, μg	Conc., $\mu\text{g/ml}$	Mass, $\mu\text{g}^{(a)}$	Conc., $\mu\text{g/g}$	Mass, μg						
Ag	<0.5	<2.39E+3	<0.5	<2.45E+3	<0.5	<2.58E+3	<0.5	<2.59E+3	<0.5	<2.56E+3	3.02E+3	1.62E+6
Al	3.10E+3	1.44E+7	1388	335024	438	0	150	1.50E+5	55	1.10E+5	4.91E+4	2.64E+7
Bi	67	3.09E+5	49	9.59E+4	35	8.43E+4	37	1.32E+5	10	8.47E+3	186	1.00E+5
Ba	<0.2	<957	<0.2	<980	<0.2	<1.03E+3	<0.2	<1.03E+3	<0.2	<1.02E+3	398	2.14E+5
Bi	1.1	4.87E+3	<2	0	<2	<1.03E+4	<2	<1.03E+4	<2	<1.02E+4	562	3.03E+5
Ca	<5	<2.39E+4	<5	<2.45E+4	<5	<2.58E+4	<5	<2.59E+4	<5	<2.56E+4	5.48E+3	2.95E+6
Cd	<0.3	<1.43E+3	<0.3	<1.47E+3	<0.3	<1.55E+3	<0.3	<1.55E+3	<0.3	<1.54E+3	78	4.19E+4
Cr	58	2.67E+5	37	5.80E+4	13	0	4.3	3.88E+3	2.7	8.33E+3	711	3.82E+5
Cu	2.8	1.30E+4	2.1	4.06E+3	0.61	0	<1	1.36E+4	<0.5	<2.56E+3	58	3.13E+4
Fe	10	4.42E+4	10	3.00E+4	0.80	0	3.1	1.36E+4	7.9	3.36E+4	1.36E+5	7.31E+7
Mg	<2	<9.57E+3	<2	<9.80E+3	<2	<1.03E+4	<2	<1.03E+4	<2	<1.02E+4	1.32E+3	7.08E+5
Mn	<1	<4.78E+3	<1	<4.90E+3	<1	<5.15E+3	<1	<5.17E+3	<1	<5.12E+3	2.85E+3	1.53E+6
Na ^(b)	1.10E+5	9.06E+7	8.58E+4	0	3.29E+4	4.30E+6	1.51E+4	2.87E+7	1.24E+4	4.18E+7	1.13E+5	6.09E+7
Nd	<2	<9.57E+3	<2	<9.80E+3	<2	<1.03E+4	<2	<1.03E+4	<2	<1.02E+4	364	1.96E+5
Ni	<0.6	<2.87E+3	<0.6	<2.94E+3	<0.6	<3.09E+3	<0.6	<3.10E+3	0.28	1.29E+3	1.09E+3	5.86E+5
P	283	1.31E+6	147	1.25E+5	71	8.23E+4	41	1.02E+5	20	5.35E+4	3.48E+3	1.87E+6
Pb	31	1.43E+5	23	4.65E+4	<2	0	<2	<1.03E+4	<2	<1.02E+4	3.31E+3	1.78E+6
Si	295	1.37E+6	315	8.95E+5	180	3.08E+5	122	3.52E+5	48	1.06E+5	6.66E+4	3.58E+7
Sr	<0.3	<1.43E+3	<0.3	<1.47E+3	<0.3	<1.55E+3	<0.3	<1.55E+3	<0.3	<1.54E+3	71	3.83E+4
Tl	<0.5	<2.39E+3	<0.5	<2.45E+3	<0.5	<2.58E+3	<0.5	<2.59E+3	<0.5	<2.56E+3	995	5.35E+5
Zr	4.1	1.88E+4	2.6	3.91E+3	<1	0	<1	<5.17E+3	<1	<5.12E+3	1.05E+3	5.65E+5
¹³⁷ Cs	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	15	8.14E+3
TIC	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	5.10E+3	2.74E+6
TOC	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured	4.61E+4	2.48E+7

(a) Mass values represent the mass of material dissolved in a given step. These results have been corrected for interstitial liquid carried over from the previous step.

A value of zero represents more material predicted to be carried over in interstitial liquid than what was determined analytically.

(b) Accounts for the Na⁺ added as NaOH & NaNO₃.

Table 3.3. Anion Concentrations in the Various C-106 Process Solutions

Component	First Caustic Leach		Second Caustic Leach		First Water Wash		Second Water Wash		Third Water Wash		Residue	
	Conc. µg/ml	Mass, µg	Conc. µg/ml	Mass, µg ^(a)	Conc. µg/ml	Mass, µg ^(a)	Conc. µg/ml	Mass, µg ^(a)	Conc. µg/ml	Mass, µg ^(a)	Conc. µg/g	Mass, µg ^(a)
Cl ⁻	<250	<1.1E+6	<250	<1.2E+6	<250	<1.2E+6	<250	<1.2E+6	<250	<1.1E+6	92	5.31E+4
NO ₂ ⁻	6.85E+3	3.18E+7	2.90E+3	1.04E+6	1.29E+3	1.04E+6	730	1.82E+6	540	1.80E+6	2.07E+3	7.41E+5
NO ₃ ⁻	3.35E+2	1.55E+6	260	5.53E+5	<20	<9.4E+4	40	8.77E+4	30	1.00E+5	2.07E+3	4.06E+5
PO ₄ ³⁻	335	3.59E+6	260	3.33E+5	150	5.65E+3	40	4.50E+4	20	4.46E+4	756	7.67E+4
SO ₄ ²⁻	1.80E+3	8.34E+6	720	<9.4E+4	<20	<9.4E+4	70	6.30E+4	30	7.17E+4	409	2.11E+5
C ₂ O ₄ ²⁻	2.50E+3	1.16E+7	1.90E+3	3.95E+6	5.70E+3	2.45E+7	1.45E+4	6.19E+7	2.00E+4	7.85E+7	4.70E+2	8.20E+7
	Conc. N		Conc. N		Conc. N		Conc. N		Conc. N		Conc. N	
OH ⁻	2.7	2.16E+8	3.2	1.65E+8	1.1	0	0	0	<3E-2	<4.2E+6		

(a) Amounts represent that found in a given step. These results have been corrected for interstitial liquid carried over from the previous step. A value of zero represents more material predicted to be carried over in interstitial liquid than what was determined analytically.

Table 3.4. Concentrations of Radioactive Tank C-106 Components in Various Process Streams

Component	First Caustic Leach		Second Caustic Leach		First Water Wash		Second Water Wash		Third Water Wash		Residue	
	µCi/g	µCi	µCi/g	µCi ^(a)	µCi/g	µCi ^(a)	µCi/g	µCi ^(a)	µCi/g	µCi ^(a)	µCi/g	µCi
Total Alpha	<2E-3	<8.1	6.82E-3	37	6.17E-3	<11	<3E-3	<11	<3E-3	<10	6.8	3.53E+3
Total Beta	no analysis	no analysis	no analysis	no analysis	no analysis	no analysis	no analysis	no analysis	no analysis	no analysis	2.06E+3	1.07E+6
⁹⁰ Sr	0.29	1.58E+3	0.19	452	4.06E-2	46	1.96E-2	46	1.32E-2	44	730	3.78E+5
¹³⁷ Cs	40	2.16E+5	34	1.05E+5	10	0	3.1	0	1.5	4.12E+3	495	2.56E+5
⁶⁰ Co	<8E-4	<3.8	<8E-4	<2.2	<9E-4	<2.8	<8E-4	<2.9	<5E-4	<1.9	0.49	255
¹⁵⁴ Eu	<2E-3	<9.6	<3E-3	<6.7	<2E-3	<6.2	<2E-3	<7.1	<2E-3	<7.5	3.8	1.97E+3
¹⁵⁵ Eu	<2E-2	<9.6	<3E-2	<81	<2E-2	<62	<7E-3	<25	<5E-3	<19	3.1	1.62E+3
²⁴¹ Am	<3E-2	<144	<3E-2	<81	<2E-2	<62	<1E-2	<36	<7E-3	<26	3.1	1.62E+3
¹⁵⁵ Cs	no analysis	no analysis	no analysis	no analysis	no analysis	no analysis	no analysis	no analysis	no analysis	no analysis	2.86E-3	1.5
²³⁹ Pu + ²⁴⁰ Pu	<2E-3	<8.1	6.10E-3	33	5.44E-3	17	<3E-3	<11	<3E-3	<10	no analysis	no analysis
²³⁸ Pu/ ²⁴¹ Am	<2E-3	<8.1	7.21E-4	3.9	7.28E-4	2.5	<3E-3	<11	<3E-3	<10	no analysis	no analysis
²³² Th	5.81E-4	3.2	2.60E-4	3.44E-2	9.73E-5	0	2.75E-5	4.68E-3	1.63E-5	5.09E-2	5.60E-3	0.80

(a) Activities represent that found in a given step. These results have been corrected for interstitial liquid carried over from the previous step. A value of zero represents more material predicted to be carried over in interstitial liquid than what was determined analytically.

Table 3.5. Distribution of Nonradioactive Tank C-106 Sludge Components Between the Various Process Streams

Analyte	First Caustic Leach	Second Caustic Leach ^(a)	First Water Wash ^(a)	Second Water Wash ^(a)	Third Water Wash ^(a)	Predicted Residue
Ag	<0.2	<0.2	<0.2	<0.2	<0.2	<100, >99
Al	30	1	0	0.3	0.2	69
B	41	13	11	17	1	17
Ba	<0.3	<0.4	<0.4	<0.4	<0.4	>98
Bi	2	0	<3	<3	<3	<98, >89
Ca	<0.7	<0.7	<0.7	<0.7	<0.7	>96
Cd	<2	<2	<2	<2	<2	>90
Cr	39	8	0	0.6	1	51
Cu	11	4	0	0	<2	<84, >82
Fe	0.05	0.03	0	0.02	0.04	100
Mg	<1	<1	<1	<1	<1	>95
Mn	<0.2	<0.2	<0.2	<0.2	<0.2	>99
Na	31	0	1	10	14	43
Nd	<3	<3	<3	<3	<3	>85
Ni	<0.4	<0.4	<0.4	<0.4	0.2	<100, >98
P	27	3	2	2	1	65
Pb	6	2	0	<0.4	<0.4	<92, >91
Si	3	2	0.7	0.8	0.2	93
Sr	<3	<3	<4	<4	<3	>83
Ti	<0.4	<0.4	<0.4	<0.4	<0.4	>98
Zr	3	0.5	0	<0.7	<0.7	<97, >95
¹³⁷ Cs			not determined			46
TIC			not determined			18
TOC			not determined			45

(a) Amounts reported represent material dissolved in a given step. These results have been corrected for interstitial liquid carried over from the previous step. A value of zero represents more material predicted to be carried over in interstitial liquid (or added to the system) than what was determined analytically.

Table 3.6. Distribution of Radioactive Tank C-106 Sludge Components Between the Various Process Streams

Analyte	Component Distribution, % ^(a)						Residue
	First Caustic Leach	Second Caustic Leach	First Water Wash	Second Water Wash	Third Water Wash	Residue	
Total Alpha	<0.2	1	0.5	<0.3	<0.3	<98.5, >97.8	
Total Beta	no analysis	no analysis	no analysis	no analysis	no analysis	68 ^(b)	
⁹⁰ Sr	0.3	0.1	0	0.009	0.009	99.6	
¹³⁷ Cs	32	16	0	0	0.6	51.3	
⁶⁰ Co	<1	<0.7	<1	<1	<0.6	>95.7	
¹⁵⁴ Eu	<0.5	<0.3	<0.3	<0.4	<0.4	>98.1	
¹⁵⁵ Eu	<6	<5	<4	<2	<1	>82	
²⁴¹ Am	<7	<4	<3	<2	<1	>83	
¹³⁵ Cs	no analysis	no analysis	no analysis	no analysis	no analysis	39 ^(b)	
²³⁹ Pu + ²⁴⁰ Pu	no analysis	no analysis	no analysis	no analysis	no analysis	(c)	
²³⁸ Pu/ ²⁴¹ Am	Not Determined	Not Determined	Not Determined	Not Determined	no analysis	(c)	
⁹⁹ Tc	8	0	0	0	0.1	91.8	

- (a) Activities represent that found in a given step. These results have been corrected for interstitial liquid carried over from the previous step. A value of zero represents more material predicted to be carried over in interstitial liquid than what was determined analytically.
- (b) Obtained by comparing the amount of material in the residue to the amount in the original solids.
- (c) Analysis not performed on initial or final solids.

Table 3.7. Mass Recoveries for the Nonradioactive Tank C-106 Components

Analyte	Total Mass, μg		Recovery, %
	Direct Analysis	Summation Method ^(a)	
Ag	1.41E+6	1.77E+6	125
Al	4.78E+7	4.64E+7	97
B	2.94E+5	7.60E+5	259
Ba	2.63E+5	2.42E+5	92
Bi	3.19E+5	3.41E+5	107
Ca	3.28E+6	3.29E+6	100
Cd	5.90E+4	4.81E+4	82
Cr	6.85E+5	7.92E+5	116
Cu	1.14E+5	6.03E+4	53
Fe	8.72E+7	8.23E+7	94
Mg	7.97E+5	7.92E+5	99
Mn	2.09E+6	1.75E+6	84
Na	2.91E+8	2.57E+8	88
Nd	2.81E+5	2.25E+5	80
Ni	6.65E+5	6.57E+5	99
P	4.81E+6	4.05E+6	84
Pb	2.35E+6	2.21E+6	94
Si	4.32E+7	4.34E+7	100
Sr	4.17E+4	4.27E+4	102
Ti	5.53E+5	5.93E+5	107
Zr	7.42E+5	6.66E+5	90
¹³³ Cs	2.27E+4	1.05E+4	46
TIC	3.59E+7	6.49E+6	18
TOC	7.18E+7	3.23E+7	45

(a) Solution concentrations assumed to be zero if below the detection limit.

Table 3.8. Mass Recoveries for the Radioactive Tank C-106 Components

Component	Total Activity, μCi		Recovery, %
	Direct Analysis	Summation Method ^(a)	
Total Alpha	4.09E+3	4.01E+3	98
Total Beta	1.58E+6	1.24E+6	78
⁹⁰ Sr	4.88E+5	4.31E+5	88
¹³⁷ Cs	6.67E+5	6.51E+5	98
⁶⁰ Co	305	287	94
¹⁵⁴ Eu	2.02E+3	2.18E+3	108
¹⁵⁵ Eu	1.59E+3	1.79E+3	113
²⁴¹ Am	2.00E+3	1.83E+3	91
¹³⁵ Cs	4	2	49
²³⁹ Pu + ²⁴⁰ Pu	no analysis	50	(b)
²³⁸ Pu/ ²⁴¹ Am	no analysis	6	(b)
⁹⁹ Tc	39	4	10

(a) Solution concentrations assumed to be zero if below the detection limit.

(b) Analyses performed on supernatant only.

