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**Tank Waste Treatment Science
Task Quarterly Report for
January - March 1995**

J. P. LaFemina (Task Leader)

April 1995

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
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Tank Waste Treatment Science Task Quarterly Report for January - March 1995

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Summary

This report describes the work performed by the Pacific Northwest Laboratory during the second quarter of FY 1995 (January - March 1995) under the Tank Waste Treatment Science Task of the Tank Waste Remediation System Pretreatment Technology Development Project. Work was performed in the following areas: 1) analytical methods development, 2) sludge dissolution modeling, 3) sludge characterization studies, 4) sludge component speciation, 5) pretreatment chemistry evaluation, and 6) colloidal studies for solid-liquid separations. Significant accomplishments during the second quarter FY 1995 are highlighted below:

- The particle size analysis system for measuring of particulates in solution is ready for general research use, with user-verified operating procedures.
- Computer code modifications were completed, which allow the computation of parameters for the ESP model using our extensive thermodynamic properties database.
- A model for plutonium solubility in mixed NaOH/NaNO₃/NaNO₂ systems was developed that provides predictions in good agreement with the experimental data.
- Transmission electron microscopy studies of Tank T-111 samples indicates that sludge washing removes the soluble phosphate salts [e.g., Na₂H(PO₃)₃]; does not affect the other major components of iron, bismuth, manganese, and silicon, which appear to exist as amorphous Fe₂Bi(SiO₄)₂OH; and causes the larger agglomerates to disperse into fine aggregates with a primary aggregate size of ~ 50 nm, making solid-liquid separations difficult.
- X-ray diffraction analysis of Tank S-104 sludge indicates that the majority crystalline phase is boehmite. The colloidal properties of boehmite have been extensively studied in this task, and boehmite has been observed to form a variety of stable colloidal dispersions.
- Strontium incorporation into calcium minerals in several tank sludges was confirmed by x-ray absorption spectroscopy.
- Studies were initiated that were designed to develop sludge wash factors for single-shell tank wastes via analysis of experimental and historical tank inventory data.
- A preliminary statistical analysis using the SORWT model to evaluate tank waste physical properties indicated that centrifuged solids density is the only physical property with significant differences between SOWRT groups.
- Studies of Fe(OH)₃ and Tank C-103 sludge simulant suspensions indicate that their colloidal properties are qualitatively the same as those of boehmite and gibbsite, and that baseline assumptions concerning solid-liquid separations may be inadequate.

- Results suggest the sensitivity of sedimentation rate to container geometry is due to an "instability" regime in the formation of floc networks, which must be accounted for in the design and interpretation of sedimentation experiments.
- Studies of Tank C-103 simulant suggest that apatite is capable of scavenging fine particles from basic supernatant liquids via a heterocoagulation process.

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1.0 Introduction

The Pretreatment Technology Development Project is one of seven Tank Waste Remediation (TWRS) system projects being conducted at the Pacific Northwest Laboratory.^(a) A key objective of this Project, and of the Tank Waste Treatment Science Task within it, is to provide the technical basis and scientific understanding to support TWRS baseline decisions and actions; in particular, TPA Milestone M50-03, the 1998 sludge pretreatment decision regarding the level of pretreatment to be incorporated into the tank waste process flowsheets. Work performed by this task during the second quarter of FY 1995 (January - March 1995) is detailed in this report. Work for the first quarter is reported in *Tank Waste Treatment Science Task, Quarterly Report for October-December 1994*^(b). An overview of activities is given below.

Analytical Methods Development. To decrease analytical turnaround times; to increase sensitivity of the measurement; and/or to decrease waste volumes associated with obtaining analytical data for the project.

Sludge Dissolution Modeling. To provide the key thermodynamic data to be used in process flowsheet development models and to provide a bounding case on dissolution reactions via direct experimental data on which tanks sludges will dissolve under specified processing conditions.

Sludge Characterization Studies. To identify the major solid phases in sludge; to determine how radionuclides are partitioned among the observed phases; to characterize the behavior of phases during processing; and to use the resulting database on sludge chemistry to help evaluate pretreatment technologies.

Sludge Component Speciation. To provide data on the chemical speciation of specific components in tank wastes that are important to developing pretreatment options. These data will allow the prediction of how different tank wastes will respond to different pretreatment processes, as well as assist in the interpretation of existing pretreatment process chemistry data.

Pretreatment Chemistry Evaluation. To gather, evaluate, and integrate data on the characteristics of tank wastes that are relevant to the pretreatment end function.

Colloidal Studies for Solid-Liquid Separations. To determine how colloidal interactions in tank waste impact the major steps in tank waste processing, in particular, solid-liquid separations, as a function of waste processing conditions.

It is important to note that the scope of activities for the Tank Waste Treatment Science task encompasses all aspects of tank waste processing. It is also important to recognize that there are complementary efforts going on at Hanford and at other U.S. Department of Energy sites as part of the Efficient Separations Processes Cross-Cutting Program and the Tanks Focus Area. To make the most

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(b) PNL-10762.

efficient use of our resources, all possible effort is being made, and will continue to be made, to keep the lines of communication open among these activities so as to avoid duplication of effort and, most importantly, create a cooperative, synergistic environment for performing the required technical work.

2.0 Analytical Methods Development

Brian M. Rapko, Scott M. Tingey, Gregg J. Lumetta, and Ingrid E. Burgeson

The purpose of this subtask is to purchase and install several analytical instruments to support the analysis of Hanford waste samples necessary for the development of pretreatment technologies. Table 2.1 summarizes the instruments to be installed and optimized during FY 1995. These instruments were selected in order to decrease analytical turnaround times, increase the sensitivity of the measurement, and decrease the waste volumes associated with obtaining analytical data. However, these new instruments, which in some cases introduce new analytical methods, require developmental work to be optimized for the complex and unique matrices associated with the TWRS sludge pretreatment project.

Because of a project change request, the listings in Table 2.1 differ from those given last quarter. During the second quarter of FY 1995, optimization work continued for two of the instruments: the capillary ion analyzer and the particle size analyzer, and work began on the installation and testing of the gamma spectrometer. The details of operation and technical issues associated with each of the following systems were described last quarter. Only the progress made in the second quarter is described below.

2.1 Particle Size Analysis System

During the first quarter, NIST^(a) traceable standards, which covered the operating range (0.015 to 400 microns), were purchased and tested with the instrument. Good agreement was found between the standards and the instrument's measured values. During the second quarter, a procedure for operating the instrument was prepared. Testing the procedure with inexperienced users led to some refinements in the procedure, and the instrument is now ready for general research use.

Table 2.1. Analytical Instruments Associated with the Analytical Methods Development Subtask

Instrument	Analytical Function
Particle Size Analyzer	Determination of particle sizes
Capillary Ion Analyzer	Anion analysis in dissolved Hanford tank pretreatment matrices
Capillary Ion Analyzer	Cation analysis in dissolved Hanford tank pretreatment matrices
Gamma Spectrometer	Identification and quantification of gamma-emitting radionuclides

(a) National Institute of Standards and Technology

2.2 Capillary Ion Analyzer

During the first quarter, the instrument was installed and its anion separation and detection performance verified with a standard solution that contained Br, Cl, F, PO₄, SO₄, NO₂, CO₃, and NO₃ anions, each at a level of 1 to 2 ppm. With more complex matrices, designed to simulate actual tank waste-derived solutions [indicated by ion chromatography (IC) results from actual samples submitted during sludge washing and caustic leaching of sludge from Tank B-201], the separation proved unsatisfactory, with nitrate, nitrite, and sulfate being unresolved. By the end of the first quarter, a two-step approach seemed most likely to succeed. The first step would involve detection of all anions but sulfate, nitrate, and nitrite. The second step would involve a separate measurement under conditions designed to quantify at least two of the three anions, since the third could be determined by difference.

During the second quarter, a chloride-based electrolyte system, using the capillary ion analyzer with an ultraviolet (UV)-detection at 214 nm, was developed and tested by the instrument manufacturer, Waters/Millipore. This system seemed to give good detection and separation of nitrite and nitrate, with poor response for the other ions. However, in combination with the standard, chromate-based system with UV-detection at 254 nm, a successful analysis appeared possible with the simulated tank samples. Consequently, a 214 lamp/filter assembly was purchased and installed. Unfortunately, the results reported by Water/Millipore could not be duplicated here. The reasons for this discrepancy remain unclear.

A second approach was initiated involving the use of longer columns (silica gel-coated copper) to increase resolution. If resolution of the anions is sufficiently increased, then the original chromate-based system could be maintained and all necessary analytical information obtained in a single run. The primary disadvantage of using longer columns is the increased run time required. However, as the run times for this capillary electrophoresis system were substantially shorter than for IC, improvement in current analysis time may still be possible compared to IC even with these longer columns. A set of longer columns was purchased at the end of the second quarter, and work in this area will begin in the third quarter.

2.3 Installation of Gamma Spectrometer

Gamma counting equipment designed for quantitative determination of gamma-emitting isotopes was installed and will be used to analyze solutions generated during sludge pretreatment studies.

An energy calibration was performed using a multinuclide standard source. The gamma spectrum recorded for the standard is shown in Figure 2.1. The most commonly encountered gamma-emitting nuclides in Hanford tank sludge are ²⁴¹Am and ¹³⁷Cs. As can be seen in Figure 2.1, resolution and quantification of these isotopes should be straightforward using this equipment. Occasionally, ⁶⁰Co, ¹⁵⁴Eu (122.9 and 1275 keV), and ¹⁵⁵Eu (86.6 and 105.4 keV) are also observed in tank waste samples. Again, resolution of these isotopes is possible using the described gamma spectroscopy equipment.

Figure 2.1. Spectrum of Multinuclide Gamma Standard

Future work will involve counting samples from sludge washing experiments. Parallel samples will be submitted to the Analytical Chemistry Laboratory (ACL) at Pacific Northwest Laboratory. The results obtained with this system will be compared with those reported by the ACL to confirm the performance of the system. Ultimately, a technical procedure will be written for operating the gamma spectroscopy equipment.