Table 3.9. Distribution of Various Tank C-106 Sludge Components Compared to Data from Lumetta et al. (1996a)

CURRENT WORK

Analyte	Component Distribution, % ^(a)			Residue
	First Caustic Leach	Second Caustic Leach	Final Water Wash(es)	
Al	30	1	1	69
Cr	39	8	2	51
Fe	0.05	0.03	0	100
Na	31	0	36	43
P	27	3	6	65
Pb	6	2	<1.2	<92, >91
Si	3	2	2	93
Total Alpha	<0.2	1	0.5	<98.5, >97.8
⁹⁰ Sr	0.3	0.09	0	99.6
¹³⁷ Cs	32	16	0.7	51

LUMETTA ET AL (1996) WORK

Al	39	6	1	53
Cr	24	7	0	68
Fe	0	0	0	100
Na	Not Determined	Not Determined	Not Determined	13.5(b)
P	59	6	3	32
Pb	4	2	0	94
Si	2	6	2	91
Total Alpha	0	<1	<6	>93
⁹⁰ Sr	0	0	0	100
¹³⁷ Cs	50	9	1	40

(a) Amounts reported represent material dissolved in a given step. These results have been corrected for interstitial liquid carried over from the previous step. A value of zero represents more material predicted to be carried over in interstitial liquid than what was determined analytically.

(b) Obtained by compared the amount of Na in the residue to the amount in the original solids.

phosphorus obtained from ICP-AES on similar samples, the percentage of phosphorus that is phosphate could be determined for each washing step. In the caustic leaches, ~89% of the phosphorus was measured as phosphate. In the subsequent washes, the percentage of phosphate dropped to less than 25% of the phosphorus. The mass of oxalate ion removed, unlike the other anions studied, actually increased during the water wash steps. The significance of this will be discussed further below. The hydroxide concentration was within 0.2 M of what could be expected based on interstitial carryover during decanting for all the water washes, indicating good washing efficiency to remove the excess NaOH using settle/decant.

As can be seen in Table 3.7, no significant alpha emitters were removed by the caustic leach. Total alpha in the supernatant samples were $\leq 0.007 \mu\text{Ci/g}$ (highest in the second caustic leach at 1% of the total

alpha in the sludge stayed in the supernate) for each step of the enhanced sludge washing process. Similarly, ^{90}Sr remained in the solids fraction and only small traces were found in the supernate samples. The first caustic leach contained the most ^{90}Sr : $\sim 0.29 \mu\text{Ci/g}$ or 0.3% of the total ^{90}Sr in the sludge stayed in the supernate during this step. Other radionuclides such as ^{60}Co , ^{241}Am , and isotopes of Eu were below detection levels for all supernates analyzed, indicating that they were not removed during the enhanced sludge wash process. In contrast to other radionuclides, $\sim 32\%$ of the ^{137}Cs was removed in the first caustic leach and $\sim 16\%$ was removed in the second caustic leach. The overall ^{137}Cs removal is reasonably consistent with the other isotopes of cesium measured (removal of 61% for ^{135}Cs , 54% for ^{133}Cs , 48% for ^{137}Cs).

3.1.2 Final Three Water Washes

Very little material was dissolved in the final three washing steps. The only nonradioactive analytes of any significance were Na and oxalate (discussed below), P and B. 5% of the total P and 29% of the total B in the sludge was removed during the three water washes. Not including sodium and oxalate, only ~ 2 grams of material was leached from the solids during the water washes. Furthermore, no additional radionuclides were removed ($\sim 0.5\%$ Total Alpha emitters, $\sim 0.02\%$ ^{90}Sr , and $\sim 0.6\%$ ^{137}Cs).

The oxalate in the sludge is believed to be in the form of partially soluble sodium oxalate, with the solubility product constant (K_{sp}) written as follows:

$$K_{sp} = [\text{Na}^+]^2[\text{C}_2\text{O}_4^{2-}]$$

where units are in molarity. If this hypothesis is correct, the following would occur. When the sodium concentration in solution is high during the caustic leaching steps, the sodium oxalate would remain as a solid. As the sodium concentration from NaOH decreases following the caustic leaching steps, the sodium oxalate would then dissolve. With each subsequent water wash after the NaOH is removed, the sodium and oxalate concentration would remain relatively constant until all the sodium oxalate leaches out of the sludge. An analogous phenomenon was observed for removal of sodium phosphate from tank T-104 sludge (Rapko et al. 1996).

The experimental results are consistent with this hypothesis. Significant quantities of both sodium and oxalate ion were removed during the water washes. In fact, 90% of the oxalate washed out during the enhanced sludge wash process was removed during the three water washes. Approximately 240 grams of sodium and oxalate washed from the solids during the water washes. In addition, 125 grams of sodium and oxalate were found in the supernate of the final wash solution. In both cases, the sodium and oxalate are present in the supernate in nearly stoichiometric proportions. Furthermore, the calculated solubility product constant (K_{sp}) for the final steps of the water wash is $\sim 0.07 \text{ M}^3$, compared to the literature value of 0.08 M^3 (Weast 1984).

In summary, the water washes removed nearly half of the 758 grams of solids present as sodium oxalate following the second caustic leach. Because there are large amounts of oxalate in a sludge, the removal of a large fraction of the sodium during the enhanced sludge washing process may be suppressed, requiring additional water wash steps at low solids concentration to remove the sodium down to acceptable levels.

3.1.3 Mass Recoveries

The mass recoveries are determined by adding the amount of a species removed during each enhanced washing step to the amount of the species remaining in the final product and then comparing the result to the amount of the species in the initial material. If the mass recovery for a given species is close to 100%, it is assumed that none of that species was lost or inaccurately measured. If the mass recoveries for all species are close to 100%, this indicates that no sludge was lost during processing.

The mass recoveries for the tank C-106 analytes, given in Tables 3.7 and 3.8, were generally below 100%, indicating that there was some hold-up of sludge in the equipment. After rinsing the equipment following testing, ~20 to 30 grams of sludge (dry basis) was recovered. This would account for a 5% to 10% low recovery. Of the major analytes, phosphorus had a low recovery (84%) and chromium had a high recovery (116%), aluminum, barium, calcium, iron, magnesium, nickel, lead, and silicon had recoveries of 95%±5%.

The low mass recovery may impact the leaching results for phosphorus and chromium. The fraction of phosphorus removed from the sludge, for example, could actually range from 29% to 45% if the low recovery is due to analytical measurement error or loss of phosphorus in the sludge residue or the supernates, respectively. This range of phosphorus removal efficiencies provided an upper and lower bound for the value of 35% phosphorus removal presented in Table 3.5. Similarly, the chromium fraction removed could range from 41% to 57%. However, it is more likely that the losses were produced by both the sludge and the supernate analysis, and the estimated removals in the Table 3.5 are reasonable values.

Similar to the nonradioactive components, the radioactive components mass recoveries are less than 100% (see Table 3.8). The lower mass recoveries are primarily due to material loss in the equipment and analytical variability. The technetium result, however, shown in Tables 3.6 and 3.8, are contradictory. Analytical results of the supernatant samples indicate that less than 7.9% of the technetium was removed. However, the mass recovery for technetium with this assumption is 10%. Based on the results of screening tests (Lumetta 1996a) and past sludges (Lumetta 1996b), 90% of the technetium was removed during the washing steps.

3.1.4 Comparison to Screening Test Results

A comparison of the above results with those the screening test from Lumetta et al. (1996a) can be seen in Table 3.9. Most of the results are fairly similar and will only be presented here. The differences in the aluminum, phosphorus, chromium, and sodium leachability are of particular interest and will be discussed further. The screening test sample leached 47% of the aluminum present in the sludge compared to the bench-scale removal of 31%. Similarly, the screening test leached 68% of the phosphorus compared to 35% in the bench scale test. The screening test sample leached more sodium (86.5% compared to 57%) and less chromium (32% compared to 49%) than the bench-scale test. While the reasons for these differences are not completely understood, three possible reasons will be presented: 1) differences in the sludge samples; 2) differences in the analyses; and 3) differences in the experiment.

3.1.4.1 Differences in Sludge Samples

The concentrations of aluminum, phosphorus, chromium, and sodium in the initial C-106 sludge are shown in Table 3.10. Because the screening test was performed with a subsample of the material used in this study, the sample concentrations should be similar. However, the aluminum concentration is significantly *higher* in the screening test sample than in the bench-scale work here. In contrast, the phosphorus concentration is significantly *lower* in the screening test sample. Both differences in component concentrations are greater than could be accounted for by analytical variability alone. Thus, the differences in both initial sludge concentration and washing efficiency may be the result of sample inhomogeneity.

By multiplying the initial sludge concentration by the percentage leached, the mass of species leached (or remaining) can be determined. In the case of aluminum and phosphorus, the results are interesting. While there is a higher concentration of aluminum in the screening test sample, so also is there a higher fraction leached in the screen test sample; thus the amount of aluminum *remaining* in both the screening and bench-scale is very similar. In contrast, there is a lower concentration of phosphorus in the screening test sample, but a higher fraction is removed, thus the amount of phosphorus *removed* in both the screening and bench-scale test is very similar. Thus different species as well as concentrations of aluminum and phosphorus may exist in the two samples, possibly accounting for the different leach efficiencies.

3.1.4.2 Differences in Data Analysis

The differences in quantities leached may also be tied to the data analysis. As mentioned previously, the mass recovery is an indication of mass loss and the accuracy of the measured concentrations. Phosphorus, for example, had a mass recovery of 84% for the bench-scale test and 130% for the screening test. Thus, less material was recovered than indicated by the initial concentration for the bench-scale test, and more material was recovered than expected for the screening test. Such results may account for some of the leaching efficiency and initial concentration differences.

3.1.4.3 Differences in the Experiment

Differences in the experiments are also shown in Table 3.11. These differences may impact the leaching efficiencies of each component. The bench-scale test, for example, performed settling at elevated

Table 3.10. Key Component Concentrations in the Original C-106 Solids ($\mu\text{Ci/g}$ dry solids)

Species	Screening Test (Lumetta 1996a)	This Study	
		KOH Fusion	Na_2O_2 Fusion
Aluminum	48,500	37,300 \pm 1900	36,600 \pm 1200
Chromium	606	621 \pm 30	531 \pm 36
Sodium	231,000	225,000 \pm 6300	--
Phosphorus	2140	3710 \pm 130	3240 \pm 230

Table 3.11. Characteristics of the Screening and Bench-Scale Study and Their Impact on Leaching, Settling Rate, and Sludge Compaction

Characteristic	Screening Test	Bench-Scale Test	Leaching is Improved by...	Settling Rate is Increased by...	Sludge Compaction is Increased by...
Time	5 hrs @ 100°C;	5 hours @ 100°C;	Increasing	N/A	Increasing
Temperature	24 hours @ ~25°C	2-3 days @ 85°C	Increasing	Increasing	Increasing
Solids Loading	~3 wt%	~6 wt%	Decreasing	Decreasing	Increasing
[OH ⁻]	2.6-3.0	2.7-3.2	Increasing	Decreasing	Decreasing
Column Diameter	~3 cm	10 cm	No Effect	Increasing	No Effect
Sludge Height	1-1.2 cm	10-20 cm	No Effect	No Effect	Increasing

temperatures to model what might happen in an actual tank. These higher temperatures improve settling and compaction but they also could improve the leaching efficiency. Furthermore, the bench-scale test also had a slightly higher free OH⁻ concentration, which could improve leaching. In contrast, the lower solids loading of the screening test may improve leaching efficiencies of some species.

One particular example of the effect of differences in the experiment is sodium. As discussed above, it is believed that a significant quantity of the sodium in the bench-scale test was precipitated as slightly soluble sodium oxalate. Because the screening test was performed at approximately 3 wt% solids instead of 6 wt% solids (see Table 3.11), the screening test used nearly twice as much wash water as the bench-scale test. If the solubility of sodium oxalate is equilibrium-limited, more total sodium oxalate could be removed during the screening test washes than in the bench-scale test. While in the bench-scale test this can be verified with analytical data, oxalate and/or TOC measurements were not taken during the screening test. Therefore, it is difficult to determine if all the oxalate was leached out or even if it was present in the screening test.

As noted in Table 3.10, more chromium was removed from the bench-scale sample than from the screening test sample. The bench-scale chemical processing tank (C-202) uses an air bubbler (at 1 scfh) to measure the level and specific gravity of the sludge. The laboratory experiment is completely sealed. It has been postulated that this air purge during the caustic leaching process may oxidize the Cr⁺³ to the more soluble Cr⁺⁶ state allowing more chromium to leach from the sludge.

3.2 Results of the Bench-Scale Settling Experiments

As discussed in Section 2.1.2, one settling experiment was performed for each step in the enhanced sludge washing process. All of the sludge settled in the column in every settling test. The settling conditions, velocities, and compacted solids concentrations are provided in Table 3.12. As described in Section 2.2, the wt% solids during settling is based on the insoluble material in the sludge residue. As indicated by the data in the last two columns in Table 3.12, the sludge compaction increases with each subsequent enhanced sludge washing step. This increase in wt% caustic-insoluble solids is in part the result of solids loss during the caustic leaching and water washing steps (especially sodium oxalate). Although, even when this effect is included, the solids compact more with each subsequent step.

The first four settling experiments (first and second Leaches and first and second Washes) settled with a single, very distinct interface between the solids and the supernate. A picture of the bench-scale settling apparatus showing the supernate/solids interface during one of these settling experiment is shown in Figure 3.1. The light supernatant was clearly distinguishable from the dark sludge. For these first four experiments, the supernate/solids interface developed within the first 50 minutes of settling and within the first 5 cm from the top of the liquid surface in the settling column.

The settling experiment from the third wash had the following differences from the previous settling experiments. First, there was considerable sludge foaming. A small amount of foam was also produced during fluidization of the second wash; however, approximately 35% of the total slurry volume was foam

Table 3.12. Bench-Scale C-106 Settling Test Results

Step	Initial Wt.% Solids ^(a)	Temp. (°C)	Free Settling Rate (cm/hr)	Hindered Settling Rate (cm/hr)	Final Compaction ^(b) (vol.%)	Final Compaction ^(c) (wt.%)
Caustic 1	5.9	81	---	3.4	39	14
Caustic 2	6.5	81	---	5.5	35	16
Wash 1	6.9	31	---	4.4	26	22
Wash 2	7.2	30	35.6	6.2	21	28
Wash 3	7.5	31	~100	6.3	18	32

(a) All wt% solids are based on final caustic leached solids of 14.2% of original sludge.

(b) Final compaction (volume) is the percentage of the total volume of supernatant and solids occupied by the final settled solids.

(c) Final compaction (weight) is the mass of caustic insoluble solids divided by the mass of the settled solids.



Figure 3.1. Bench-Scale Settling Column During C-106 Settling Experiment. Note the distinct line between the light supernatant and the dark sludge.

when first pumped into the top of the column during the final wash. The foam disappeared within 5 minutes of its formation and was not considered a problem in data-taking but is mentioned here as a difference from previous runs. Secondly, the sludge initially settled very fast (~100 cm/hr), and the particles settled individually rather than as a distinct interface. Both the rate and the manner in which the particles settled indicate free settling rather than hindered settling.