3.0 Sludge Dissolution Modeling

Andrew R. Felmy, S. Michael Sterner, Linfeng Rao, and James R. Rustad

The solubility of the solids present in Hanford tank wastes is a critical factor in evaluating the effectiveness of pretreatment technologies. The solubility of these solid phases is affected by a variety of factors that include the pretreatment solutions, temperature, and mixing conditions. This subtask is focused on developing a thermodynamic model that predicts the solubility of important tanks solids as a function of the composition of the major electrolyte components of the waste, i.e., NaOH, NaNO₃, NaNO₂, etc., and the operating temperature. Such a model can then be used to predict the performance of pretreatment strategies, such as the optimum NaOH concentration and temperature for each waste type. As a result, the amount of experimental work required to verify the optimum pretreatment solutions/strategies can be minimized. The data developed in this subtask will be of direct use to process flowsheet development efforts across the entire disposal program, including pretreatment and vitrification. Moreover, these data are being used to improve the process flowsheet modeling efforts currently under way at WHC.

Thermodynamic data for specific ion interactions in the solution and for important solid phases must be evaluated in order to construct the model. The specific ion interactions are parameterized beginning with data on simple binary systems, i.e., NaOH, NaNO₃, etc., where the effects of each electrolyte component can be determined. In the second quarter of FY 1995 work was initiated in the following areas: 1) major electrolyte studies, 2) alkaline earth cation inclusion, 3) actinide studies, and 4) bismuth studies. The following text summarizes progress made in these areas during this period.

3.1 Major Electrolyte Studies

Computer code modifications have been implemented to utilize the existing parameter calculation code NONLIN to calculate the parameters for the Environmental Simulation Program (ESP) model. These code modifications are presently being tested by comparison with output from the existing ESP code. Modifying the code allows existing data files on solubility and osmotic data to be used to calculate the ESP parameters. The use of existing ESP fitting routines is very cumbersome when ion association species are included in the treatment.

3.2 Alkaline Earth Cation Inclusion

Isopiestic investigations were performed to determine osmotic coefficients in strontium, calcium, and magnesium nitrate and nitrite binary brines at 100°C (Figures 3.1 and 3.2). This information, together with available data at room temperature, allows evaluation of specific ion interactions necessary for inclusion of these metals into our polythermal, major electrolyte model for Hanford tank waste.

Solubility experiments for strontium, calcium and magnesium phosphates, and strontium and calcium carbonates in concentrated Na₂CO₃ solutions are in progress. Parallel studies of strontium, calcium and magnesium phosphate, and hydroxide solubilities in concentrated NaOH solutions have also been initiated.

Figure 3.1. Experimentally Determined Osmotic Coefficients for Strontium and Calcium Nitrates and Nitrites

Figure 3.2. Experimentally Determined Osmotic Coefficients for Magnesium Nitrate and Nitrite

3.3 Actinide Studies

Progress was made in the development of a model for plutonium solubility in concentrated NaOH, NaOH/NaNO₃/NaNO₂, and NaOH/NaAl(OH)₄ solutions utilizing experimental data (Figures 3.3 and 3.4) from Delegard (1986, 1987). These solubility data cover the following concentration ranges: NaOH, 1-15 M; NaNO₃, 0-4 M; NaNO₂, 0-4 M; NaAl(OH)₄, 0-2 M; Na₂CO₃, 0-1 M. The solid phase was identified by x-ray diffraction (XRD) as amorphous PuO₂·nH₂O. Absorption spectra indicated that plutonium exists as Pu(V) in an aqueous solution of 15 M NaOH. In the solutions of lower [NaOH], the concentration of plutonium was not high enough for spectroscopic identification. A recent paper by Peretrukin et al. (1994) provided evidence for the existence of PuO₂(OH)₄³⁻ as the dominant (and limiting) species in alkaline solutions ([OH] > 1.3 M).

Based on the above information, the data sets of NaOH and NaOH/NaNO₃/NaNO₂ by Delegard were interpreted by the solid-liquid equilibrium between PuO₂(s) and PuO₂(OH)₄³⁻. Pitzer ion interaction parameters for Na⁺-PuO₂(OH)₄³⁻ were developed from the NaOH system and then tested with the mixed NaOH/NaNO₃/NaNO₂ system. The predicted concentrations of plutonium are in very good agreement with the experimental data for the NaOH system as shown in Figures 3.5 through 3.10, and in fairly good agreement with those for the NaOH/NaNO₃/NaNO₂ system as shown in

Figure 3.3. Plutonium Concentration in Sodium Hydroxide (oversaturation)

Figure 3.10. The decrease in the solubility of plutonium with time (Figure 3.7) was interpreted as being due to the increase in the crystallinity of the $\text{PuO}_2(\text{s})$ phase with time.

Modeling of the data for the $\text{NaOH}/\text{NaAl}(\text{OH})_4$ system is under way and has shown some promise. The modeling of the $\text{NaOH}/\text{Na}_2\text{CO}_3$ system might be difficult if we have to assume the formation of highly charged Pu/carbonate species. Preparation for the experimental work with $\text{Np}(\text{V})$ is also under way.

3.4 Bismuth Studies

Solubility studies of bismuth phosphate in concentrated NaOH solutions have been initiated, and 5- and 20-day sampling and analyses have been completed. The results show that the solubility of bismuth phosphate increases with increasing pH. The observed concentrations at $\text{pH} = 8.0$ are approximately $10^{-7.5}$ M, while those in 5.0 M NaOH are approximately $10^{-3.5}$ M. At the higher NaOH

Figure 3.4. Plutonium Concentration in Sodium Hydroxide (line = oversaturation; point = undersaturation)

Figure 3.5. Solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in NaOH (oversaturation, 768 days; undersaturation, 974 days; and predicted)

Figure 3.6. Solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in NaOH (oversaturation, 317 days; and predicted)

Figure 3.7. Solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in NaOH (oversaturation, 153 days; and predicted)

Figure 3.8. Solubility of $PuO_2 \cdot xH_2O$ in NaOH (oversaturation, 56 days; undersaturation, 56 days; and predicted)

Figure 3.9. Solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in NaOH (56, 153, 317, and 768 days)

Figure 3.10. Solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in $\text{NaOH}/\text{NaNO}_3/\text{NaNO}_2$

concentrations, visual observation of the samples indicate that bismuth phosphate is not the stable phase. Analysis of the solid phase(s) is presently under way.

3.5 References

Delegard, C. H. 1986. *Solubility of PuO_2 by H_2O in Alkaline Hanford High-Level Waste Solutions*. RHO-RE-SA-75P, Westinghouse Hanford Company, Richland, Washington.

Delegard, C. H. 1987. *Radiochim. Acta.* 41:11-21

Peretrukin et al. 1994. *Radiochim. Acta.* 65:161-166

4.0 Sludge Characterization Studies

Jun Liu, Larry E. Thomas, Yuan L. Chen, and Li-Qiong Wang

The objectives of this subtask are to identify the major solid phases present in sludge; determine how radionuclides are partitioned among the observed phases; characterize the ion exchange, colloidal chemistry, and dissolution behavior of phases during sludge processing; and use the resulting database on sludge chemistry to help evaluate existing sludge pretreatment technologies and develop new sludge pretreatment schemes. Work within this subtask is divided into three activities: 1) analysis of actual sludges; 2) analysis of simulated sludges; and 3) supplemental studies using analysis techniques such as nuclear magnetic resonance (NMR). NMR provides additional information about the chemistry and chemical reactions in simulants.

4.1 Analysis of Tank Sludges

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and x-ray diffraction (XRD) analyses have been performed on sludge samples from Tanks T-111 and S-104. Waste in Tank T-111 originated from the second (2C) and final (224) decontamination cycles of the bismuth phosphate process. Waste in Tank S-104 originated from REDOX and REDOX aluminum cladding wastes. Preliminary results are discussed in the following text.

4.1.1 Tank T-111 Sludge Samples

TEM and SEM analyses indicated a large amount of phosphate salt exists in the unwashed sludge sample from Tank T-111. Preliminary analysis of the phosphate diffraction pattern suggested that this phosphate phase is sodium hydrogen phosphate $[\text{Na}_2\text{H}(\text{PO}_3)_3]$.

SEM of the unwashed samples revealed agglomerates up to $100\text{ }\mu\text{m}$ (Figure 4.1a). After washing, these large agglomerates broke into smaller agglomerates of about $5\text{ }\mu\text{m}$ (Figure 4.1b). TEM analysis further revealed the existence of a large number of even smaller aggregates that ranged from 50 nm to a few microns (Figure 4.2). It appears that the primary aggregate size is as small as 50 nm . The unwashed sample consists of denser agglomerates of these primary aggregates.

Observed effects of washing include:

- Soluble salts, such as sodium hydrogen phosphate, are removed with washing.
- Other major components, such as iron, bismuth, manganese, and silicon, do not appear to be affected by washing.
- Washing causes some of the larger agglomerates to break up into fine aggregates. The smallest primary aggregates are about 50 nm in size.

These observations suggest that the current washing procedure is not effective in removing the major solid materials in the T-111 sludge. The breaking-up of the agglomerates during washing implies that the agglomerates in this sludge are not strongly bound and can be easily redispersed into

Figure 4.1. Scanning Electron Microscopy Image of T-111. Washing caused the large agglomerates to break up. (a) Before washing: needle-like particles are sodium phosphate. (b) After washing.

smaller aggregates. The existence of small aggregates less than $0.1 \mu\text{m}$ will make it more difficult to separate the solid and the liquid phases by techniques such as sedimentation and filtration.

The major (<90%) insoluble phases consist of iron, bismuth, and silicon compounds. These compounds are aggregates of very fine particles. The primary particles are $<10 \text{ nm}$, and the primary agglomerate size is about 50 nm . These materials are poorly crystalline, and the composition changes slightly from one area to another. A small amount of uranium is also detected in these regions. The only compound found in literature that contains iron, silicon, and bismuth is bismuth iron silicate hydroxide (bismuth ferrite), $\text{Fe}_2\text{Bi}(\text{SiO}_4)_2\text{OH}$. The diffraction pattern from these regions was not well defined, and only two rings were identified. These peak positions do match those from the bismuth ferrite. We believe that most of the phases are a homogeneous and amorphous mixture of the hydroxide of bismuth, silicon, and iron. Certain regions have better crystalline structure that is similar to bismuth ferrite. XRD analysis of T-111 samples confirmed that most of the solid materials are amorphous.