In free settling, the individual particles are not influenced by others around them and can be characterized by Stoke's free fall velocity. It is generally faster than hindered settling, in which particles interact with each other, retain their position relative to their neighbors, and settle as a single distinct interface. Following this short, rapid free settling, a clear interface formed and hindered settling commenced. A similar short, rapid settling followed by a slower settling was also seen in the second water wash, but a distinct interface existed. Whether this was also free settling is unclear.

All experiments completed their hindered settling and began compaction within the first 9 hours after settling commenced. The solids pumped from tank to tank fluidized easily, suggesting that gel formation of Tank C-106 sludge did not occur during any step of the enhanced sludge washing process.

The settling rate is improved over the TWRS base case settling rate of >1-2 cm/hr for all steps of the enhanced sludge wash. The TWRS base case for final wt% solids in the compacted sediment is >20 wt% solids. In this bench-scale experiment, this goal of 20 wt% solids was achieved for the water washes, but not for the caustic leach settling experiments. These sludge compaction results, however, cannot be scaled directly to a million-gallon tank. It is still possible that with the higher sludge layers that would be encountered in an actual double-shell tank, the sludge would compact to 20 wt% solids during caustic leaches. Further testing and modeling would be required to verify this, as was done with C-107 sludges.^(a) Additionally, the solids concentration described here is for the caustic-insoluble solids (392 grams). If the sodium oxalate solids are included in the solids concentration (758 grams after first caustic leach and dropping to 126 grams by the third water wash), the compacted solids would contain 28 and 31 wt% solids for caustic leach 1 and 2, respectively. The compacted solids of the water washes would be approximately 40 wt% if the sodium oxalate solids were included in the solids concentration.

The curves for the five settling tests run are shown in Figures 3.2 and 3.3. Figure 3.2 shows the entire data for the settling test following each step of the enhanced sludge washing process. Figure 3.3 shows the same data as in Figure 3.2, but the time scale on the X-axis is reduced to highlight the differences between the curves in the free and hindered settling regime. Generally, the overall settling rate and solids compaction increase with each subsequent enhanced sludge washing step. These results are surprising because the ionic concentration and pH decrease with each subsequent washing step. Lower ionic strength and pH should reduce the interparticle attraction (less blinding of the double-layer), reducing the floc size and/or density. This should result in a decreased settling rate and compaction. The fact that the settling rate and

(a) Brooks, K. P., J. R. Phillips, R. L. Myers, K. G. Rappe, D. R. Rector, and P. A. Smith. 1996. "Sludge Pretreatment Studies Using Hanford Tank C-107," White Paper Prepared for TWRS Low-Level Waste Addback Program by Pacific Northwest National Laboratory, Richland, Washington.

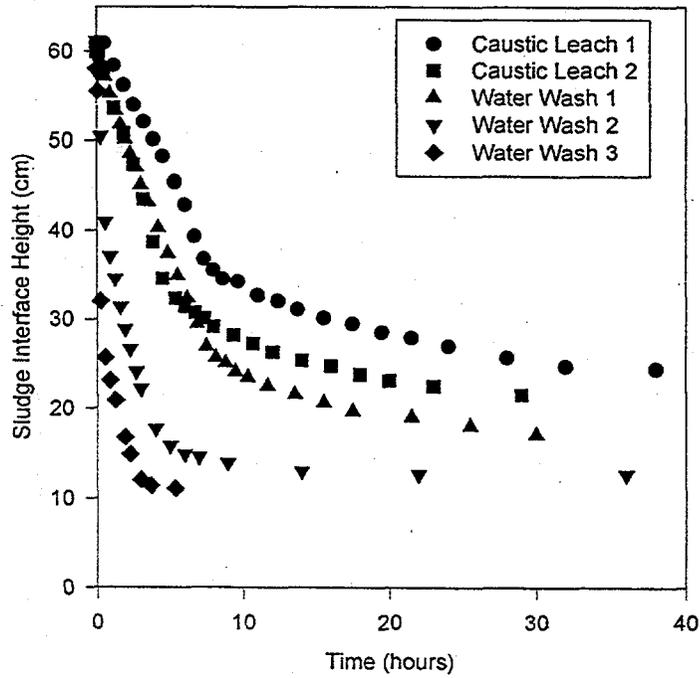


Figure 3.2. Dimensional Settling Curve for Each Step of the Enhanced Sludge Wash Process for Tank C-106

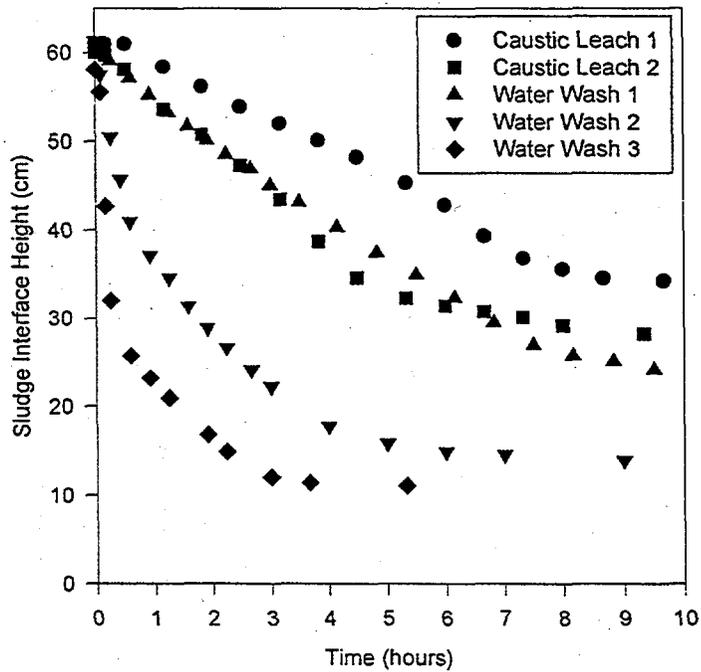


Figure 3.3. Expanded-Scale Settling Curve for Each Step of the Enhanced Sludge Wash Process for Tank C-106

compaction actually increase suggests that the floc size and/or density is actually increasing. One exception to the steady increase in settling rate is the second caustic leach and the first water wash, where the initial settling rates are very nearly identical.

The settling conditions and results of the screening test are shown in Table 3.13. The initial wt% solids for the screening test was lower than for the bench-scale test in all cases. These lower solids concentrations should result in increased maximum settling rate (see Table 3.11). In a smaller system, the sludge may adhere to the walls of the settling container, slowing the settling rate of the sludge agglomerates near the wall. In small containers, these "wall effects" are significant enough to decrease the settling rate of all of the sludge. Overall, the increased settling rate due to lower solid concentration and decreased rate due to wall effects appear to cancel out resulting and settling rates fairly comparable to those in the bench-scale test.

As the sludge settles in the bottom of a container, a network of sludge agglomerates forms. This structure possesses the ability to support itself, stopping the sludge particles from settling further. However, as more sludge accumulates above the network, the pressure increases on the sludge below, causing the network to deform. The sludge layers compress, and the concentration of solids in the sediment increases. As would be expected, the wt% solids in the gravity-settled sludge is higher for the bench-scale system in all cases as compared to the screening test. The taller sludge layer allows higher solids fraction in the final compacted sludge. The wt% solids in the settled sludge of a full-scale system would be even higher than those reported here due to even taller sediment height.

Table 3.13. Screening Test Settling Results

Step	Initial Wt% Solids ^(a)	Temp. (°C)	Maximum Settling Rate (cm/hr)	Final Compaction (vol%)	Final Compaction (wt%)
Caustic 1	3.3	Ambient	4.1	21	13
Caustic 2	3.9	Ambient	2.7	22	12
Wash 1	2.8	Ambient	19.8	16	13
Wash 2	2.9	Ambient	14.4	13	~13
Wash 3	3.0	Ambient	24.6	14	16

(a) All wt% solids are based on final caustic leached solids.

Because the settling done in the screening test was performed on smaller samples, the settling curve requires normalization to compare the bench-scale settling experiments. The settling data were normalized according to formulas recommended by Graham MacLean.^(a)

$$t^* = t v_{\max} / z_0 \quad \text{and} \quad z^* = z / z_0$$

where t^* and z^* are the normalized time and height, t is the dimensional time, v_{\max} is the maximum settling velocity, and z and z_0 are the dimensional interface height and initial height, respectively. By non-dimensionalizing the data, the shapes of the settling curves can be compared with similar experiments performed in containers with other geometries.

Using normalized data as described above, the settling test data were compared with data from the screening test reported by Lumetta (1996a). The results of this comparison are shown in Figures 3.4, 3.5, 3.6 and 3.7, where the screening tests data are shown with lines and the bench-scale test are shown data points. Figure 3.4 shows the normalized data from the caustic leach settling tests while Figure 3.5 shows the normalized data from the water wash settling tests. Figure 3.6 and 3.7 show the same data as Figures 3.4 and 3.5, but on a logarithmic scale on the X-axis to highlight the differences between the curves in the hindered settling regime. In general, the screening tests and bench-scale tests have similar shaped settling curves. In the case of the compaction regime, for both the caustic leaches and water washes, the bench-scale curves begin compaction before the screening test curves. This is likely due to the higher solids concentration in the bench-scale tests. In the case of the linear settling portion of the curve, most of the laboratory-scale settling test results fit within the bounding limits of the bench-scale tests. In Figure 3.7 the settling curve for the bench-scale third water wash are shifted to the right due to an enlarged "induction period." This result occurs because of the high maximum settling velocity used in the calculation of the dimensionless time value. This value is nearly 30 times greater than the lowest maximum settling. The third water wash for the screening test shows similar large time scale and "induction period" as the result of its high settling velocity.

As mentioned previously, for a solid/liquid separation technique to be considered viable, the TRU concentration in the final LLW product must be less than 100 nCi/g. Assuming that each supernatant would be individually vitrified in a 20 wt% Na₂O glass matrix, the alpha in the final waste form would be less than 33.6 nCi/g for each step of the process (see Table 3.14). Assuming blend of all solutions, the final waste form would be less than 13 nCi/g. The DF is another measure of the ability of settle/decant to remove the TRU from the supernatant. The DF here is defined as the total alpha in the solids (μCi) divided by the total alpha in the supernatant (μCi) for each step. Results show DFs ranging from 180 to >770 (limited by the analytical technique). Evaluation of the alpha spectrum indicate the alpha is primarily associated with ²³⁹Pu and ²⁴⁰Pu rather than ²³⁸Pu and ²⁴¹Am.

To be considered efficient, the ⁹⁰Sr should also be removed from the supernatant by the settle/decant process. The ⁹⁰Sr concentration in the final LLW form was estimated to be between 0.348 and 1.16 Ci/m³

(a) Westinghouse Hanford Company Internal Memo, From Graham MacLean To Dave Place, June 18, 1996.

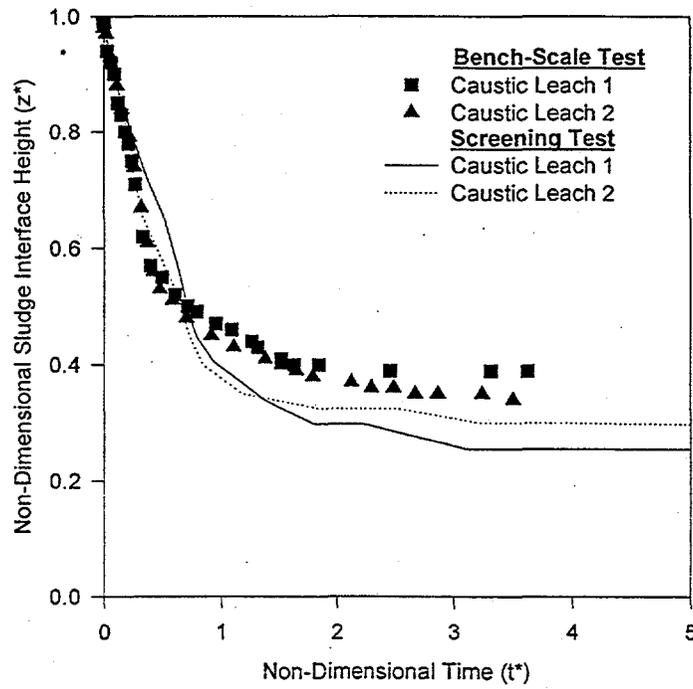


Figure 3.4. Non-Dimensional Settling Curves for Tank C-106 Caustic Leaches Comparing Screening and Bench-Scale Test

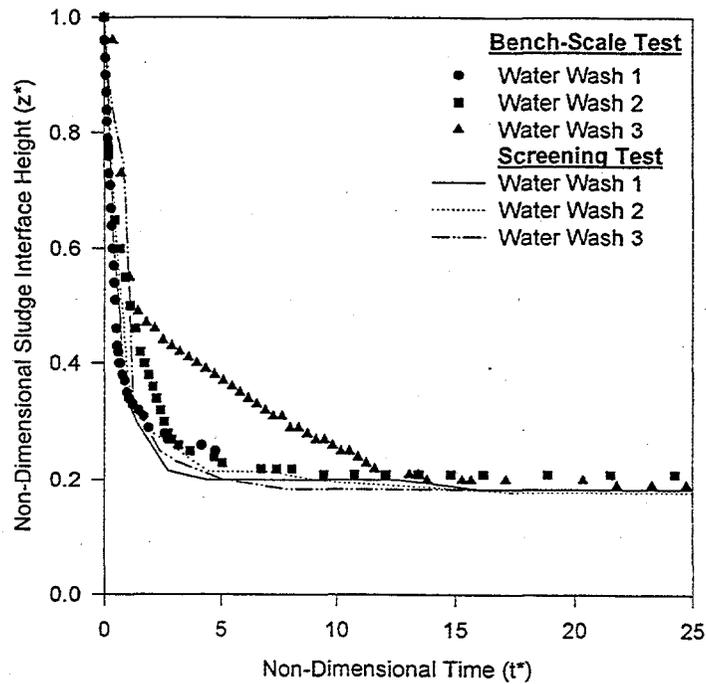


Figure 3.5. Non-Dimensional Settling Curves for Tank C-106 Water Washes Comparing Screening and Bench-Scale Test