The following phases have been confirmed by electron dispersive x-ray (EDS) and electron diffraction patterns analyses:

Figure 4.2. Transmission Electron Microscopy of T-111. (a) Large agglomerates before washing, (b) Small agglomerates after washing. The primary agglomerate size is about 50 nm.

- hydroxyapatite (HAP) $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, rod-like, $0.1 \mu\text{m}$ in length
- iron manganese oxide (Jacobsite) Fe_2MnO_4 , plate-like, $0.5 \mu\text{m}$ in width
- goethite FeOOH , rod like, $0.5 \mu\text{m}$ in length
- lanthanum phosphate $\text{La}_4(\text{P}_2\text{O}_7)_3$, irregular shape, $0.5 \mu\text{m}$ in size.

4.1.2 Tank S-104 Sludge Samples

XRD analysis of Tank S-104 has been completed, and TEM characterization is under way. XRD analysis indicated that most ($>50\%$) of the crystalline phase in S-104 is boehmite. The line broadening from the XRD pattern suggests the presence of fine boehmite particles. The TWRS Sludge Treatment Technology Development Task has noted that solids do not settle well in the wash phase; this may be attributed to the behavior of boehmite.

The Colloidal Studies subtask (Section 7.0) performed extensive studies on the dissolution, aggregation, viscoelastic property, sedimentation, and pressure filtration of boehmite under different pH, electrolyte concentrations, and solids loading. It was observed that boehmite suspensions do not settle and filter easily, and it is difficult to control the viscosity and increase the solids loading. The suspension either has dispersed nm-sized particles or forms low density gels. With boehmite as a major phase in S-104, the information provided by the colloidal studies becomes important.

4.2 Analysis of Simulated Sludges

TEM analysis of sludge simulants is performed as part of this subtask to support the Initial Pretreatment Module (IPM) Solid-Liquid Separations Simulant Development Task by comparing particle size and morphology of the simulants with actual tank waste.

4.2.1 Tank C-103 Simulated Sludge

Tank C-103 simulant was obtained from the IPM Solid-Liquid Separations Simulant Development Task. TEM analysis of the simulant was performed to study the mixing and aggregation behavior of the various components in the simulant and to confirm particle size measurements performed with optical means. Major observations are listed below:

- Boehmite (commercial nm-sized) and colloidal silica (commercial, 0.1 μm) tended to form mixed aggregates. Iron hydroxide (commercial, nm-sized) and aluminum hydroxide (commercial, μm -sized) were not present in this mixed aggregate region. Therefore, it seems boehmite did not mix with iron hydroxide and aluminum hydroxide.
- HAP did not mix with boehmite; however, HAP did mix with iron hydroxide.
- There appeared to be no extensive chemical reactions between the different particles mixed together; however, some surface reactions could not be ruled out.
- A small amount of HAP can affect the sedimentation behavior of the simulant.
- The agglomerate sizes in the sample without HAP are considerably smaller than those in the sample with HAP.
- After a long period of sedimentation, the supernatant solution from the simulant without HAP was sampled. Many suspended solid particles were observed; these particles were mainly silica.

This study suggests that HAP likely influences the aggregation of the suspension through the binding with silica particles.

4.2.2 Tank T-111 Simulated Sludge

Because the majority of the solid phases in actual T-111 sludge are an amorphous mixture of iron, bismuth, and silicon compounds, a simple scheme for preparing T-111 simulant material through homogeneous mixing and coprecipitation was suggested. The parameters that needed to be controlled include composition, primary particle size and agglomerate size, and agglomerate structure. TEM analysis showed that materials prepared in this manner are amorphous, and the particle size is in the nm-size range.

4.3 Supplemental Analysis Studies

Supplementary analyses using NMR spectroscopy are being performed to more completely characterize the chemical behavior of the phases identified via TEM analysis. In particular, solid-state ^{29}Si NMR experiments are being carried out to study the reactions between colloidal aluminum and silicon species in the sludge simulants that may be responsible for cement-like sediment formation in actual waste tanks. The interactions between these species may greatly affect the solubility of the aluminum species and the rheological properties of the suspension.

Eight samples (different pH and with/without AlOOH) that were prepared by the IPM Solid-Liquid Separations Simulant Development Task have been examined. Preliminary results showed that AlOOH at $\text{pH} > 11$ interacts strongly with SiO_2 in presence of NaNO_3 . Further studies, using techniques such as Raman spectroscopy, are under way to understand the role of AlOOH in such reactions.

Formation of cancrinite-type zeolitic materials has been reported in tank wastes containing aluminum, silicon hydroxides, and NaNO_3 under alkaline conditions. Pure cancrinite has been synthesized by the IPM Solid-Liquid Separations Simulant Development Task and confirmed using a Si-magic angle spinning (MAS) NMR technique.

5.0 Sludge Component Speciation

David L. Blanchard, Steven D. Conradson (LANL), Richard L. Gordon, Nancy J. Hess, J. Craig Hutton, Marc M. Lamoureux, and David L. Styris

The chemical speciation of sludge components is perhaps the single most important factor in determining how they will respond to any chemical processing. For example, in the current baseline strategy, a large fraction of the phosphorus and chromium must be removed from the sludge in order to minimize the volume of high-level waste (HLW) that is produced. The key to designing an effective pretreatment strategy is knowing whether the phosphorus is present as BiPO_4 , $\text{Ca}_3(\text{PO}_4)_2$, or some other low soluble form, such as calcium hydroxyapatite $[\text{Ca}_5(\text{OH})(\text{PO}_4)_3]$ or apatite $[\text{Ca}_5\text{F}(\text{PO}_4)_3]$. Is the bismuth phosphate in waste really metathesized to bismuth oxide by enhanced sludge washing? Is the major phosphate species left by enhanced sludge washing truly calcium phosphate, or do other phosphate species contribute to the residual solids? Is chromium in the sludge found in pure phases, such as Cr_2O_3 or CrO_3 , or in minerals, such as FeCr_2O_4 ? Because these solids have different solubilities that vary extensively with pH and the concentration of other ions, the extent of phosphorus and chromium removal will be determined by these details. In addition, chemical speciation data will provide direction for future technology development, should it be needed.

Chemical speciation is defined in this context as identification of the chemical compounds and phases and the *physical location* of sludge constituents, e.g., coprecipitation vs. precipitation in separate phases or at the surface of another phase, etc. This detail is required because elemental information is not sufficient for predicting how a complex mixture will respond to a given treatment. The purpose of this subtask is to provide data on the chemical speciation of specific components of tank wastes that are important to developing the pretreatment baseline. These data will allow prediction of how different tank wastes will respond to pretreatment processes, as well as assist in the interpretation of existing pretreatment process chemistry data.

In FY 1994, this subtask performed a survey of existing analytical techniques for chemical speciation. As a result of this study, x-ray absorption spectroscopy (XAS) and laser ablation/mass spectroscopy (LA/MS) were chosen as the most appropriate techniques for providing speciation information. In addition to the ability to provide this information, these techniques require minimal sample preparation and disruption during measurement. These techniques also are complementary. XAS can readily provide information on low concentration elements (down to 10 ppm) that may not be present in pure phases. Such inclusions are more difficult to identify with LA/MS techniques. In turn, LA/MS is very effective at identifying organic species and compounds of low atomic weight elements, which are difficult to identify with XAS.

Although there is currently a LA/MS system at PNL for the elemental analysis of radioactive samples, there is no system capable of elucidating *speciation* in samples. As a result, this task will pursue the use of Raman spectroscopy to help elucidate speciation information. Raman will be used to follow changes in the relative concentrations and speciation of the various anions, i.e., phosphate, sulfate, nitrate, nitrite, etc., in tank waste caused by enhanced sludge washing. These polyanions can be easily distinguished in Raman spectra of tank waste (Lombardi et al. 1994). However, overlap of the spectral features of the many similar chemical species makes the interpretation challenging. A secondary goal of this study is to determine the amount of useful information Raman can provide about tank waste.

5.1 Phosphate Speciation

Last year, XAS data of strontium in tank wastes were collected. Attempts to fit the spectra using standard strontium compounds (hydroxide, phosphate, etc.) were not successful. Because of the high concentration of calcium relative to strontium, the strontium appeared to be incorporated, i.e., coprecipitated, with calcium minerals. Therefore, spectra were calculated assuming strontium was incorporated in calcium minerals and used to fit the experimental spectra. It was shown that a combination of strontium incorporated in calcite and aragonite (two phases of CaCO_3) and calcium hydroxyapatite [$\text{Ca}_5(\text{OH})(\text{PO}_4)_3$] fit the experimental data well.

Samples of strontium coprecipitated with calcium minerals were prepared at the beginning of this quarter, and the XAS spectra taken at the Stanford Synchrotron Radiation Laboratory (SSRL). The strontium in calcium hydroxy phosphate was prepared by first dissolving calcium and strontium nitrates (in a 1000:1 ratio) in aqueous solution at pH 12 (pH achieved with NH_4OH). A solution of $(\text{NH}_4)_2\text{HPO}_4$ (at pH 12) was then added drop-wise with vigorous stirring. After complete addition, the resulting reaction mixture was gently boiled for 10 min, then filtered, washed, and dried. The strontium in calcium carbonate was prepared by dissolving both calcium and strontium carbonate (at the appropriate 1000:1 ratio) by bubbling CO_2 through the stirred solution. Undissolved carbonate was removed by filtering. The dissolved carbonate was re-precipitated by evolving the CO_2 through boiling. The precipitate was then filtered and dried. The structure of the precipitates is believed to be that of calcium hydroxyapatite and aragonite, respectively. X-ray diffraction of the samples for structure determination is planned.

Figure 5.1a shows the extended x-ray absorption fine structure (EXAFS) of strontium in Tank C-112, Core 36. Figure 5.1b is the radial structure plot (RSP) for Figure 5.1a. The peak positions in the RSP give a rough indication (within approximately $0.5 \text{ \AA}$) of the bond distance from the absorber (Sr) to the scatterer (O for the peak just below $2 \text{ \AA}$). These data were well fit using a linear combination of the spectra of the experimental samples of strontium in calcium hydroxyapatite and strontium in calcium carbonate (70% and 30% respectively). Figures 5.1c and 5.1d show plots of the analogous strontium XAS data from Tank C-109, Core 49. This spectrum was well fit using 80% of the strontium in calcium hydroxyapatite and 20% of the strontium in calcium carbonate. Although the values for the contributions of the species are somewhat different from those determined using calculated spectra, the fit provides confidence that the strontium is indeed incorporated in calcium minerals, and more generally, that the use of calculated spectra can help identify species when experimental standards are not immediately available. These results also show that a significant portion of the calcium in the untreated sludge in these tanks is found in carbonate species. In subsequent experiments planned this year, the bismuth and calcium in sludge samples before and after enhanced sludge washing will be probed directly to determine how this pretreatment affects the phosphates present; i.e., how much is removed, how much metathesizes to insoluble calcium species, etc.

5.2 Chromium Speciation

Speciation of chromium in tank samples will also be investigated this year. The ratio of Cr^{3+} to Cr^{6+} will be determined in samples before and after enhanced sludge washing to assess how this pretreatment affects the distribution of chromium oxidation states. In addition, the chromium chemical species will be identified, concentrations permitting. To this end, chromium XAS data of mixtures of $\text{K}_2\text{Cr}_2\text{O}_7$ and Cr_2O_3 were taken at SSRL at the beginning of this quarter.

Figure 5.1. (a) EXAFS of Sr in Tank C-112, Core 36. The EXAFS was fit by 70% strontium in calcium hydroxy phosphate and 30% strontium in calcium carbonate. (b) Radial structure plot for XAS in (a). (c) EXAFS of Sr in Tank C-109, Core 49. The EXAFS was fit by 80% strontium in calcium hydroxy phosphate and 20% strontium in calcium carbonate. (d) Radial structure plot for XAS in (c).

Figure 5.2a shows the EXAFS from a series of mixtures of $\text{K}_2\text{Cr}_2\text{O}_7$ to Cr_2O_3 . It is clear that the EXAFS varies continuously from pure $\text{K}_2\text{Cr}_2\text{O}_7$ to pure Cr_2O_3 . Therefore, the composition of a mixture of these materials may be determined by fitting with a linear combination of the spectra from pure samples. An x-ray absorption pre-edge feature may also be used to determine the ratio of $\text{Cr}^{3+}:\text{Cr}^{6+}$. Results obtained from fitting the EXAFS agree quantitatively with results obtained by using this established pre-edge analysis procedure. However, pre-edge analysis only yields the $\text{Cr}^{3+}:\text{Cr}^{6+}$ ratio, whereas the EXAFS analysis yields the actual chemical species information.

Figure 5.2b shows an example of fitted results for a mixture of chromium standards: the solid line is the experimentally measured EXAFS for the 59% Cr_2O_3 :41% $\text{K}_2\text{Cr}_2\text{O}_7$ sample; the dashed line is the fit results using a linear combination of the two pure standards (59% and 41%, respectively). This result verifies that the use of such a procedure to determine the amount of Cr_2O_3 and $\text{Cr}_2\text{O}_7^{2-}$ in the tank sample will yield accurate results.

5.3 Other Studies

Samples obtained from the Efficient Separations Program were incorporated into this study to investigate coordination of strontium by various ion exchangers. Ion exchangers were loaded with strontium. Some were dried, some kept moist. The strontium k-edge XAS RSPs for strontium-loaded IE-96 is shown in Figure 5.3. Data for wet and dried samples are shown. The peak at approximately 2 Å is due to the first shell of coordinating oxygens. The similarity in this peak indicates that drying the sample does not significantly change the first shell coordination. However, the lower intensity in the small peak at 3.5 Å in the wet sample suggests that drying the sample causes more ordering in this coordination shell. Therefore, for information on coordination by the first shell oxygen atoms, a dried sample is probably sufficient. (The use of a dry sample reduces the difficulty of the experiment somewhat.) However, information about higher coordination shells in the exchangers under processing conditions will require wet samples.

A comparison of the coordination of strontium in three different exchangers is shown in Figure 5.4. The sodium titanate (NaTi) and IE-96 exchangers appear very similar in the coordination of strontium by first shell oxygens. The amplitude of the coordination peaks gives an indication of the average number of atoms in a coordination shell. Therefore, the lower amplitude of the first (oxygen) coordination shell of the hydrous titanium oxide (HTO) suggests fewer coordinating oxygens in this shell in this exchanger. This correlates with the distribution coefficient (k_d) for these exchangers for strontium at long times. The NaTi and IE-96 k_d values are very similar at long times (greater than 1000 hr), while the k_d for HTO is nearly an order of magnitude greater after a similarly long time, according to Dr. J. E. Amonette, PNL. The source of the correlation is unclear. Further analysis is in progress to understand these preliminary results.

5.4 Reference

Lombardi, D. R., et al. 1994. *Applied Spectroscopy* 48:875.

(a)

(b)

Figure 5.2. (a) Continuous Variation in the EXAFS from Pure $\text{K}_2\text{Cr}_2\text{O}_7$ to Pure Cr_2O_3 Using Mixtures of These Two Compounds. (b) An Example of Fitted Results for the Mixture of Chromium Standards. The solid line is the experimentally measured EXAFS for the 59% Cr_2O_3 :41% $\text{K}_2\text{Cr}_2\text{O}_7$ sample; the dashed line is the fitted results using the appropriate linear combination of the two pure standards.

Figure 5.3. Comparison of the Radial Structure Plots for Wet and Dry Samples of Strontium-loaded Ion Exchanger, IE-96

Figure 5.4. Comparison of the Radial Structure Plots for Strontium-loaded Ion Exchangers Sodium Titanate, IE-96, and Hydrous Titanium Oxide

6.0 Pretreatment Chemistry Evaluation

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The objective of this subtask is to gather, evaluate, and integrate data on the characteristics of tank wastes that are relevant to the pretreatment end function. Activities within this subtask are summarized below:

Process Chemistry Evaluation. Chemical analyses data and chemical flowsheet compositions are being used to define waste stream compositions in terms of chemical species present in the tanks. The results from these activities will provide insight into the partitioning behavior of different waste streams during pretreatment processing, as well as insight into the chemical composition of the waste streams that are sent to high-level waste vitrification.

Data Evaluation Using the Sort on Radioactive Waste Type (SORWT) Model. This activity is focused on 1) systematically determining how physical properties vary from tank to tank and across SORWT groups and 2) using an electronic data set of historical sample analyses to generate tank-by-tank estimates of waste characteristics. These tank-by-tank estimated compositions based on analysis will be compared with the chemical inventories predicted by Los Alamos National Laboratory (LANL).

Efforts in the first quarter centered on data gathering; during the second quarter, efforts have focused on data evaluation.

6.1 Process Chemistry Evaluation

The effect of the enhanced sludge wash strategy on final waste volumes is evaluated in systems engineering studies using waste inventory estimates along with assumptions about the chemical and physical behavior of the wastes. Tank inventory estimates for single-shell tank (SST) wastes are derived from the Tank Layer Model (TLM) and defined waste types that were developed by LANL (Agnew 1994b). Tank-specific wash factors, i.e., the fraction of each waste component in a particular tank that will partition in the aqueous phase during the wash processing step, need to be established in order to use these inventories in systems engineering studies. The goal for this activity is to help develop these wash factors for SST wastes.

One overall approach to establishing tank-specific wash factors is to assign wash factors to each of the defined waste types and then use the TLM to weight the contribution of these wash factors to formulate wash factors for a specified tank waste. Wash factor information can be extracted from experimental data for some defined waste types; however, for others, this information may have to be predicted based on chemical species assumed to be present in the waste type. An important point to note is that the results from systems engineering studies will be only as good as the inventory estimates/data and wash factor assumptions used in the evaluation.

6.1.1 Review of Tank Inventory Estimates

During the second quarter, a review of the tank inventory estimates (bulk components) was initiated. In *Hanford Defined Wastes: Chemical and Radionuclide Compositions* (Agnew 1994a),

S. F. Agnew of LANL summarizes three methods for establishing defined wastes: 1) knowledge of process, 2) chemicals used and waste volume produced, and 3) analysis of characteristic waste. While the LANL methodology favored Methods 1 and 2, this activity is using Methods 1 and 3 for comparative purposes.

Concentrations of constituents in first cycle waste that contained approximately 24% aluminum cladding waste, REDOX waste (Flowsheet HW#4), and REDOX cladding waste were derived from technical flowsheets. Estimated concentrations for selected constituents are presented in Table 6.1. Constituents were grouped into three categories based on their expected partitioning behavior: 1) aqueous phase constituents, 2) solid phase constituents, and 3) constituents that partition between both phases. Initial efforts are centered on reviewing constituents that partition predominantly in one phase, i.e., Groups 1 and 2. Note that this initial partitioning behavior may not necessarily reflect the partitioning behavior of the same constituents as they exist in aged wastes.

Flowsheet concentrations for nitrate, nitrite, and sulfate (aqueous phase constituents), and for bismuth, iron, and silicon (solid phase constituents) were entered onto a spreadsheet that calculated the concentration of these species in μg constituent/g wet sludge (solids + interstitial liquid). Calculations were based on the following assumptions:

Aqueous Species: The interstitial liquid in a specific tank sludge is affected by all wastes that contact the sludge. The concentration of species that partition predominantly in the aqueous phase, i.e., nitrate, nitrite, and sulfate for this exercise, may be calculated by summing the contributions from each waste volume that contacted the sludge.