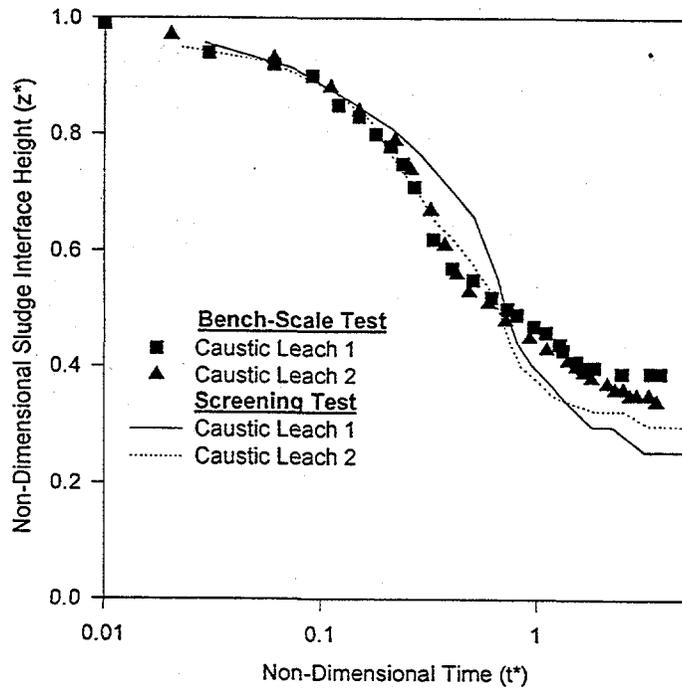


Figure 3.6. Logarithmic Scale Non-Dimensional Settling Curves for Tank C-106 Caustic Leaches Comparing Screening and Bench-Scale Test

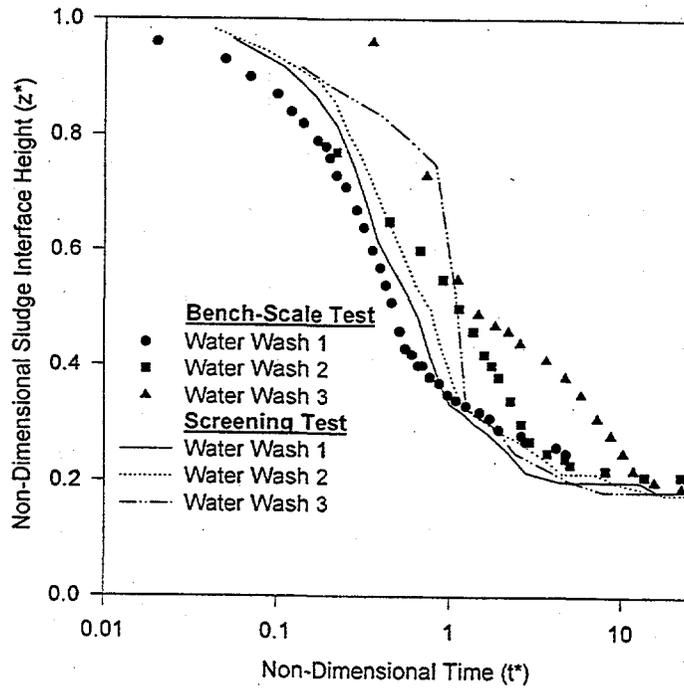


Figure 3.7. Logarithmic Scale Non-Dimensional Settling Curves for Tank C-106 Water Washes Comparing Screening and Bench-Scale Test

Table 3.14. Alpha Separation Efficiencies

Enhanced Sludge Washing Step	Total Alpha ($\mu\text{Ci/g}$) (μCi)	Sodium ($\mu\text{g/g sol'n}$)	Alpha in Final LLW Form (nCi/g) ^(a)	Total Alpha DF ^(b)
Initial Sludge ^(c)	3.16E+00 4092	---	---	---
Caustic Leach 1 ^(d)	<1.70E-03 <5.28	93400	< 2.7	>770
Caustic Leach 2	6.82E-03 22.4	75500	13.4	180
Water Wash 1	4.74E-03 18.1	31000	22.6	225
Water Wash 2	<3.10E-03 <12.4	14400	<32.1	>330
Water Wash 3	<2.70E-03 <10.6	11900	<33.6	>380
Overall Blend ^(e)	<3.79E-03 <68.9	41900	<13.4	>59.4

(a) Assumes streams are not mixed and are vitrified separately and 20 wt% Na₂O in LLW glass final product.

(b) DF = (total alpha in the solids [μCi])/(total alpha in the supernatant [μCi]).

(c) Initial sludge is in $\mu\text{Ci/g}$ of dry solids.

(d) Enhanced sludge washing steps here are not corrected for interstitial liquid carry-over. Only describes decanted liquid concentrations.

(e) Overall Blend is a composite of all caustic leach and water wash solutions.

for the individual decanted solutions and 0.88 Ci/m³ in the blend. These all would be considered NRC Class B (between 0.04 and 150 Ci/m³) (see Table 3.15). As expected, the ¹³⁷Cs was leached into the supernatant and would be found in relatively large quantities in the LLW form. The ¹³⁷Cs concentrations range between 46 and 168 Ci/m³ for the various streams processed to a borosilicate glass containing 20 wt% Na₂O. In this case, the resultant LLW glass would be considered NRC Class C (between 44 and 4600 Ci/m³). The DF for ⁹⁰Sr is defined as the total ⁹⁰Sr in the solids (μCi) divided by the total ⁹⁰Sr in the supernatant (μCi) for each step. Results show DFs increasing from 539 for the first caustic leach to 11,100 for the final water wash.

Table 3.15. ⁹⁰Sr and ¹³⁷Cs Separation Efficiencies

Enhanced Sludge Washing Step	⁹⁰ Sr ($\mu\text{Ci/g sol'n}$) (μCi)	¹³⁷ Cs ($\mu\text{Ci/g sol'n}$) (μCi)	⁹⁰ Sr in Final LLW Form (Ci/m^3) ^(a)	¹³⁷ Cs in Final LLW Form (Ci/m^3)	⁹⁰ Sr DF ^(d)
Initial Sludge ^(b)	376 4.87E+05	515 6.67E+05	---	---	---
Caustic Leach 1 ^(c)	0.291 904	39.8 1.24E+05	1.16	158	539
Caustic Leach 2	0.193 632	34.3 1.12E+05	0.948	168	770
Water Wash 1	0.0406 155	10.2 3.93E+04	0.485	122	3130
Water Wash 2	0.0196 78.8	3.13 1.26E+04	0.505	80.7	6190
Water Wash 3	0.0112 44.0	1.48 5.81E+03	0.348	46.0	11100
Overall Blend ^(e)	0.100 1810	16.2 2.94E+05	0.883	143	268

(a) Assumes streams are not mixed and are vitrified separately, 20 wt% Na₂O in LLW glass final product and a LLW glass density of 2.5.
 (b) Initial sludge is in $\mu\text{Ci/g}$ of dry solids.
 (c) Enhanced sludge washing steps here are not corrected for interstitial liquid carry-over.
 (d) $\text{DF} = (\text{Total } ^{90}\text{Sr in the solids } [\mu\text{Ci}] / (\text{Total } ^{90}\text{Sr in the supernatant } [\mu\text{Ci}])$.
 (e) Overall Blend is a composite of all caustic leach and water wash solutions.

4.0 Conclusions

Of the major nonradioactive components, those that were significantly removed with enhanced sludge washing included aluminum (31%), chromium (49%), sodium (57%), and phosphorus (35%). In the case of phosphorus, the percentage removed for C-106 is lower than that estimated in the TWRS baseline. Most of the aluminum and phosphorus were removed during the first caustic leach with very little removed during the second caustic leach and subsequent washing steps. The sodium remaining in the sludge appears to be tied up in insoluble sodium aluminosilicates and sparingly soluble sodium oxalate. Approximately half of the solids present after the second caustic leach were sodium oxalate.

The results of these tests differ somewhat from those of the screening test performed by Lumetta et al. (1996a) where considerably more phosphorus and considerably less chromium were leached. These differences could be attributable to both differences in experimental conditions (the screening test experiments were performed at lower wt% solids), differences in the sludge material (the small screening test sample not being representative of the bench-scale sample), and differences in the data analysis. More sodium may have been washed from the sludge during the water wash steps in the screening test because the wt% solids for the screening tests were nearly half those of the bench-scale tests. Thus, the quantity of sodium (and oxalate) removed from the C-106 sludge during full-scale washing may depend more on the total amount of water contacting the sludge rather than the number of washes performed.

Of the radioactive components, a significant amount of ^{137}Cs (49%) were removed during the enhanced sludge wash. Only a very small fraction of the remaining radionuclides were removed, including ^{90}Sr (0.4%) and TRU elements (1.5%). These results are consistent with those of the screening test. All of the supernatants (both individually and as a blend) removed from these washing steps, once vitrified as LLW glasses (at 20 wt% Na_2O), would be less than NRC Class C in TRU elements and less than NRC Class B in ^{90}Sr .

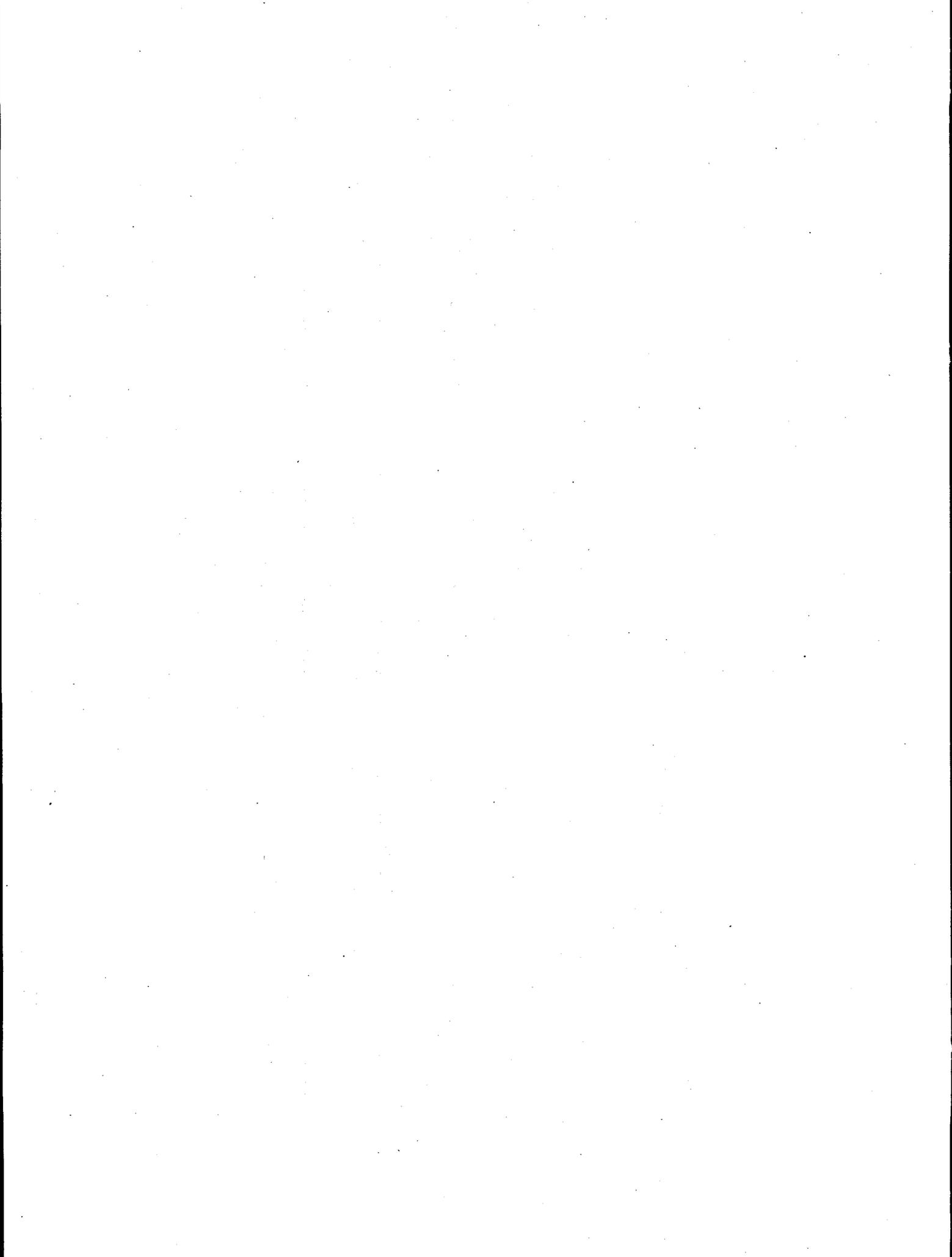
Gravity settle/decant appears to be a viable approach to solid/liquid separations for Tank C-106 sludge considering its settling rate. The solids in the compacted sludge, however, were lower than the TWRS estimate of 20 wt% during the caustic leach steps. The solids generally settled as a single, distinct interface at initial rates ranging from 3.4 to 100 cm/hr as compared to the TWRS estimates for settling rate of 1-2 cm/hr. The initial settling rate increased with each subsequent step of the enhanced sludge wash. The final solids concentration in the sediment after the caustic leaches were 14 wt% and 16 wt% caustic-insoluble solids, respectively. The final solids concentrations in the sediment for each subsequent water wash were 22 wt%, 28 wt%, and 32 wt% caustic-insoluble solids, respectively. These sediment concentrations are 10 to 15 percentage points higher if the sodium oxalate solids are included in the solids concentrations. Higher sludge layers encountered during full-scale operations will increase these solids concentrations even more and may bring them well beyond the TWRS estimate of 20 wt%.

These settling results are fairly consistent with those of the screening tests. Settling rates are similar in spite of the lower solids loading and smaller container used in the screening tests. The wt% solids in the

final compacted sludge were in all cases lower for the screening tests than for the bench-scale tests. These results are consistent with the fact that hindered settling is slowed due to wall effects in smaller settling vessels, and compaction is lower with a smaller quantity of sludge.

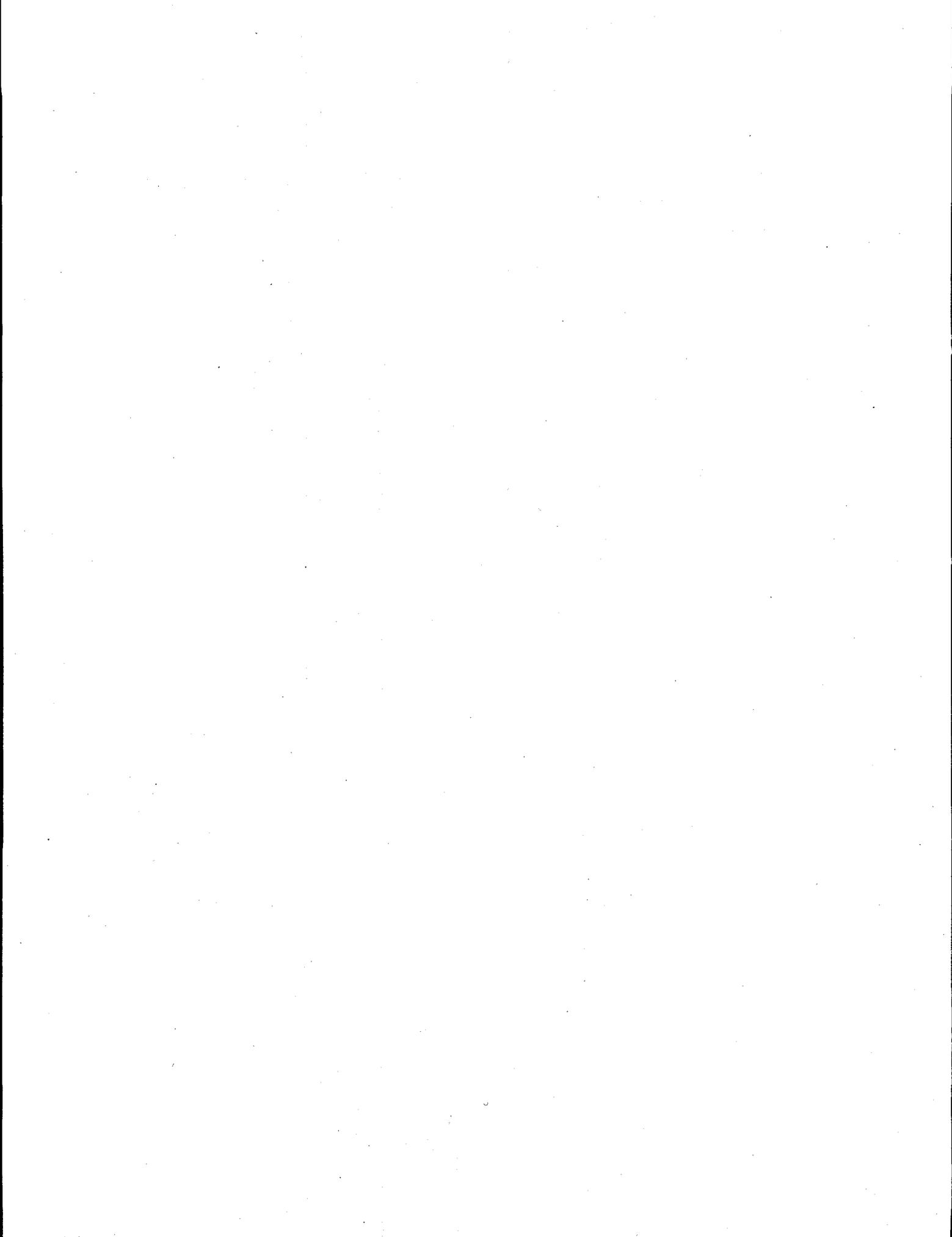
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Appendix A

WSU Project Report 12/30/94 - 9/15/95



Appendix A

WSU Project Report 12/30/94 - 9/15/95

A.1 Introduction

During FY 1995, Washington State University (WSU) performed several simulant sludge settling tests as part of the sludge pretreatment demonstration (SPD) of Hanford's Tank Waste Remediation System (TWRS) project. The purpose of the work performed by WSU was to evaluate the settling behavior of sludge simulants. Of particular interest was the effect of varying solids concentration, settling vessel diameter, temperature, and the use of a rake mechanism on interface settling velocity (ISV).

The two simulants ultimately chosen for analysis were a mixture of kaolin clay and water, and a recipe designed to approximate the contents of Hanford's tank C-106. The solids concentration of the actual sludge following in-tank sludge washing has been estimated at between 5% and 15%. Therefore, these values were targeted in the tests performed by WSU. Ultimately, triplicate test runs were performed on kaolin at 5%, 10%, and 15% solids concentration in 10-cm-diameter and 30-cm-diameter settling columns at both 20 and 50°C.

The same combination of tests were performed for the tank C-106 simulant as kaolin, except that due to time constraints only 8% and 5% solids concentrations were analyzed. Additionally, tests were performed on both simulants utilizing a rake mechanism to evaluate any effect of wall effects on the ISV.

A.2 Experimental Methods

The ISV tests were performed in clear cast acrylic columns both 10-cm-diameter and 30 cm-diameter and about 90 cm tall. Temperature for the heated tests was maintained by placing the 10- and 30-cm-diameter columns inside 20 and 37-cm-diameter columns, respectively, and pumping temperature-controlled water in between the columns. The water temperature was strictly maintained to within 0.1 C with a Haake Model A81 laboratory hot water bath. Cast acrylic lids were fitted atop all columns during testing to minimize evaporative losses. The raked tests were performed utilizing materials and methods described in procedure 2710E of Standard Methods (1992). Total solids concentration for the kaolin simulant was analyzed according to Procedure 2540E Standard Methods (1992), and the total suspended solids of the tank C-106 simulant was determined according to Procedure 2540D Standard Methods (1992).

A sufficient volume of each simulant was mixed in a baffled 55-gallon Nalgene drum using one of two custom electric mixers. The kaolin simulant was mixed by adding the appropriate weight of kaolin clay with deionized water to yield the desired solids concentration. Following the addition of clay, the simulant was allowed to stand for one week to allow for complete hydration of the clay particles. The desired solids

concentrations of the C-106 simulant were obtained by dilution with inhibited water (0.01M NaOH and 0.01M NaNO₂ in deionized water). Following the dilution, the pH of the C-106 simulant was adjusted to 12 with nitric acid. In the event that either simulant was allowed to settle for several days, the large mixer (1 horsepower, 1750 RPM, with 3-bladed, 6-inch stainless steel impeller) was used to insure adequate resuspension of the sludge particles. Following several minutes of mixing at high intensity, the small mixer (½ horsepower, 1750 RPM, with 3-bladed, 3-inch stainless steel impeller) was used to maintain suspension of the particles while the sludge was being pumped into the cylinders.

Sludge was pumped to the cylinders using a Masterflex model # 7549-30 peristaltic pump outfitted with a #82 pump head (Cole Palmer Instrument Comp.) The suction line was held rigid in the mixing drum by placing a 3-ft section of 1/8-inch stainless steel tubing inside the #82 tubing. Two of each 10-cm-diameter and 30-cm-diameter columns were filled to approximately 85 cm with simulant. One each of the 10- and 30-cm-diameter columns were heated to 50°C with the hot water bath and allowed to equilibrate overnight. After the sludge temperature was stabilized, the peristaltic pump was used to resuspend the sludge particles in all columns. The discharge line of the pump was positioned at the bottom of the settling vessel and held rigid with a length of 1/8-inch stainless steel tube. The suction line was positioned near the top of the sludge and a combination of pumping, stirring with the discharge line, and air sparging by raising the suction line above the sludge surface was used to resuspend the sludge particles. After resuspension was complete, interface settling height was recorded over time until the sludge-supernate interface was well into the compression zone of settling. At the end of each test run, the sludge was pumped back into the mixing drum and mixed while the columns were cleaned in preparation for a subsequent run.

A.3 Results and Discussion

The final averaged results of normalized interface height (NIH) as a function of time from all test runs performed on both Kaolin and C-106 simulants are illustrated in Table A.1. Normalized interface height is the sludge-supernate interface height divided by the original sludge height in the column at time zero. Additionally, a statistical analysis was performed on the individual results from each test run in an attempt to quantify the significance of varying column diameter, temperature, and interaction between column diameter and temperature on ISV. The results listed in Table A.1 for the C-106 simulant at 8% solids is individual test data from test Run #3. Results were not averaged for the three test runs because of a significant decrease in the ISV between the three test runs. This decrease was hypothesized to be a result of the chemical nature of the simulant changing with time. Additional tests performed in 10-cm-diameter columns at 20°C approximately 2 weeks following the completion of Run #3 confirmed that the chemical nature of the simulant had stabilized, and the results from test Run #3 are reliable. Since only one test run was used to quantify the ISV behavior of this simulant, no statistical analysis could be performed.

A.3.1 Statistical Analysis of Data

The statistical analysis was implemented utilizing a two-factor, two-level experimental design within an 8 X 8 Hadamard matrix (Diamond 1981). For eight runs per simulant, this configuration provided a 90% chance of detecting a 2.5 standard deviation difference using a 90% confidence test.

Table A.1. Normalized Interface Height (NIH) Summary Data

kaolin 5% solids summary data			
column	.5 hr	1 hr	48 hr
20C 10 cm	0.738	0.422	0.168
20C 30 cm	0.752	0.462	0.165
50C 10 cm	0.424	0.359	0.172
50C 30 cm	0.442	0.358	0.168

kaolin 10% solids summary data				
column	.5 hr	1 hr	48 hr	72 hr
20C 10 cm	0.843	0.616	0.316	0.291
20C 30 cm	0.829	0.576	0.300	0.274
50C 10 cm	0.685	0.596	0.304	0.294
50C 30 cm	0.639	0.557	0.284	0.273
60C 10 cm	0.634	0.581	N/A	N/A
70C 10 cm	0.612	0.560	0.304	0.300
80C 10 cm	0.621	0.570	0.304	0.300
20C 10 cm rak	0.898	0.699	N/A	N/A
20C 55 cm	0.848	0.602	N/A	N/A

kaolin 15% solids summary data					
column	.5 hr	1 hr	48 hr	72 hr	144 hr
20C 10 cm	0.942	0.846	0.464	0.426	0.369
20C 30 cm	0.952	0.907	0.498	0.451	0.368
50C 10 cm	0.836	0.759	0.422	0.391	0.366
50C 30 cm	0.866	0.817	0.420	0.379	0.341

C-106 5% solids summary data				
column	12 hr	24 hr	48 hr	72 hr
20C 10 cm	0.823	0.624	0.395	0.351
20C 30 cm	0.831	0.654	0.391	0.353
50C 10 cm	0.561	0.409	0.342	0.305
50C 30 cm	0.623	0.406	0.343	0.305

C-106 8% solids summary data				
column	12 hr	24 hr	48 hr	72 hr
20C 10 cm	0.897	0.803	0.584	0.544
20C 30 cm	0.917	0.828	0.614	0.570
50C 10 cm	0.697	0.629	0.568	0.529
50C 30 cm	0.728	0.665	0.597	0.550
20C 10 cm rak	0.969	0.923	0.828	0.726

The statistical output generated from the Hadamard matrix model is listed in Table A.2 for every solids concentration tested for each simulant. The term XT20-XT50 is a measure of the significance of temperature, 20°C compared to 50°C, on the NIH. The term XD10-XD30 is a measure of the significance of varying column diameter, 10-cm Versus 30-cm, on the NIH. The term X+AB - X-AB is a measure of any interaction between column diameter and simulant temperature on NIH. Xhigh - Xlow is the objective criterion, which is a function of the variance, sample size, and desired confidence interval. The absolute value of each term of interest is compared to the objective criterion in order to establish a statistically verifiable difference. For example, if the absolute value of the term XT20-XT50 is less than the objective criterion, then no statistical difference in NIH exists for tests conducted at 20°C or 50°C. If the absolute value of the temperature term is greater than the objective criterion, there is said to be a significant statistical impact of temperature on the NIH. The Hadamard matrix model used for these analyses was constructed such that a negative value for the temperature or column diameter term, of magnitude greater than the objective criterion indicates a positive effect on NIH. For example, if the objective criterion were 0.015, and the temperature and column diameter terms were both -0.02, then it can be concluded that tests performed at either warmer temperature or in the larger settling vessel led to an increase in settling velocity (decrease in NIH for a given time interval).

A.3.2 Effect of Temperature

Analysis of Table A.2 indicates a trend of reduced significance of the effect of temperature on NIH with settling time during a test run, for each solids concentration of both simulant tested, as indicated by the reduced difference between the temperature term, XT20 - XT50 and the objective criterion. For most tests, even after 48 hours, the Hadamard matrix model implied a statistically significant increase in ISV with increased temperature. Although a statistical difference is shown, the practical significance of this difference must be examined. For example, for kaolin at 15% solids and time 144 hours, the temperature term = -0.0153 and the objective criterion is 0.0089, implying that temperature has a statistically significant effect on NIH. Analysis of Table A.1 (kaolin 15% solids), however, reveals that the difference in NIH at time 144 hours for the test in the 10-cm-diameter column is only 2.55 mm $[(0.369-0.366) \times 85\text{cm}]$, which poses little, if any practical significance in an 85-cm-tall column. The greatest difference in NIH of approximately 0.05 at time 72 hours is seen in Table A.1 for the C-106 simulant at 5% solids. This difference in an 85-cm-tall column equated to just under 4 cm or approximately 5%. Although this could be considered practically significant, analysis of the raw data for this test run reveals that at time 118 hours, the difference reduces to 2.7 cm. This reduction in difference with time again reinforces the trend in reduced significance of the effect of temperature on NIH with time during the test run.

A.3.3 Effect of Column Diameter

It was more difficult to find a trend in the effect of column diameter on ISV. Analysis of the NIH in Table A.1 for kaolin at 5% and 15% solids shows that the average ISV was slightly less for the larger diameter column until the test time reached 48 hours and 144 hours, respectively. For kaolin, the final NIH reached at the end of each test run was slightly less for sludge settled in the larger diameter columns. The NIH of the C-106 simulant at 5% solids followed a similar pattern, except the final NIH at time 72 hours was

Table A.2. Hadamard Matrix Statistical Analysis for Individual Test Runs

kaolin 5% 0.5 hr		kaolin 5% 1 hr		kaolin 5% 48 hr	
S_{avg}^2	0.0001	S_{avg}^2	0.0002	S_{avg}^2	0.0000
S_{avg}	0.0111	S_{avg}	0.0125	S_{avg}	0.0015
$X_{T20} - X_{T50}$	-0.3143	$X_{T20} - X_{T50}$	-0.0728	$X_{T20} - X_{T50}$	0.0037
$X_{D10} - X_{D30}$	0.0183	$X_{D10} - X_{D30}$	0.0218	$X_{D10} - X_{D30}$	-0.0037
$X_{+AB} - X_{-AB}$	0.0013	$X_{+AB} - X_{-AB}$	0.0248	$X_{+AB} - X_{-AB}$	0.0012
$X_{high} - X_{low}$	0.0120	$X_{high} - X_{low}$	0.0136	$X_{high} - X_{low}$	0.0016
kaolin 10% 0.5 hr		kaolin 10% 1 hr		kaolin 10% 48 hr	
S_{avg}^2	0.0003	S_{avg}^2	0.0005	S_{avg}^2	0.0001
S_{avg}	0.0166	S_{avg}	0.0219	S_{avg}	0.0076
$X_{T20} - X_{T50}$	-0.1965	$X_{T20} - X_{T50}$	-0.0255	$X_{T20} - X_{T50}$	-0.0133
$X_{D10} - X_{D30}$	-0.0265	$X_{D10} - X_{D30}$	-0.0325	$X_{D10} - X_{D30}$	-0.0178
$X_{+AB} - X_{-AB}$	0.0005	$X_{+AB} - X_{-AB}$	0.0000	$X_{+AB} - X_{-AB}$	0.0018
$X_{high} - X_{low}$	0.0179	$X_{high} - X_{low}$	0.0237	$X_{high} - X_{low}$	0.0082
kaolin 10% 72 hr		kaolin 15% .5 hr		kaolin 15% 1 hr	
S_{avg}^2	0.0000	S_{avg}^2	0.0001	S_{avg}^2	0.0011
S_{avg}	0.0063	S_{avg}	0.0100	S_{avg}	0.0325
$X_{T20} - X_{T50}$	0.0008	$X_{T20} - X_{T50}$	-0.1025	$X_{T20} - X_{T50}$	-0.1050
$X_{D10} - X_{D30}$	-0.0188	$X_{D10} - X_{D30}$	0.0170	$X_{D10} - X_{D30}$	0.0290
$X_{+AB} - X_{-AB}$	0.0023	$X_{+AB} - X_{-AB}$	-0.0105	$X_{+AB} - X_{-AB}$	0.0065
$X_{high} - X_{low}$	0.0069	$X_{high} - X_{low}$	0.0108	$X_{high} - X_{low}$	0.0352
kaolin 15% 48 hr		kaolin 15% 72 hr		kaolin 15% 144 hr	
S_{avg}^2	0.0003	S_{avg}^2	0.0002	S_{avg}^2	0.0001
S_{avg}	0.0166	S_{avg}	0.0123	S_{avg}	0.0082
$X_{T20} - X_{T50}$	-0.0633	$X_{T20} - X_{T50}$	-0.0565	$X_{T20} - X_{T50}$	-0.0153
$X_{D10} - X_{D30}$	0.0153	$X_{D10} - X_{D30}$	0.0065	$X_{D10} - X_{D30}$	-0.0113
$X_{+AB} - X_{-AB}$	0.0208	$X_{+AB} - X_{-AB}$	0.0200	$X_{+AB} - X_{-AB}$	0.0133
$X_{high} - X_{low}$	0.0180	$X_{high} - X_{low}$	0.0133	$X_{high} - X_{low}$	0.0089