Table 6.1. Waste Stream Compositions Estimated from Process Flowsheets

	1st Cycle BiPO ₄ / Al Cladding, <u>M</u>	REDOX (HW#4) <u>M</u>	REDOX Al Cladding, <u>M</u>
NO ₃ ⁻	1.59	3.62	0.980
NO ₂ ⁻	0.216		1.27
SO ₄ ²⁻	0.0524	0.029	
Bi ³⁺	0.0120		
Fe ³⁺	0.0263	0.014	
Si ⁴⁺	0.0329		0.020
U	0.0006	0.0075	0.001
Al ³⁺	0.288	1.05	1.7
Cr ^{3+/6+}	0.0017 ⁽³⁺⁾	0.053 ^(6+/3+)	
PO ₄ ³⁻	0.279		
F ⁻	0.197		

Sum [molarity x formula weight x 1e6 $\mu\text{g/g}$ x void fraction x 1e-3 L/mL $\div$ density of sludge x fraction of waste x liquid concentration factor x liquid dilution factor]

Void fractions used in the calculations are based on LANL-predicted void fractions. The density of the sludge is obtained from analytical data. The fraction of each waste volume and the liquid dilution factor are calculated from waste volumes given in Agnew (1994b). The dilution factor accounts for water added to the tanks. The liquid concentration factor accounts for concentration of the liquids in the tanks and is estimated from tank level histories. Using waste volumes from Anderson (1995) and Tank S-104 as an example:

Concentration factor for REDOX contribution

<u>kgal</u>	<u>conc. factor</u>	<u>total conc. factor</u>
758 --> 458	1.6	
734 --> 623	1.2	
763 --> 711	1.1	2.1

Concentration factor for Cladding Waste contribution

807 --> 543	1.5	
307 --> 299	1.0	1.5

Solid Species: The concentration of species that partition predominantly in the solid phase, i.e., bismuth, iron, and silicon for this exercise, may be calculated by summing the contributions from each solids volume that comprises the tank sludge.

Sum [molarity x formula weight x 1e6 $\mu\text{g/g}$ x characteristic solids concentration factor x 1e-3 L/mL $\div$ characteristic density of sludge type x fraction of solids waste]

This assumption is consistent with the LANL methodology.

Each sludge type is assumed to have a characteristic density, and the characteristic density for each sludge type is based on analytical or flowsheet data. The fraction of each solids volume is calculated from tank level history information or from the TLM summaries. The characteristic solids concentration factor accounts for the concentration of solids when they precipitate from solution and is based on LANL-defined waste information or on analytical data.

6.1.2 Results

Results from the preliminary spreadsheet evaluation of Tanks T-104, S-104, and U-110 are provided in Figure 6.1. Note that results for Tank U-110 do not include the solid species because of anomalies with tank level history information. While it is too early in the review to draw any conclusions, the following observations are noted:

- Tank T-104 contains only one waste type, first concentration cycle bismuth phosphate that contains approximately 24% cladding waste. Spreadsheet-calculated inventories for this waste compared favorably with inventories projected from analytical data. The concentrations entered into the spreadsheet were derived from a Bismuth Phosphate Process flowsheet, and only one concentration factor was assumed for the solids. The tank solids volume projected

T-104									
1.15 density									
0.3 fraction solids (wt)									
1 dilution factor	Calculated	Calculated	Analytical	Calculated	% diff	Analytical	LANL	% diff	
	1C - process	1C - waste							
	M	ug/g	ug/g	ug/g	kg	kg	kg		
void fraction	0.7								
fraction waste	1								
conc factor-soil	7.4								
conc factor-liq	1								
MW									
62 NO3	1.59	6.00E+04	60005	58025	115000	3	112000	50400	-55
46 NO2	0.216	6.05E+03	6048	4067	11600	48	7830	9920	27
96 SO4	0.0524	3.06E+03	3062	3885	5890	-21	7470	7620	2
209 Bi	0.012	1.61E+04	16138	18875	31000	-15	36300	25600	-29
55.8 Fe	0.0263	9.44E+03	9443	9015	18200	5	17300	36600	112
28 Si	0.0329	5.93E+03	5928	6440	11400	-8	12400	5790	-53

S-104											
1.5 density	1.3		1.8								
0.65 fraction solids (wt)								INVENTORY			
1.01 dilution factor	Calculated			Calculated	Analytical	Calculated	% diff	Analytical	LANL	% diff	
	Redox - process	Redox - waste	RCW - process	RCW - waste							
void fraction	0.67		0.67								
wt factor-S	0.73		0.27								
conc factor-sol	8.7		12								
conc factor-liq	2.1		1.5								
wt factor-L	0.865		0.135								
MW	M	ug/g	M	ug/g	ug/g	ug/g	kg	kg	kg		
62 NO3	3.62	1.80E+05	0.98	5.44E+03	185742	185667	309000	0	309000	101000 -67	
46 NO2	0	0.00E+00	1.27	5.23E+03	5232	20816	8730	-75	34600	8470 -76	
96 SO4	0.029	2.24E+03	0	0.00E+00	2236	2365	3720	-5	3930	952 -76	
209 Bi	0	0.00E+00	0	0.00E+00		0	0	-100	65	0 -100	
55.8 Fe	0.014	3.82E+03	0	0.00E+00	3816	2486	6370	54	4140	4310 4	
28 Si	0	0.00E+00	0.02	1.01E+03	1008	1460	1680	-31	2430	2010 -17	

U-110															
1.5 density	1.15		1.3		1.8		1.5								
0.65 fraction solids (wt)															
1.12 dilution factor	Predicted		Predicted		Predicted		Predicted		Calculated	Analytical	Calculate % diff	Analytical	95% Cont	LANL	% diff
	1C - process	1C - waste	Red - process	Redox - waste	RCW - process	RCW - waste	MW - process	MW - waste							
void fraction	0.7		0.66		0.67		0.67								
wt factor-S	0.78		0.05		0.11		0.05								
conc factor-soil	7.4		4.8		10		4.8								
conc factor-liq	1		1		1		1.6								
wt factor-L	0.39		0.33		0.225		0.055								
										</					

Figure 6.1. Calculated Inventories for Selected Constituents - Tanks T-104, S-104, and U-110

from this method would be 467 kgal less 5 kgal that were transferred to another tank for a total of 462 kgal. Tank T-104 is reported to contain 442 kgal. The difference between the calculated and measured waste is equivalent to approximately 7.5 in. of waste in the tank.

Note the differences between the LANL-predicted inventories for bismuth, iron, and silicon and the inventories for these elements based on analytical data. The LANL tank inventory estimate is based on two defined wastes for the first concentration cycle with 24% cladding waste that differ in solids volume percent (one defined waste concentrates by a factor of 7.3 and the other by a factor of 4) for very similar defined waste compositions. Agnew (1994a), notes that this change in solids percent is not understood.

- Tank S-104 contains REDOX and REDOX aluminum cladding wastes. Spreadsheet inventories for aqueous species compare favorably with inventories based on analytical data. This observation suggests that additional waste contributions and self-concentrating/boiling effects may play an important role in determining the concentration of the aqueous species in the interstitial liquid. Tank solids volume projected for this tank is 303 kgal. Tank S-104 is reported to contain 293 kgal. The LANL-predicted inventories for iron and silica look good, as do the tank projected solids. This observation lends support to the tank layering approach for solids as well as for the defined waste composition.
- Tank U-110 contains first concentration cycle bismuth phosphate with 24% aluminum cladding waste; REDOX waste; REDOX aluminum cladding waste; and possibly bismuth phosphate metal waste. Spreadsheet inventories for aqueous species again compare favorably with inventories based on analytical data. Again, this observation may suggest that additional waste contributions might need to be factored into calculations for aqueous species in the interstitial liquid.

Near-term plans for this activity are to evaluate constituents that partition between both liquid and solids phases and to complete spreadsheet calculations for all sludges that have been characterized. While this is a "dry-lab" approach in some respects, this review approach provides a means of identifying any potential sources of error and might lead to improvements in some tank-specific inventory estimates.

6.2 Data Evaluation Using the Sort on Radioactive Waste Type (SORWT) Model

The SORWT model (Hill et al. 1995) has been used successfully to categorize Hanford SSTs into groups of tanks that are expected to exhibit similar chemical and physical characteristics based on their major waste types and processing histories. This methodology is being used to look at the variability in physical and rheological properties across individual tanks and SORWT groups, as well as to evaluate a historical sample analysis data set to provide a tank-by-tank estimate of analyte concentrations.

6.2.1 Evaluation of Physical Properties

Several physical and rheological analyses have been conducted on core samples since the mid-1980s. The properties analyzed are listed below:

Physical Data

Weight Percent Water
Weight Percent Undissolved Solids
Volume Percent Settled Solids
Time to Settle
Weight Percent Centrifuged Solids
Bulk Density
Centrifuged Solids Density
Centrifuged Supernatant Density
Penetration Resistance
Weight Percent Oxides
Particle Size Distribution by Volume
Particle Size Distribution by Number

Rheological Data

Shear Strength
Yield Point
Viscosity
Critical Reynold's Number for Turbulent Flow

Thermal analyses have also been conducted, specifically, differential scanning calorimetry and thermogravimetric analysis.

Sufficient data to complete a preliminary statistical analysis are available for only a fraction of the properties listed above (see Table 6.2). Viscosity data were not included in the preliminary statistical

Table 6.2. Availability of Physical Property Data for Waste in Single-Shell Tanks

Physical Property	Number of Tanks Included in the Statistical Analysis	Percentage of Waste Sampled Based on Tank Volume
Bulk Density (g/mL)	11	7%
Mean Particle Size by Number (μm)	9	5%
Mean Particle Size by Volume (μm)	9	5%
Wt% Water	12	8%
Wt% Centrifuged Solids	10	6%
Centrifuged Solids Density (g/mL)	10	6%
Vol% Centrifuged Solids	10	6%
Vol% Settled Solids	10	6%

analysis at this time because of the difficulty in extracting the necessary information from the original data packages. This task may be performed at a later date if the information is deemed useful. Data from the differential scanning calorimetry and the thermogravimetric analysis also were not included because of uncertainties regarding how to meaningfully incorporate such information in a statistical study. Any additional properties that were not included in the analysis were excluded due to lack of available data.

Table 6.3 presents the results of the preliminary statistical analysis. Note that the 95% confidence range represents the range of numbers within two standard deviations of the mean value. The results from this preliminary analysis indicate that centrifuged solids density is the only physical property with significant differences between SORWT groups. The lack of significant differences between SORWT groups for the other properties may be an artifact of the lack of available and/or meaningful data; may indicate the need for a revised grouping strategy for physical properties; or may indicate a lack of physical property variability over all tanks.

It is apparent that a considerable amount of additional data is necessary before generalizations about the physical properties can be made. If additional data and further statistical analysis indicate that the physical properties do not exceed acceptable ranges set by pretreatment, retrieval, and other related operations, then general characterization of sludge physical properties over all SSTs may be considered. However, if further analysis indicates that the physical properties do exceed acceptable ranges, then a revised grouping strategy will be needed to reduce the variability of the physical properties within groups of tanks. This revised grouping strategy may be determined through cluster analysis or some other statistical analysis technique.