Table A.2. (contd)

C-106 5% 12 hr		C-106 5% 24 hr		C-106 5% 48 hr	
S_{avg}^2	0.0005	S_{avg}^2	0.0019	S_{avg}^2	0.0000
S_{avg}	0.0220	S_{avg}	0.0434	S_{avg}	0.0049
$X_{T20} - X_{T50}$	-0.2355	$X_{T20} - X_{T50}$	-0.2315	$X_{T20} - X_{T50}$	-0.0508
$X_{D10} - X_{D30}$	0.0350	$X_{D10} - X_{D30}$	0.0140	$X_{D10} - X_{D30}$	-0.0013
$X_{+AB} - X_{-AB}$	-0.0270	$X_{+AB} - X_{-AB}$	0.0170	$X_{+AB} - X_{-AB}$	-0.0023
$X_{high} - X_{low}$	0.0238	$X_{high} - X_{low}$	0.0470	$X_{high} - X_{low}$	0.0053
C-106 5% 72 hr					
S_{avg}^2	0.0000				
S_{avg}	0.0034				
$X_{T20} - X_{T50}$	-0.0493				
$X_{D10} - X_{D30}$	-0.0017				
$X_{+AB} - X_{-AB}$	-0.0018				
$X_{high} - X_{low}$	0.0037				

approximately equal for both diameter columns. The NIH of the C-106 simulant at 8% solids was slightly greater for the larger diameter column at the end of the test run, but this difference was only about 2 cm in an 85-cm-tall column.

A.3.4 Interaction Between Column Diameter and Temperature

An additional bonus provided by the Hadamard matrix model is a statistically defensible quantification of the effect of interaction between column diameter and temperature on the ISV. Analysis of Table A.2, however, indicates that the magnitude of the interaction term is less than the objective criterion for nearly all test runs. It can, therefore, be concluded that no significant interaction between temperature and column diameter effects the ISV.

A.3.5 Effect of Rake Mechanism

Preliminary tests were performed on both simulants utilizing a rake mechanism (Procedure 2710 E, Standard Methods 1992) to evaluate the effect of the rake on ISV in the 10-cm-diameter settling column.

Use of the rake during an ISV test of kaolin at 10% solids resulted in a decrease in the initial settling velocity. However, as the test proceeded the NIH decreased to a value that was unattainable in either diameter column previously tested.

Use of the rake mechanism on the C-106 simulant drastically reduced the ISV and NIH compared to unraked tests. A comparison of raked and unraked tests for both simulants is illustrated in Figure A.1 and Figure A.2.

A.3.6 Final Settled Solids Concentration

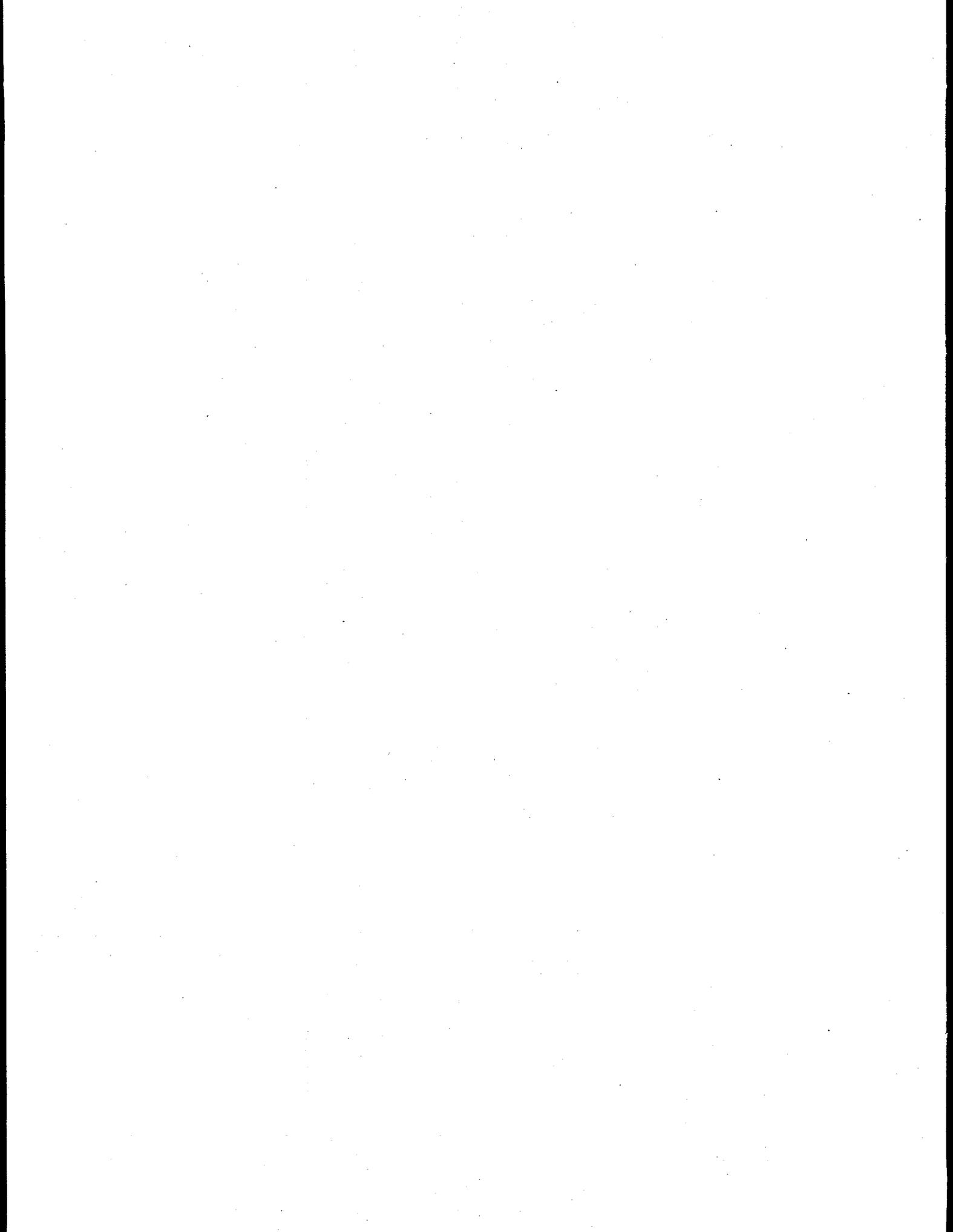
An additional practical item of concern is the average solids concentration of the sludge layer in the bottom of the test column following completion of the ISV test. A few tests were performed on the Kaolin at 15% solids to determine the concentration. After the ISV was well into the compression zone of settling, an aliquot of sludge was taken both approximately 3 cm below the sludge-supernate interface and above the bottom of the settling column. These samples were analyzed for solids concentration and averaged to determine the average solids concentration of the settled sludge layer. The average sludge concentration can also be calculated by assuming negligible suspended solids in the supernate and dividing the initial solids concentration (15%) by the normalized interface height. The resulting solids concentrations determined by both methods are illustrated in Table A.3.

A.4 Conclusion

The ISV of both simulants, Kaolin and C-106, was found to be independent of both sludge temperature and column diameter. Although increased sludge temperature significantly increases the ISV during the hindered zone of settling, this effect becomes relatively insignificant as the settling regime progresses into the compression zone, the region of practical application. The use of a rake actually slowed the ISV of the C-106 simulant, but assisted the kaolin to settle to a low NIH not attainable in the large diameter settling vessel. This was an interesting result and may warrant further investigation regarding mechanisms that could be employed in the field to enhance solids concentration. The data indicate that the use of a rake is not necessary when using a small diameter column to evaluate ISV and NIH.

A.5 Reference

Diamond, W. J. 1981. *Practical Experimental Design for Engineers and Scientists*, Lifetime Learning Publications, Belmont, California.



Appendix B

Test Conduct: Detailed Operations Description

Appendix B

Test Conduct: Detailed Operations Description

B.1 Retrieval Slurry Preparation

B.1.1 Tank Waste Sample Preparation

The C-106 tank waste sample was received from the 325 Building in two containers. The net weight of the sample was 3900 grams, and the insoluble solids concentration was 38 wt.%. Of this sample, 3074 grams were used in the TWRS Privatization Contractor Sample tests, a quantity limited by the capacity of the sludge settler. The amount of inhibited water (0.01 M NaOH/0.01 M NaNO₂) required was calculated to be 1003 grams, and this amount was made up and added to the cold chemical tank. This water was used as rinse water by pumping from the cold chemical tank through the quick disconnect into a bottle in the cell. This bottle was used to pour water on the funnel and into the sample containers for rinsing. The sample containers were triple-rinsed to remove all of the C-106 sludge, and two additional bottles of deionized rinse water were required. During handling with the manipulator, the plastic rinse bottle split and spilled approximately 50 mL of water. Thus, the total amount of rinse water used was 1965 grams (mL), and all but approximately 50 mL was added to the sludge in the sludge receipt tank.

The off-gas system was started, and the agitator in the sludge receipt tank was turned on. Data required for the determination of the level and density (PIR102 and PIR103) of the slurry in the sludge receipt tank were taken, but did not look reasonable. Instruments later were obviously malfunctioning and may have been going bad at this time. The option in the procedure to run the slurry through a high-speed centrifugal pump, simulating the retrieval mixer pumps, was not done during this test.

The slurry in the sludge receipt tank was recirculated through pump P-203, and five slurry samples were obtained from the sample port. Initial attempts to obtain these samples were unsuccessful, but after replacing the hose in pump P-203 and allowing the slurry to mix with the agitator in the sludge receipt tank for 2 days, they were obtained.

The retrieval wash and subsequent settling test and axial supernate sampling were skipped and not performed as part of the C-106 Privatization Contractor Sample preparation.

B.2 First Caustic Leach and Settling Test

B.2.1 Add Caustic Solution, Heat, and Agitate

The amount of 10 M caustic leach needed to achieve the desired final concentration of 3 M NaOH with an insoluble solids concentration of five wt.% was calculated to be 2340 grams. This amount of caustic leach was added to the cold chemical tank and transferred to the sludge receipt tank.

The off-gas system was set for heating, and the heater in the sludge receipt tank was turned on. While the slurry was heating, the agitator continued to operate. The determination of the level and density (PIR102 and PIR103) of the slurry in the sludge receipt tank was not possible because of instrument malfunctions. The option in the procedure to run the slurry through a high-speed centrifugal pump, simulating the retrieval mixer pumps, was not done during this test. The slurry in the sludge receipt tank was heated to 100°C and held at that temperature for 5 hours while mixing with the agitator. Meanwhile, the temperature of the water in the circulating hot water bath was heated to 80°C.

B.2.2 First Caustic Leach Settling Test

When the slurry had mixed at 100°C for 5 hours and the temperature in the circulating hot water bath was at 80°C, the slurry was transferred from the sludge receipt tank to the sludge settler. Immediately after the transfer, the settling test was started. At the start of the settling test, the slurry volume was 4825 mL, corresponding to a height of 13 ¼ inches in the sludge settler.

During regular work hours, the solids/liquid interface was visually observed and recorded on data sheets. The entire settling process was also recorded on videotape (SPD1-C106-001), so the entire settling rate and solids/liquid interface can be documented. Electronic data were monitored and recorded on a data disk (disk C106DAS, FILE C106.xls) automatically by the data acquisition system. Two hours short of three days from the start of testing, the settling test was terminated. The final total volume was 4750 mL, corresponding to 13 ¾ inches in the sludge settler. The final volume of the solids was 1900 mL, corresponding to 27 5/8 inches height in the sludge settler.

B.2.3 Axial Sampling

While attempting to obtain axial location supernate samples following the gravity settling test, only a few drops of supernate could be held in the sample tube. After checking the pump drive tube, the flexible tube in the sample line, and all fittings in the line for leaks, samples still could not be obtained. Finally, the sample tube flexible hose was replaced, the fittings were tightened, and samples could be successfully obtained. Three samples were used to check out the equipment (SPD1-C106-006 through SPD1-C106-008). Some solids were disturbed during the process and allowed to settle overnight. Three 15-mL in situ samples (SPD1-C106-009 through SPD1-C106-011) of the supernate were taken at axial elevations of 16, 21, and 27 inches from the top of the sludge settler (measured on the sludge settler ruler). The samples were obtained by 1) inserting the sample tube into the supernate to the desired sample location (upper samples first), 2) running the peristaltic pump (P-301) clockwise to draw the sample into the tube, 3) raising the sample tube

out of the sludge settler, 4) placing the sample bottle under the sample tube, and 5) running the pump (P-301) counter clockwise to discharge the sample into the bottle. To obtain the desired 15-mL volume, the peristaltic pump volume setting was set at 60. Weights of the top, middle, and bottom supernate samples were 22.7, 16.4, and 19.9 grams, respectively.

The supernate was decanted by lowering the sample tube to within 2 inches of the solids layer and slowly pumping the supernate into the batch collection tank. As the liquid level came near the end of the sample tube, the sample tube was incrementally lowered until it was within 1/8 inches of the solids level. The amount of supernate removed in the process was 2650 mL, as determined from observations of the liquid height in the sludge settler before and after decanting.

B.2.4 Supernate Sampling and Transfer

The supernate from the first caustic leach and settling test in the batch collection tank, C-301, was recirculated from the tank through pump P-302 back to the tank. After recirculating for 5 minutes, two supernate samples (SPD1-C106-012 and SPD1-C106-013) were obtained from the in-line sample port. These samples weighed 19.7 and 15.0 grams, respectively. After these samples were obtained, all of the supernate in tank C-301 was transferred to the supernate holding tank, C-302.

B.2.5 Inhibited Water/Caustic Leach Addition and Solids Resuspension

Instead of adding inhibited water (0.01 M NaOH and 0.01 M NaNO₂) at this point and 10 M caustic (NaOH) during the beginning of the next procedure, as described in the procedures, 3 M caustic (NaOH) solution was added at this time. The amount added (3286 grams) was calculated to replace the inhibited water that was to be added now plus the 10 M caustic to be added in the early part of the second caustic leach test. This amount (3286 grams) of 10 M caustic was prepared, weighed, and added to the cold chemical tank. Approximately 500 mL was then pumped into the sludge settler.