The primary conclusion from this preliminary analysis is that more data are necessary before an accurate assessment of the tank waste physical characteristics can be made. There is concern as to whether the physical properties currently being studied actually provide meaningful information for pretreatment, retrieval, and other related operations. The results from this study may help to identify those types of data that do not provide sufficient information from an operations point of view.

Table 6.3. Summary of Single-Shell Tank Waste Physical Properties

Physical Property	Mean Value	Standard Deviation	Range 95% Confidence
Bulk Density (g/mL)	1.32	0.218	0.889-1.76
Mean Particle Size by Number (μm)	1.21	0.247	0.718-1.71
Mean Particle Size by Volume (μm)	24.7	15.1	0-55.0
Wt% Water	52.7	40.0	0-100
Wt% Centrifuged Solids	81.2	14.5	52.2-100
Centrifuged Solids Density (g/mL) ^(a)	1.51	0.196	1.19-1.90
Vol% Centrifuged Solids	78.4	15.9	46.5-100
Vol% Settled Solids	100	0.505	98.9-100
(a) Only property showing significant differences between SORWT groups.			

6.2.2 Evaluation of Historical Data Set

A preliminary analysis was initiated using a PC software package called SYSTAT.^(a) Unfortunately, this package could not support the Braun Data Set because the data contained 11,500 records by 20 fields per record. The PC system was configured to accept X-windows from a Unix-based machine in order to conduct a preliminary statistical analysis using the SAS statistical software package.^(b)

Original plans were to develop a model to estimate the analyte concentration in the tanks based on the information provided in the Braun Data Set. An attempt was made to group several of the sample types based on densities and concentrations using an analysis of variance (ANOVA) and TUKEY analyses. However, the Braun Data Set proved to have a number of anomalies that provided ambiguous results. Some examples of the anomalies that were identified in the data set are given below:

- Approximately +90% of the data does not identify the methods used to prepare or analyze the samples, e.g., water leach for ion chromatography, acid digestion for inductively coupled plasma spectroscopy, etc.
- Some wastes with high analyte concentrations also reported "0" concentration for the same analytes. The zero may infer that no analysis was performed or that the concentration may have been less than detection limits.
- Conversion errors were identified throughout the data set. In some cases, the original analyte concentrations were increased by three orders of magnitude.

When data that were obviously in error, e.g., 4,000,000 μg analyte/g sample, and outliers were eliminated, the data set provided some clustering consistencies when compared with Group I established by the SORWT model. Based on this result, limited statistical analyses will proceed to see whether the data may be used to characterize the analyte concentration across tanks and SORWT groups.

6.3 References

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(a) SYSTAT for Windows, Version 5, SYSTAT, Inc.

(b) SAS Version 6.09, SAS., Inc.

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7.0 Colloidal Studies for Solid-Liquid Separation

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Tank waste sludges contain fine particles of insoluble oxides, hydroxides, and salts. During many critical phases of tank waste processing, these insoluble particles will be dispersed in aqueous solutions and form colloidal suspensions. The objective of the Colloidal Studies subtask is to understand and model the behavior of such colloidal suspensions and determine how colloidal interactions impact major steps in tank waste processing.

The Colloidal Studies subtask consists of three major activities: 1) experimental studies aimed at characterizing the interactions between model colloids and understanding how those interactions influence properties of importance to sludge processing such as viscosities, sedimentation behavior, and filtration; 2) theoretical studies aimed at developing mathematical models to describe, explain, and predict colloidal behavior; and 3) preparation of a facility designated as a Hot Colloids Laboratory in which predictions based on "cold" studies on simulants and modeling efforts can be directly compared with the behavior of real sludge samples.

Experimental work performed during the second quarter of FY 1995 addressed various colloidal properties, i.e., agglomeration, viscosity, sedimentation, and filtration. A brief discussion of progress on the Hot Colloids Laboratory is also presented.

7.1 Experimental Studies

Existing analyses of sludge [elemental, x-ray, and transmission electron microscopy (TEM)] suggest that major colloids expected to be present either in initial or processed sludges include submicron particles such as $\text{Al}(\text{OH})_3$ (gibbsite), boehmite (AlOOH), $\text{Fe}(\text{OH})_3$, ZrO_2 , phosphates, and aluminosilicates. The emphasis of this subtask is to study the properties of slurries containing such particles as a function of solids loadings, pH, and salt content (ionic strength). These parameters are systematically varied to span the range of solution conditions and particle types likely to be encountered during processing. Results are used to help define the general principles that govern such colloidal suspensions in order to predict and/or control the properties of sludge suspensions, regardless of sludge composition or processing conditions.

Examples of the properties of interest and their impact on sludge processing are given in Figure 7.1. For retrieval and transport, a major property of concern is slurry viscosity. In the baseline process, the desire is to produce slurries with maximum solids loadings (to minimize waste volumes) and still maintain low (< 60 cp) viscosities to allow pumping. For storage, washing, and leaching steps, solid-liquid separations in the current baseline call for settle-decant processes to divide supernatant liquids (the low-level waste stream) from insoluble solids (going to high-level waste). Here, critical parameters are sedimentation velocities (which need to exceed 3 cm/hr in the current baseline process) and final sediment densities (which influence separations efficiencies by controlling the relative volumes of entrapped interstitial liquids and supernatant liquids that can be removed).

Fe(OH)₃ Suspensions

Three different sources of Fe(OH)₃ were evaluated as potential simulants for the Fe(OH)₃ observed in tank wastes: commercial Fe(OH)₃ suspensions supplied by Noah Technologies Corp. (13 wt%), commercial Fe(OH)₃ supplied by Pfaltz and Bauer (60 wt%), and fresh iron nitrate precipitates prepared at PNL via precipitation with NaOH. Transmission electron micrographs indicate all three materials contain primary particles that are roughly equiaxial and 5 to 10 nm in diameter. All three resemble the Fe(OH)₃ seen in TEM micrographs of actual tank waste. Most of the work contained in this quarterly was performed using the Noah powder. However, the agglomeration properties of the aged Fe(OH)₃ suspension are somewhat unusual and may not resemble fresh Fe(OH)₃ (see Agglomeration below).

This quarter, the behavior of Fe(OH)₃ suspensions has been investigated to provide direct comparisons with boehmite and gibbsite suspensions. Similarities between Fe(OH)₃ and boehmite are that both materials exhibit similar surface charge characteristics (with isoelectric points between pH 9 and 10) and that both contain submicron primary particles. Major differences between the particles are 1) the primary particles in Fe(OH)₃ are equiaxed rather than plate-like; 2) the Fe(OH)₃ forms 1.6- μ m agglomerates that are difficult to disperse regardless of solution conditions (see Agglomeration); and 3) the Fe(OH)₃ is less soluble than AlOOH at all pH values (most apparent in strong base conditions). The similarities and differences between the two particle types are reflected in the physical properties of the particle suspensions and will be described below.

Tank C-103 Simulant

Simple chemical simulants for Tank C-103 developed in the IPM Solid-Liquid Separations Simulant Development Task have been investigated in sedimentation and agglomeration studies reported below. Simulants were prepared using commercial colloidal phases. Components in the simulant include Fe(OH)₃, SiO₂, Al(OH)₃, AlOOH, and apatite (Ca₅(PO₄)₃OH). The presence or absence of apatite will be shown to have a significant impact on the colloidal behavior of the mixed systems. The constituents were added in ratios similar to those indicated in the chemical analysis of actual C-103 sludge. However, the phases present in C-103 are unknown at this time, so the phases present in the simulant may not represent the phases present in the actual waste. Two simulants were prepared. Simulant 103-7 contains the phosphate mineral apatite, while apatite is absent in the simpler simulant 103-4. Compositions of both simulants, along with primary particle components, are listed in Table 7.1.

Table 7.1. Estimated Simulant 103-4, 103-6, and 103-7 Composition

Constituent	Primary Particle Size (nm)	103-4 wt%	103-6 wt%	103-7 wt%
Fe(OH) ₃	10 nm	3.5	3.0	2.6
SiO ₂	60 nm	3.5	3.0	2.6
Al(OH) ₃	250 nm	0.75	0.65	0.57
AlOOH	20 nm	0.23	0.2	0.17
Ca ₁₀ (OH) ₂ (PO ₄) ₆	50 nm	0	1.2	2.1
Total Solid		7.9	8.0	8.0
NaNO ₃		1.2 M	1.0 M	0.8 M

7.1.2 Discussion of Properties

Agglomeration

Although techniques such as TEM clearly show that most of the primary particles (by both number and volume percent) in actual tank sludges are smaller than $0.1\ \mu\text{m}$ in diameter, indirect measurements of particle size using techniques such as sedimentation and light scattering indicate that most of the particles are larger than $1\ \mu\text{m}$. The apparent discrepancy between the two sets of measurements is due to the fact that, under many slurry conditions, the primary particles are heavily agglomerated.

However, it is critical to understand that an agglomerate with an effective diameter of around $1\ \mu\text{m}$ does not behave anything like a primary particle having the same diameter. Predictions based either on normal particle size distributions or on TEM results alone can be equally misleading.

In general, the material in sludge can be viewed on a wide range of length scales, each of which provides useful information regarding ultimate properties (Figure 7.2). At the smallest length scale (probed by TEM), the size of the primary particles can be determined. TEM images suggest that many of the primary particles in sludge are as small as 5 to 10 nm. Under many processing conditions, the primary particles agglomerate to form fractal clusters. The sizes of these clusters typically range from approximately $0.1\ \mu\text{m}$ to a few microns in diameter. On a larger length scale, the fractal clusters can associate to form flocs that can range anywhere from $10\ \mu\text{m}$ up to particles larger than 1 mm. The size of the large flocs is usually determined by the level of shear and Brownian motion in the solution, which tends to break up the larger flocs. Shear can also partially disrupt the smaller fractal clusters.