The solids in the sludge settler were then resuspended by 1) placing the sample tube approximately 2 inches below the liquid level and 2) circulating the slurry through the sample tube, pump P-202, and back through a port in the bottom of the sludge settler. When the slurry was homogenous (as determined by visual observation), the valve at the bottom of the sludge settler was opened, and the slurry was transferred to the sludge receipt tank. The pump continued to run for a minute to clear the line.

The remaining 3 M caustic (2150 mL corresponding to a height of 26 1/2 inches on the sludge settler) was pumped into the sludge settler. It was circulated through the sample tube, pump P-202, and back, as described above, for 10 minutes to rinse the sludge settler. During this rinse, the drive hose in pump P-202 split, spraying the caustic over the equipment on the table. The pump was immediately shut off, but approximately 450 mL of caustic was lost. This amount is based on the observed liquid level in the sludge settler, 28 3/4 inches, and the corresponding volume (1700 mL). The liquid lost drained from the table into the secondary catch pan on the floor and activated the secondary containment liquid level alarm, including the visible, audible, and automatic computer phone dialing procedure. After cleaning up the spill, the alarm was reset. An additional 503 grams of 3 M caustic were added to the sludge settler to replace that which was lost.

After replacing the hose on pump P-202, the recirculating rinse procedure was repeated. This rinse leach was then drained into the sludge receipt tank. The agitator in the sludge receipt tank was turned on.

B.3 Second Caustic Leach and Settling Tests

B.3.1 Add Caustic Solution, Heat, and Agitate

The amount of 3 M caustic (NaOH) needed was calculated and added during the first caustic leach test. Therefore, no liquid was added at the beginning of the second caustic leach and settling test. The off-gas system was set for heating, and the heater in the sludge receipt tank was turned on. While the slurry was heating, the agitator continued to operate. Determining the level and density (PIR102 and PIR103) of the slurry in the sludge receipt tank was not possible because of instrument malfunctions. The option in the procedure to run the slurry through a high-speed centrifugal pump, simulating the retrieval mixer pumps, was not done during this test. The slurry in the sludge receipt tank was heated to 100°C and held at that temperature for 5 hours while mixing with the agitator. Meanwhile, the temperature of the water in the circulating hot water bath was heated to 80°C.

B.3.2 Second Caustic Leach Settling Test

When the slurry had mixed at 100°C for 5 hours and the temperature in the circulating hot water bath was at 80°C, the slurry was transferred from the sludge receipt tank to the sludge settler. Immediately after the transfer, the first settling test was started. The volume of slurry in the sludge settler at the start of the settling test was 4800 mL, which corresponds to 13 ½ inches height.

During regular work hours, the solids/liquid interface was visually observed and recorded on data sheets. The entire settling process was also recorded on videotape (SPD1-C107-002) so the entire settling rate and solids/liquid interface can be documented. Electronic data were monitored and recorded on a data disk (disk C106DAS, file C106.xls) automatically by the data acquisition system. One day and 14 hours after the start of testing, the settling test was ended. The final total volume was 4600 mL, corresponding to 14 ½ inches in the sludge settler. The final volume of the solids was 1700 mL, corresponding to 28 ¾ inches in the sludge settler.

B.3.3 Axial Sampling

Three 15-mL in situ samples (SPD1-C107-014 through SPD1-C107-016) of the supernate were taken at axial elevations of 16, 22, and 27 inches from the top of the sludge settler (measured on the sludge settler ruler). The samples were obtained by 1) inserting the sample tube into the supernate to the desired sample location (upper samples first), 2) running the peristaltic pump (P-301) clockwise to draw the sample into the tube, 3) raising the sample tube out of the sludge settler, 4) placing the sample bottle under the sample tube, and 5) running the pump (P-301) counter clockwise to discharge the sample into the bottle. The samples were weighed and the top, middle, and bottom supernate sample weights were 24.9, 22.7, and 22.8 grams, respectively.

Solids samples were not obtained after this gravity settling test.

B.3.4 Supernate Decant and Transfer

The supernate was decanted by lowering the sample tube to within 2 inches of the solids layer and slowly pumping the supernate into the batch collection tank. As the liquid level came near the end of the sample tube, the sample tube was incrementally lowered until it was within 1/8 inches of the solids level. The amount of supernate removed in the process was 2850 mL, as determined from observations of the liquid height in the sludge settler before and after decanting.

B.3.5 Supernate Sampling and Transfer

The supernate in the batch collection tank, C-301, from the second caustic leach and settling test was recirculated from the tank through pump P-302 back to the tank. After recirculating for 5 minutes, two supernate samples (SPD1-C106-017 and SPD1-C106-018) were obtained from the in-line sample port. These samples weighed 20.6 grams each. After these samples were obtained, all of the supernate in tank C-301 was transferred to the supernate holding tank, C-302.

B.3.6 Inhibited Water Addition and Solids Resuspension

The amount of inhibited water (0.01 M NaOH and 0.01 M NaNO₂) to be added for the first water wash and settling test was calculated to be 3164 grams. This amount of inhibited water was prepared, weighed, and 1185 grams of it were added to the cold chemical tank. This water was pumped into the sludge settler. The solids in the sludge settler were then resuspended by 1) placing the sample tube approximately two inches below the liquid level and 2) circulating the slurry through the sample tube, pump P-202, and back through a port in the bottom of the sludge settler. When the slurry was homogenous (as determined by visual observation), the valve at the bottom of the sludge settler was opened and the slurry was transferred to the sludge receipt tank. The pump continued to run for a minute to clear the line.

Remaining inhibited water (1979 grams) was placed in the cold chemical tank and pumped into the sludge settler. It was circulated through the sample tube, pump P-202, and back into the sludge settler for 10 minutes to rinse the sludge settler. This rinse water was then drained into the sludge receipt tank. The agitator in the sludge receipt tank was turned on.

B.4 First Water Wash and Settling Test

Inhibited water (0.01 M NaOH and 0.01 M NaNO₂) required for this test was added at the end of the second caustic leach and settling test. The resulting slurry was in the sludge receipt tank at the beginning the first water wash and settling test.

B.4.1 Agitate and Heat

The slurry was cooled to ambient temperature and mixed with the agitator in the sludge receipt tank. The option in the procedure to run the slurry through a high-speed centrifugal pump, simulating the retrieval mixer pumps, was not done during this test. Meanwhile, the temperature of the water in the circulating hot water bath was cooled to ambient temperature.

B.4.2 Gravity Settle Test

When the slurry had cooled to ambient and the temperature in the circulating hot water bath reached lower than 40°C, the slurry was transferred from the sludge receipt tank to the sludge settler. Immediately after the transfer, the settling test was started. The slurry volume at the start of the settling test was 4850 mL, corresponding to a height of 13 ¼ inches in the sludge settler. The temperature, as recorded on the circulating hot water bath inlet, was 37.1°C.

During regular work hours, the solids/liquid interface was visually observed and recorded on data sheets. Also, the entire settling process was recorded on videotape (SPD1-C107-003), so the entire settling rate and solids/liquid interface can be documented. Electronic data were monitored and recorded on a data disk (disk C106DAS, file C106.xls) automatically by the data acquisition system. After 2 days and 20 hours of settling, the settling test was ended. The final total volume was 4800 mL, corresponding to 13 3/8 inches in the sludge settler. The final volume of the solids was 1250 mL, corresponding to 31 inches in the sludge settler.

B.4.3 Axial Sampling

Four 15-mL in situ samples (SPD1-C107-019 through SPD1-C107-022) of the supernate were taken at axial elevations of 15, 23, and 30 inches from the top of the sludge settler (measured on the sludge settler ruler). The bottom sample was taken twice because of the low volume obtained the first time. The samples were obtained by 1) inserting the sample tube into the supernate to the desired sample location (upper samples first), 2) running the peristaltic pump (P-301) clockwise to draw the sample into the tube, 3) raising the sample tube out of the sludge settler, 4) placing the sample bottle under the sample tube, and 5) running the pump (P-301) counter clockwise to discharge the sample into the bottle. The samples were weighed and the top, middle, and bottom supernate sample weights were 18.4, 22.4, 7.7, and 25.6 grams, respectively.

Supernate was decanted by lowering the sample tube to within 2 inches of the solids layer and slowly pumping the supernate into the batch collection tank. The first attempts to decant the supernate were unsuccessful, even when higher pump speeds were used. A kink in the drive hose for pump P-301 was straightened, and the problem was solved. However, some solids had been stirred up by backflow from the sample tube when the pump was turned off. They were allowed to settle for about 6 hours, and the decanting process was resumed. As the liquid level came near the end of the sample tube, the sample tube was incrementally lowered until it was within 1/8 inches of the solids level. Supernate removed in the process was 3550 mL, determined from observations of the liquid height in the sludge settler before and after decanting.

B.4.4 Supernate Sampling and Transfer

The supernate from the first water wash that was decanted after the settling test and was in the batch collection tank, C-301, was transferred to the supernate holding tank, C-302. Samples of this supernate were not obtained.

B.4.5 Inhibited Water Addition

The amount of inhibited water (0.01 M NaOH and 0.01 M NaNO₂) to be added for the second water wash and settling test was calculated to be 3626 grams. This amount of inhibited water was prepared, weighed, and added to the cold chemical tank. Approximately 575 mL of inhibited water was pumped into the sludge settler. A considerable amount of foaming was observed as the water was added to the sludge settler.

The solids in the sludge settler were then resuspended by 1) placing the sample tube approximately 2 inches below the liquid level and 2) circulating the slurry through the sample tube, pump P-202, and back through a port in the bottom of the sludge settler. When the slurry was homogenous (as determined by visual observation), the valve at the bottom of the sludge settler was opened, and the slurry was transferred to the sludge receipt tank. The pump continued to run for a minute to clear the line.

The remaining inhibited water (3050 mL) was pumped into the sludge settler and was circulated to rinse the sludge settler. This rinse water was then drained into the sludge receipt tank, and the agitator in the tank was turned on.

B.5 Second Water Wash and Settling Test

Inhibited water (0.01 M NaOH and 0.01 M NaNO₂) required for this test was added at the end of the first water wash and settling test (Section B.4). The resulting slurry was in the sludge receipt tank at the beginning of the this second water wash and settling test.

B.5.1 Heat, and Agitate

The slurry was mixed with the agitator in the sludge receipt tank. The option in the procedure to run the slurry through a high speed centrifugal pump, simulating the retrieval mixer pumps, was not done during this test. The slurry in the sludge receipt tank was maintained at ambient temperature for 30 minutes while mixing with the agitator. Meanwhile, the temperature of the water in the circulating hot water bath also remained at ambient.

B.5.2 Second Water Wash Settling Test

With the slurry and the hot water bath at ambient temperature, 4900 mL of slurry was transferred from the sludge receipt tank to the sludge settler. This volume corresponds with 13 inches on the sludge settler. Immediately after the transfer, the first settling test was started.

During regular work hours, the solids/liquid interface was visually observed and recorded on data sheets. The entire settling process was also recorded on videotape (SPD1-C106-004) so the entire settling rate and solids/liquid interface can be documented. Electronic data were monitored and recorded on a data disk (disk C106DAS, file C106.xls) automatically by the data acquisition system. After 1 day and 13 hours from the start of testing, the settling test was ended. The final total volume was 4850 mL, corresponding to 13 ¼ inches in the sludge settler. The final volume of the solids was 1050 mL, corresponding to 32 inches in the sludge settler.

B.5.3 Axial Sampling

Three 15-mL in situ samples (SPD1-C106-023 through SPD1-C106-025) of the supernate were taken at axial elevations of 14, 24, and 31 inches from the top of the sludge settler (measured on the sludge settler ruler). The samples were obtained by 1) inserting the sample tube into the supernate to the desired sample location (upper samples first), 2) running the peristaltic pump (P-301) clockwise to draw the sample into the tube, 3) raising the sample tube out of the sludge settler, 4) placing the sample bottle under the sample tube, and 5) running the pump (P-301) counter clockwise to discharge the sample into the bottle. The samples were weighed and the top, middle, and bottom supernate sample weights were 12.0, 13.0, and 18.7 grams, respectively.

Solids samples were not obtained after this gravity settling test.

B.5.4 Supernate Decant and Transfer

Supernate was decanted by lowering the sample tube to within 2 inches of the solids layer and slowly pumping the supernate into the batch collection tank. As the liquid level came near the end of the sample tube, the sample tube was incrementally lowered until it was within 1/8 inches of the solids level. Supernate removed in the process was 3800 mL, determined from observations of the liquid height in the sludge settler before and after decanting.

B.5.5 Supernate Sampling and Transfer

The supernate from the second water wash that was in the batch collection tank, C-301, was recirculated from the tank through pump P-302 back to the tank. After recirculating for 5 minutes, two supernate samples (SPD1-C106-026 and SPD1-C106-027) were obtained from the in line sample port. These samples weighed 18.8 and 20.5 grams, respectively. After these samples were obtained, all of the supernate in tank C-301 was transferred to the supernate holding tank, C-302.

B.5.6 Inhibited Water Addition

The amount of inhibited water (0.01 M NaOH and 0.01 M NaNO₂) to be added for the third water wash and settling test was calculated to be 3823 grams. This amount of inhibited water was prepared, weighed, and added to the cold chemical tank. Approximately 773 mL of inhibited water was pumped into the sludge settler.

The solids in the sludge settler were then resuspended by 1) placing the sample tube approximately two inches below the liquid level and 2) circulating the slurry through the sample tube, pump P-202, and back through a port in the bottom of the sludge settler. During this resuspension, a significant layer of foam was observed but no measurement was made as the amount or height of the foam. When the slurry was homogeneous (as determined by visual observation), the valve at the bottom of the sludge settler was opened, and the slurry was transferred to the sludge receipt tank. The pump continued to run for a minute to clear the line.

The remaining inhibited water (3050 mL) was pumped into the sludge settler and was circulated to rinse the sludge settler. During this circulating and rinsing, a significant foam layer was observed in the sludge settler. Then, the drive hose on pump P-202 broke and was replaced with one from pump P-203. Inhibited water lost because of this break was too small to measure (the total volume in the sludge settler was still 22 inches [3050 mL]). The rinse was completed, and the water was then drained into the sludge receipt tank. The agitator in the tank was turned on.

B.6 Third Water Wash and Settling Test

Inhibited water (0.01 M NaOH and 0.01 M NaNO₂) required for this test was added at the end of the second water wash and settling test. The resulting slurry was in the sludge receipt tank at the beginning of the first water wash and settling test.

B.6.1 Agitate and Heat

The agitator continued to mix the slurry at ambient temperature in the sludge receipt tank. Volume was not determined from the density and level indications because of instrument malfunctions. The option in the procedure to run the slurry through a high-speed centrifugal pump, simulating the retrieval mixer pumps, was not done during this test. Meanwhile, the water in the circulating hot water bath was maintained at ambient temperature.

B.6.2 Gravity Settle Test

The slurry was transferred from the sludge receipt tank to the sludge settler, and immediately after the transfer the settling test was started. Foam was observed on top of the slurry in the sludge settler. The difference between the foam layer and the slurry layer was 3 3/4 inches, corresponding to a volume of approximately 750 mL. At the start of the settling test the slurry volume was 4400 mL, corresponding to a height of 15 1/2 inches in the sludge settler. The temperature, as recorded on the circulating hot water bath inlet, was 31.0°C.

During regular work hours, the solids/liquid interface was visually observed and recorded on data sheets. The entire settling process was also recorded on videotape (SPD1-C107-005), so the entire settling rate and solids/liquid interface can be documented. Electronic data were monitored and recorded on a data disk (disk C106DAS, file C106.xls) automatically by the data acquisition system. The foam layer gradually dissipated and disappeared during the settling test. After just less than six hours of settling, the settling test was ended. The final total volume was 4650 mL, corresponding to 14 ¼ inches in the sludge settler. The final volume of the solids was 1050 mL, corresponding to 32 inches in the sludge settler.

B.6.3 Axial Sampling

Three 15 mL in-situ samples (SPD1-C107-028 through SPD1-C107-030) of the supernate were taken at axial elevations of 16, 24, and 31 inches from the top of the sludge settler (measured on the sludge settler ruler). The samples were obtained by 1) inserting the sample tube into the supernate to the desired sample location (upper samples first), 2) running the peristaltic pump (P-301) clockwise to draw the sample into the tube, 3) raising the sample tube out of the sludge settler, 4) placing the sample bottle under the sample tube, and 5) running the pump (P-301) counter clockwise to discharge the sample into the bottle. The samples were weighed and the top, middle, and bottom supernate sample weights were 17.9, 23.2, and 23.7 grams, respectively.

B.6.4 Supernate Decanting, Sampling, and Transfer

Supernate was decanted by lowering the sample tube to within two inches of the solids layer and slowly pumping the supernate into the batch collection tank. As the liquid level came near the end of the sample tube, the sample tube was incrementally lowered until it was within one/eighth inches of the solids level. Supernate removed in the process was 3675 mL, determined from observations of the liquid height in the sludge settler before and after decanting.

Axial solids samples and supernate samples from the batch collection tank, C-301, were not obtained. The supernate was transferred to the supernate holding tank, C-302.

B.6.5 Removal of Sludge Sample

Deionized water, used in place of inhibited water, was prepared and added to the solids in the sludge settler. The amount of water added was 2225.1 grams. The total volume in the sludge settler was incorrectly recorded in the procedure workplace copy as 28 ¼ inches, or 1900 mL. The total volume was the sum of the sludge in the sludge settler (875 mL, 32 7/8 inches in height) and the deionized water added, 2225.1 mL, which equals 3100 mL.

Solids in the sludge settler were then resuspended by placing the sample tube approximately two inches below the liquid level. The slurry was circulated through the sample tube, pump P-202, and back through a port in the bottom of the sludge settler. After a minimum of 10 minutes, the valve at the bottom of the sludge settler was opened, and the slurry was transferred to the sludge receipt tank. The agitator in the sludge receipt

tank was turned on and set at 75%. It was thus determined that two 2-L sample bottles would be required, beyond the five 100-mL samples to be obtained, to transfer the sludge out of the cell.

Slurry was circulated from the sludge receipt tank through pump P-203, through pump P-204 (although this pump was not operated), and back into the tank past the sampling port. After purging the sample port, five slurry samples were obtained (SPD1-C106-046 through SPD1-C106-050). Note that sample numbers SPD1-C106-031 through SPD1-C106-045 were not used. These samples weighed 90.7, 70.3, 84.7, 62.8, and 55.7 grams, respectively. Two 2-L bottles (SPD1-C106-051 and SPD1-C106-052) were filled with the remaining slurry; they weighed 1624.2 and 1523.0 grams, respectively. The total slurry weight at the end of the test was 3511.3 grams.

B.6.6 Equipment Cleanup

Liquid from the supernate holding tank, C-302, which consists of the decanted supernate and rinse water, was used to rinse the equipment. Approximately 8 L of liquid were pumped into the sludge receipt tank, agitated, and heated to 94°C. After cooling to 90°C, the liquid was transferred into the sludge settler and recirculated for 10 minutes at 1.5 gpm. It was then transferred back to the sludge receipt tank. From there it was pumped into a plastic carboy for disposition.

Appendix C

Mass Balance Spreadsheet for the Bench-Scale Test

Description	Settling Column Level (in)	Volume (mL)	Mass (g)	Density (g/mL)	Caustic Molarity (M)	Total Solids (g)	Weight Percent Undissolved Solids	Water Soluble Solids (g)	Leach Soluble Solids (g)	Insoluble Solids (g)	Notes
Effective Test Sample		2049	3073.9	1.50	0	NA	NA	859	54.6	437	Water insoluble solids = 16%
Retrieval Wash											
Deionized Water Added to C-202	NA	1930	1930.00	1	0	NA	NA	NA	NA	NA	
Deionized Water held up in line	NA	150	150	1	0	NA	NA	NA	NA	NA	Caustic insoluble solids =
Slurry Remaining in C-202	NA	3979	4854	1.22	0	492	10.1%	0	54.6	437	14.22%
Slurry Sample -001	NA	119	145.5	1.22	0	14.7	10.1%	0	1.64	13.1	
Slurry Sample -002	NA	78	95.3	1.22	0	9.66	10.1%	0	1.07	8.59	total initial sample solids =
Slurry Sample -003	NA	71	86.8	1.22	0	8.80	10.1%	0	0.98	7.82	42.16%
Slurry Sample -004	NA	71	86.2	1.22	0	8.73	10.1%	0	0.97	7.77	
Slurry Sample -005	NA	77	93.6	1.22	0	9.48	10.1%	0	1.05	8.43	
Sample -006 ^(a)	Used for Equilibrium Check										
Sample -007 ^(a)	Used for Equilibrium Check										
Sample -008 ^(a)	Used for Equilibrium Check										
Remaining Slurry in C-202	NA	3563	4347	1.22	0	440	10.1%	0	49	392	
Caustic (NaOH) Added	NA	1814	2340.00	1.29	10.11	0	0	0	0	0	
Caustic Leach Slurry	NA	5377	6687	1.24	3.41	392	5.9%	0	0	392	
Evaporation	NA	531	531	1	0	0	0	0	0	0	
Caustic Leach 1											
Initial Settling Column Conditions	13.375	4846	6156	1.27	3.41	392	6.4%	0	0	392	
Evaporation	NA	102	102	1	0	0	0	0	0	0	
Settled Solids	27.75	1912	2741	1.43	3.48	392	14.3%	0	0	392	
Supernatant	13.875	2832	3313	1.17	3.48	0	0	0	0	0	
Evaporation	NA	204	204	1	0	0	0	0	0	0	
Supernatant	14.875	2628	3109	1.18	3.75	0	0	0	0	0	
Top Supernate Sample -009	NA	19	22.7	1.18	3.75	0	0	0	0	0	
Middle Supernate Sample -010	NA	14	16.4	1.18	3.75	0	0	0	0	0	
Bottom Supernate Sample -011	NA	17	19.9	1.18	3.75	0	0	0	0	0	
Supernate Decanted and Transferred to C-301	12.875	2578	3050	1.18	3.75	0	0	0	0	0	
Sludge in C-201	27.75	1912	2741	1.43	3.48	392	14.3%	0	0	392	
Caustic Added	NA	3007.495	3338	1.11	3.00	0	0	0	0	0	
Slurry in C-202	NA	4920	6079	1.24	3.19	392	6.4%	0	0	392	
Evaporation	NA	99	99	1	0	0	0	0	0	0	
Caustic Leach 2											
Initial Settling Column Conditions	13.5	4820	5980	1.24	3.25	392	6.5%	0	0	392	
Evaporation	1	204	204	1	0	0	0	0	0	0	
Settled Solids	28.75	1708	2460	1.44	3.40	392	15.9%	0	0	392	
Supernatant	14.5	2908	3315	1.14	3.40	0	0	0	0	0	
Top Supernate Sample -014	NA	22	24.92	1.14	3.40	0	0	0	0	0	
Middle Supernate Sample -015	NA	20	22.67	1.14	3.40	0	0	0	0	0	
Bottom Supernate Sample -016	NA	20	22.79	1.14	3.40	0	0	0	0	0	
Evaporation	NA	0	0	1	0	0	0	0	0	0	
Remaining Supernate	14.75	2857	3245	1.14	3.38	0	0	0	0	0	
Supernate Decanted and Transferred to C-301	13.875	2832	3216	1.14	3.38	0	0	0	0	0	
Sludge in C-201	28.625	1733	2489	1.44	3.40	392	15.7%	0	0	392	
Inhibited Water Added	NA	1252	1252.31	1.00	0.01	0	0	0	0	0	
Slurry in C-201	NA	2986	3741	1.25	1.98	392	10.5%	0	0	392	

Description	Settling Column Level (in)	Volume (mL)	Mass (g)	Density (g/mL)	Caustic Molarity (M)	Total Solids (g)	Weight Percent Undissolved Solids	Water Soluble Solids (g)	Leach Soluble Solids (g)	Insoluble Solids (g)	Notes
Slurry Transferred to C-202	NA	2986	3741	1.25	1.98	392	10.5%	0	0	392	
Inhibited Water Wash for C-201, then Transferred to C-202	27.75	1912	1912	1	0.01	0	0	0	0	0	
Evaporation	NA	0.00	0.00	1	0	0	0	0	0	0	
Water Wash 1											
Initial Settling Column Conditions	13.125	4897	5653	1.15	1.21	392	6.9%	0	0	392	
Evaporation	0.25	51	51	1	0	0	0	0	0	0	
Settled Solids	31	1249	1790	1.43	1.22	392	21.9%	0	0	392	
Supernatant	13.375	3597	3813	1.06	1.22	0	0	0	0	0	
Top Supernate Sample - 019	NA	17	18.28	1.06	1.22	0	0	0	0	0	
Middle Supernate Sample -020	NA	21	22.35	1.06	1.22	0	0	0	0	0	
Bottom Supernate Sample -021	NA	7	7.72	1.06	1.22	0	0	0	0	0	
Bottom Supernate Sample -022 ^(b)	NA	24	25.6	1.06	1.22	0	0	0	0	0	
Supernate Decanted and Transferred to C-301	17.75	3553	3766	1.06	1.22	0	0	0	0	0	
Sludge in C-201	31.125	1223	1763	1.44	1.22	392	22.2%	0	0	392	
Inhibited Water Added	NA	592	591.82	1	0.01	0	0	0	0	0	
Slurry Transferred to C-202	NA	1815	2354	1.30	0.83	392	16.6%	0	0	392	
Inhibited Water Wash for C-201, then Transferred to C-202	22.25	3034	3034	1	0.01	0	0	0	0	0	
DI Water Added	NA	73	73	1	0	0	0	0	0	0	
Slurry in C-202	NA	4923	5462	1.11	0.31	392	7.2%	0	0	392	
Water Wash 2											
Initial Settling Column Conditions	13	4922	5462	1.11	0.31	392	7.2%	0	0	392	
Evaporation	0.25	51	51	1	0	0	0	0	0	0	
Settled Solids	32	1045	1393	1.33	0.31	392	28.1%	0	0	392	
Supernatant	13.25	3827	4018	1.05	0.31	0	0	0	0	0	
Top Supernate Sample - 023 ^(b)	NA	11	11.99	1.05	0.31	0	0	0	0	0	
Middle Supernate Sample -024	NA	12	13.01	1.05	0.31	0	0	0	0	0	
Bottom Supernate Sample -025	NA	18	18.7	1.05	0.31	0	0	0	0	0	
Supernate Decanted and Transferred to C-301	18.75	3785	3974	1.05	0.31	0	0	0	0	0	
Sludge in C-201	32	1045	1393	1.33	0.31	392	28.1%	0	0	392	
Inhibited Water Added	NA	738	737.91	1	0.01	0	0	0	0	0	
Slurry Transferred to C-202	NA	1783	2131	1.20	0.19	392	18.4%	0	0	392	
Inhibited Water Wash for C-201, then Transferred to C-202	22	3086	3086	1	0.01	0	0	0	0	0	
Slurry in C-202	NA	4718	5217	1.11	0.08	392	7.5%	0	0	392	
Water Wash 3											
Initial Settling Column Conditions	14	4718	5217	1.11	0.08	392	7.5%	0	0	392	
Evaporation	0.125	26	26	1	0	0	0	0	0	0	
Settled Solids	32.875	866	1211	1.40	0.08	392	32.3%	0	0	392	
Supernatant	14.125	3827	3980	1.04	0.08	0	0	0	0	0	
Top Supernate Sample - 028	NA	17	17.89	1.04	0.08	0	0	0	0	0	
Middle Supernate Sample -029	NA	22	23.24	1.04	0.08	0	0	0	0	0	

Description	Settling Column Level (in)	Volume (mL)	Mass (g)	Density (g/mL)	Caustic Molarity (M)	Total Solids (g)	Weight Percent Undissolved Solids	Water Soluble Solids (g)	Leach Soluble Solids (g)	Insoluble Solids (g)	Notes
Bottom Supernate Sample -030	NA	23	23.71	1.04	0.08	0	0	0	0	0	
Supernate Decanted and Transferred to C-301	18.5	3713	3862	1.04	0.08	0	0	0	0	0	
Sludge in C-201	32.625	917	1264	1.38	0.08	392	31.0%	0	0	392	
DI Water Added	28.25	893	893	1	0	0	0	0	0	0	
Slurry Transferred to C-202	NA	1810	2157	1.19	0.04	392	18.1%	0	0	392	
Deionized Water Wash for C-201, then Transferred to C-202	NA	1332	1332	1	0	0	0	0	0	0	
Slurry in C-202	NA	3142	3489	1.09	0.02	392	11.2%	0	0	0	
Slurry Sample -046	NA	83	90.66	1.09	0.02	10.17	11.2%	0	0	0	
Slurry Sample -047	NA	65	70.32	1.09	0.02	7.89	11.2%	0	0	0	
Slurry Sample -048	NA	78	84.67	1.09	0.02	9.50	11.2%	0	0	0	
Slurry Sample -049	NA	58	62.78	1.09	0.02	7.04	11.2%	0	0	0	
Slurry Sample -050	NA	51	55.68	1.09	0.02	6.25	11.2%	0	0	0	
Slurry after sampling	NA	2808	3125	1.09	0.02	351	11.2%	0	0	0	
Final Slurry Product	NA	2887	3147	1.09	0.02	353	11.2%	0	0	0	
Actual vs. Calculated	NA	-20	-22	1.09	0.02	-2	11.2%	0	0	0	
(a) Error in LRB: Samples not recorded.											
(b) Error in LRB: Sample not recorded.											
(c) Error in LRB: Sample incorrectly recorded as -022 instead of -023											

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