In simple aqueous solutions, primary particles can either be dispersed or agglomerated, depending on whether the forces between the particles are repulsive or attractive, respectively. In classical DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory (Figure 7.3), the net interparticle interaction potential (V) is the sum of a van der Waals attractive term (V_a) and an electrostatic term that can either be repulsive (V_r) (for particles of like charge) or attractive (for particles of opposite charge). The van der Waals attraction depends on the materials comprising the particles, the surrounding fluid, and

Figure 7.2. Particle Types in Tank Sludge

Figure 7.3. DLVO Potential as a Function of Separation

the particle shapes. While van der Waals attractions can be strong at short distances, the attraction becomes negligible for particles that are far apart. The electrostatic term arises from charges created at particle surfaces as a result of adsorption or desorption of species such as protons and hydroxide ions. For oxides, the charges can be positive or negative depending on solution pH and the acid-base properties of the surface. To satisfy electroneutrality, each charged surface is charge compensated by a cloud of ions extending into the solution. The counterion clouds interact, resulting in what is referred to as the double layer interaction (V_r). In dilute electrolyte solutions, the counterion clouds can extend far from the particle surface, making the double layer interaction a long-range interaction. Since the van der Waals attraction is negligible at long range, the electrostatic repulsion dominates, and a net potential energy barrier to agglomeration (top curve, Figure 7.4) is created. However, as salts are added, the double layer moves closer to the particle surface (as more ions are present in solution to neutralize the surface charge) and the magnitude of the repulsive barrier decreases. At high salt concentrations (bottom curve, Figure 7.4), the net potential is purely attractive, and there is no barrier to agglomeration.

The net interaction potential between particles can be used to predict the pH and salt concentration regimes expected to promote agglomeration. For example, agglomeration can be assumed to occur when the repulsive barrier to agglomeration is less than or equal to the thermal energy in the system (kT). (Even at 10 kT , a value commonly used by ceramic engineers, a significant number of particles have sufficient thermal energy to cross the repulsive barrier and agglomerate.) Figure 7.5 shows the pH and salt concentration (for a 1:1 electrolyte such as NaNO_3) for which the barrier height is equal to kT for boehmite particles. The stability curve shows that near the isoelectric point at pH 8.5 (where the boehmite particles are neutral), agglomeration should occur regardless of the salt concentration. As

Figure 7.4. Effect of Inverse Debye Length on DLVO Potential

Figure 7.5. Stability Map for Colloidal Boehmite

the salt concentration increases, the instability regime widens. For NaNO_3 concentrations exceeding 0.1 M, boehmite is predicted to be heavily agglomerated regardless of the pH. As will be shown below, experimental trends such as the pH and ionic strength dependence for the viscosity of both boehmite and $\text{Fe}(\text{OH})_3$ suspensions can be rationalized on the basis of such stability diagrams.

Interparticle potentials not only influence the stability of colloidal suspensions, but are also critical in determining the nature of the agglomerates formed and the kinetics of agglomeration. **A critical concept required to understand the nature of agglomerates is that agglomerates are fractal objects.** For a normal dense solid, the mass of a given particle scales as r^3 , where r is the particle radius. For a fractal three-dimensional object, the particle mass scales as r^n , where n is called the fractal dimension of the object. The fractal dimension of an agglomerate is controlled by how the agglomerate is formed. For the limiting case of diffusion-limited aggregation, there is no potential energy barrier to agglomeration. Every time a primary particle or cluster encounters another cluster, it sticks. The resulting object tends to have an open network structure with a low density and a low fractal dimension. When there is a significant barrier to agglomeration, particles tend to stick in only those regions of the agglomerate that represent the lowest potential energy sites. In this so-called reaction-limited aggregation regime, denser agglomerates form with a higher fractal dimension. Figure 7.6 shows images of real fractal agglomerates of 150-nm gold particles formed under the two limiting sets of conditions. Table 7.2 lists fractal dimensions for both particle-cluster and cluster-cluster aggregates formed under either diffusion-limited or reaction-limited conditions. For the concentrated slurries representative of sludge, cluster-cluster aggregation is expected and gives rise to limiting fractal dimensions of 1.8 to 2.1 for the diffusion-limited and reaction-limited cases. If the

Figure 7.6. Transmission Electron Micrographs of Clusters Aggregated by Use of (a) Diffusion-Limited Kinetics and (b) Reaction-Limited Kinetics

Table 7.2. Fractal Dimensions of Colloidal Aggregates

		Cluster-Cluster	
		Monomer-Cluster	Polydisperse
Diffusion-Limited	2.5	1.8	2.18
Reaction-Limited	3.0	2.1	2.25

clusters are allowed to rearrange and restructure via rotation around internal points of contact, the clusters can further densify after formation and yield fractal dimensions of 2.18 to 2.25 for the diffusion-limited and reaction-limited cases.

Using the concept of fractals, it is relatively easy to understand the differences between large primary particles and agglomerates made up of small primary particles. First, the density of the fractal object can be much less than that of the primary particle. Conversely, fractal agglomerates occupy much more space than primary particles of the same diameter at equivalent solids loadings.

The density of the fractal object depends both on its size and on its fractal dimension. For example, the $\text{Fe}(\text{OH})_3$ examined in this study contains primary particles that are 10 nm in diameter. If the $\text{Fe}(\text{OH})_3$ coagulates to form a relatively dense fractal agglomerate ($n = 2.25$) with an average agglomerate diameter of 100 nm, the mass of the agglomerate is only 17.8% that of a primary particle having a diameter of 100 nm. For the same fractal dimension, a 1000-nm (1- μm) particle has a net mass that is only 0.56% that of a dense 1- μm primary particle. A 1- μm agglomerate with a lower fractal dimension of $n = 1.7$ would have an even lower relative mass (0.012%).

The impact of fractal geometry on properties of interest can be appreciated by comparing calculated properties based on spherical primary particles with calculated properties for spherical fractal agglomerates at the same solids loading (assuming that interactions between particles are similar). The examples described below compare 0.1- μm primary particles to 0.1- μm agglomerates with a fractal dimension of 2.25 (the most likely value for sludges). Calculations performed last quarter indicate that for noninteracting spheres, solids loadings of 50 vol % can be achieved before the viscosity exceeds 100 cp. Assuming that the fractal agglomerates interact as spheres with a hydrodynamic radius equal to the particle radius, the solids loading corresponding to a viscosity of 100 cp for the agglomerates is approximately 9 vol %. This is simply because the fractal agglomerates in the example occupy almost six times more volume than dense primary particles at the same solids loading. By a similar argument, hindered sedimentation is to be expected at much lower solids loadings for the agglomerates than for dense primary particles. The solids loading calculated to drop sedimentation velocities to 10% of the unhindered, maximum sedimentation velocity is 5 vol % for the agglomerate compared with 30 vol % for solid spheres. In addition, initial unhindered sedimentation velocities for the agglomerate are expected to be lower because the density of the agglomerate is lower than that of the primary particle. Including all mass within the hydrodynamic radius of the particle [$\text{Fe}(\text{OH})_3$ and the interstitial water], the agglomerate has an effective density of 1.53 g/cm³ compared with 4 g/cm³ for dense $\text{Fe}(\text{OH})_3$. Using Stokes' Law, in which sedimentation rates are proportional to the density difference between the particle and the solution, calculated sedimentation velocities (Figure 7.7) for the 0.1- μm agglomerates should be only 17% of the velocity for the primary particles. Assuming closest packing of either

Figure 7.7. Calculated Sedimentation Velocities for $\text{Fe}(\text{OH})_3$ (Stokes' Law)

spheres or the specific fractal agglomerates in the example yields a sediment density of approximately 11 vol% for the agglomerates compared with 60 vol% for hard spheres. It is obviously an oversimplification to assume that fractal agglomerates will interact with each other the same way that hard spheres do. However, as will be shown below, many of the experimental results observed to date can be rationalized using the simple geometric arguments described above.

Several key parameters are believed to control the nature and size of the agglomerates. For Brownian flocculation, the growth rate is controlled by the collision rate between two aggregates and a parameter called the stability ratio, which measures the fraction of collisions that result in having the particles stick to each other. The stability ratio, in turn, is controlled by the magnitude of the interparticle interaction potential discussed above. Model calculations can be used to determine how aggregation kinetics change as a function of the interaction potential. A sample calculation (Figure 7.8) illustrates that once agglomeration begins, monomer concentrations ($N=1$) rapidly decrease; dimers ($N=2$) form from monomers, but are eventually destroyed to form trimers; and other

Figure 7.8. Aggregate Size Distribution as a Function of Time

larger cluster sizes also are eventually formed and destroyed. For the case where there is no barrier to agglomeration (diffusion-limited aggregation), an equation describing the average agglomerate radius at long times is given by:

$$R = (4CkT/3\eta M)^{1/n} t^{1/n}$$

where C is the initial particle concentration, η is the solution viscosity, M is the mass of the primary particle, and n is the fractal dimension. In other words, particles grow faster at higher particle concentrations and when smaller primary particles are present that can diffuse more rapidly. Particle growth stops when primary particles are consumed. Larger agglomerates can still form, but only by packing of the fractal particles ("hard sphere" packing). Expressions for the equilibrium particle size suggest that more concentrated suspensions yield solutions containing higher agglomerate concentrations but smaller agglomerate sizes (similar to nucleation and growth of particles from supersaturated solutions). Another factor influencing cluster sizes is that clusters can eventually grow to the point where they settle out of solution.

Cluster sizes also can be limited by cluster deaggregation, which may occur due to either fluid shear forces or Brownian motion. High shear rates result in smaller agglomerates. Cluster deaggregation turns out to be a key phenomenon noted experimentally this quarter in making agglomerate size measurements. The light scattering instrumentation used to measure agglomerate

sizes requires that the initial concentrated suspensions be diluted to provide the appropriate light scattering conditions. To keep particles in suspension, the instrument recirculates the solution, so the agglomerates not only experience dilution but experience shear forces as well. As a result, the agglomerates deflocculate as a function of time, and the kinetics of deagglomeration can be continuously monitored.

For $\text{Fe}(\text{OH})_3$ and C-103 simulant, the behavior depicted in Figure 7.9 is typically observed. Immediately after introduction into the instrument, a broad distribution of agglomerates that consist of particles large as $100\ \mu\text{m}$ and a mean agglomerate size of approximately $10\ \mu\text{m}$ is observed. However, within 1/2 hr, a new feature appears in the distribution at around $1.6\ \mu\text{m}$. Over several hours, the large agglomerates continue to disappear until eventually a rather monodisperse agglomerate distribution is produced with a size of $1.6\ \mu\text{m}$. The above results represent one example of how sensitive "particle size" analyses are to measurement conditions. For most sludge samples, measured particle size distributions are really agglomerate size distributions which are highly sensitive to the concentrations, pH, salt content, and shear conditions under which the measurements were made. Unless careful attention is given to conditions promoting either agglomeration or deagglomeration, typical "particle size" analyses are relatively meaningless.

A final point of interest regarding deagglomeration of $\text{Fe}(\text{OH})_3$ is that the ultimate agglomerate size of $1.6\ \mu\text{m}$ is observed regardless of initial solids loading or solution pH (Figure 7.10). Even sonication or shearing is insufficient to break up the agglomerates. These results are in sharp contrast to the

Figure 7.9. Measured Agglomerate Distributions of C-103 Simulant as a Function of Recirculation Time in the Particle Analyzer

Figure 7.10. Average Agglomerate Size as a Function of pH and Solids Loading $[\text{Fe}(\text{OH})_3]$

behavior observed for boehmite. Under mildly acidic conditions, results reported last quarter showed that boehmite agglomerates can be broken down completely to yield suspensions containing high concentrations of primary particles. Although $\text{Fe}(\text{OH})_3$ exhibits surface charge characteristics similar to boehmite, solution pH appears to have no influence on the stable agglomerate size. It appears that the 1.6- μm agglomerates represent a particle type referred to as a "hard" agglomerate, in which the 1-nm primary particles are "glued" together. We speculate that these hard agglomerates form with time and may explain some of the dramatic differences between the filtration behavior of fresh and aged $\text{Fe}(\text{OH})_3$ precipitates reported at the Solid-Liquid Separations seminar held in Richland, Washington, December 7-9, 1994.

Viscosity

AlOOH Suspensions. In the previous reporting period, viscosity studies were conducted on boehmite suspensions as a function of solids loading, pH, and ionic strength. The purpose of these studies was to establish the range of behaviors that might be encountered for suspensions that contain submicron primary particles. Results showed that dispersed boehmite suspensions can exhibit low viscosities and Newtonian behavior, even at solids loadings as high as 10 vol%. However, agglomerated suspensions can form viscous, shear-thinning gels with viscosities exceeding 20,000 cp near the isoelectric point and at low and high pH where the acid and base strengths contribute to the total ionic strength. For the conditions tested, the degree of agglomeration and the magnitude of the viscosity are controlled by the degree of electrostatic stabilization (see Agglomeration). In 10^{-2} M NaNO_3 (Figure 7.11), the viscosity measurements indicate that, while the viscosity values follow the general trends indicated in the boehmite stability diagram (Figure 7.5), the value of kT that defines the stability curve is probably set too high. A value of approximately 4 kT comes closer to describing the

Figure 7.11. Viscosity of Boehmite Samples with 10^{-2} M NaNO_3 as a Function of pH and Solids Loading (shear rate = 11.5 s^{-1})

observed viscosity behavior and indicates slight agglomeration in the basic pH regime; i.e., the observed viscosity behavior is more consistent with an electrolyte concentration of 4×10^{-2} M than the actual 10^{-2} M concentration in Figure 7.5.

In this reporting period, viscosities were measured for boehmite particles suspended in 1 M NaNO_3 solutions at different solids loadings. All suspensions in the high salt content regime exhibit shear thinning behavior associated with agglomerated particles. Although maxima in the viscosity are still seen at the isoelectric point and at high and low pH, the viscosity is high at all pH values (Figure 7.12) because none of the suspensions in 1 M NaNO_3 are dispersed, as predicted in Figure 7.5. Agglomeration is due to the high ionic strength of the solutions, which collapses the electrical double layer and inhibits electrostatic stabilization regardless of surface charge. The effect of salt on viscosity is illustrated more directly in Figure 7.13, which compares the low viscosity, Newtonian behavior of a dispersed boehmite suspension at pH 3 (0.01 M NaNO_3 curve) with the highly viscous shear-thinning behavior of a pH 3 slurry agglomerated using 1 M NaNO_3 .

For sludge processing, the current baseline specifies that slurry viscosities should not exceed 60 cp. In this reporting period, work was conducted to determine the maximum solids loading for boehmite in basic salt-containing solutions to be encountered in processing. Viscosities of such suspensions as a function of shear rate and solids loading are shown in Figure 7.14. As expected, the viscosity drops

Figure 7.12. Viscosity of Boehmite Samples with 1 M NaNO_3 as a Function of pH and Solids Loading (shear rate = 11.5 s^{-1})

with decreasing solids loading and with increasing shear rate. For shear rates thought to be representative of pumping and transport operations (10 to 100 s^{-1}), the results show that the solids loading for boehmite suspensions needs to be held below 1 vol% if the maximum desired viscosity is 100 cp. Assuming that the behavior at high shear rates can be related to the nature of the agglomerates present, the viscosity is consistent with behavior expected of fractal agglomerates with $n = 2.25$ and a particle diameter of $1.8 \text{ }\mu\text{m}$.

If the behavior of boehmite is representative of other sludge components, sludges will have to be diluted to a greater extent than is currently envisioned for baseline processing schemes to achieve desired viscosities. Estimates for the initial insoluble solids content of untreated sludge range from 5 to 25 vol% (15 to 65 wt%), depending on the tank. Aluminum-rich sludges appear to be among the denser sludges. If the initial solids loading is 20 vol%, a sludge dilution factor of around 20 would be required to achieve desired viscosities. This level of dilution will generate much more liquid waste than is desired in the baseline process, which calls for dilution factors of 3 to 4. Conversely, if the baseline conditions are adhered to, slurries having solids loading of 5 to 7 vol% would be produced, given a dilution factor of 3 to 4. The measured viscosity of a 6 vol% slurry of boehmite at a shear rate of 11.5 s^{-1} exceeds 10,000 cp. Even at a shear rate of 115 s^{-1} , the viscosity exceeds 1000 cp. Such high viscosities are likely to create severe processing problems. These results indicate one reason it is critical that the initial solids loadings in tank sludges be determined. The initial loading must be known

Figure 7.13. Viscosity vs. Shear Rate for the 10 vol% Boehmite Sample at pH = 3

Figure 7.14. Viscosity of Boehmite at Different Solids Loadings (1 M NaNO₃, 1 M NaOH)

to predict the appropriate dilution factor to achieve desired viscosities. This discussion represents a "worst case" scenario. If a large fraction of material is present as large primary particles, baseline dilution factors may be adequate.

Fe(OH)₃ Suspensions. Given the high viscosities seen for boehmite suspensions, it is important to establish whether these viscosities are representative of the colloids present in tank waste, or whether the properties are somehow unique to boehmite. Viscosity measurements performed for both as-received (13 wt% or 3.25 vol%) and diluted commercial suspensions of Fe(OH)₃ in 0.01 M NaNO₃ illustrate that the general trends seen for boehmite are duplicated for Fe(OH)₃ (Figure 7.15). Conditions expected to lead to dispersed suspensions (pH 2.8) lead to the formation of low-viscosity Newtonian fluids. However, while the viscosity of the Fe(OH)₃ suspension is low (10 cp), it is six times greater than that of an equivalent boehmite suspension. Near the isoelectric point, where enhanced agglomeration is expected due to an elimination of electrostatic stabilization, viscous shear-thinning fluids are observed (pH 7.5). At a shear rate of 11.5 s⁻¹, the agglomerated Fe(OH)₃ suspension is again more viscous (2100 cp) than a comparable AlOOH suspension (1100 cp).

The results for dispersed and agglomerated Fe(OH)₃ suggest that Fe(OH)₃ can be even more difficult to handle than AlOOH. However, Fe(OH)₃ does not always exhibit higher viscosities than AlOOH. An examination of viscosity vs. pH for a 6.5 wt% (1.6 vol%) slurry (Figure 7.16) illustrates that, while Fe(OH)₃ exhibits higher viscosities at high pH, low pH, and at the isoelectric point as does boehmite, the highest viscosities correspond to the isoelectric point. It appears that in the high and low pH regimes, Fe(OH)₃ is more "benign" than AlOOH. For example, near pH 12 and at a shear rate of 11.5 s⁻¹, a 3.25 vol% slurry of Fe(OH)₃ has a viscosity of 1300 cp compared with 2500 cp for AlOOH. At 1.6 vol%, viscosities as low as 100 cp are achieved, corresponding to the upper limit for "allowable" solids loadings.

Figure 7.15. Viscosity as a Function of pH for the 13 wt% Fe(OH)₃ Sample with 0.01 M NaNO₃

Figure 7.16. Viscosity vs. pH at Two Shear Rates for the 6.5 wt% $\text{Fe}(\text{OH})_3$ Sample with 10^{-2} M NaNO_3

Unanticipated viscosity results are obtained for 1.6 vol% (6.5 wt%) $\text{Fe}(\text{OH})_3$ at high salt concentrations (1 M NaNO_3 , Figure 7.17). The measured viscosities are almost identical to those obtained at much lower ionic strength (Figure 7.16). The results suggest that even at high salt content, viscosities are just slightly higher than desired at 1.6 vol%. The 1.6 vol% maximum loading for $\text{Fe}(\text{OH})_3$ is larger than but comparable to the 1 vol% maximum inferred for boehmite. However, an examination of tank wastes suggest that iron-rich sludges tend to exhibit lower initial solids loadings than do boehmite sludges. If the initial sludge has a solids loading as low as 5 vol%, the dilution factor of 3 to 4 suggested in the baseline process would be sufficient to disperse $\text{Fe}(\text{OH})_3$ suspensions to the point where pumping might be feasible. While the high-salt result is not well understood, it may be that high viscosities associated with collapse of the double layer are accentuated at higher solids loadings. Measurements performed at 13 wt% (Figure 7.18) come closer to exhibiting the behavior predicted on the basis of stability diagrams.

Sedimentation

For sedimentation, three major properties require characterization and understanding: 1) the kinetics of sedimentation, 2) the final density of the sediment cake, and 3) the fraction of material left in the supernatant liquid as fines. All three of these parameters have been investigated during the past quarter with an emphasis on $\text{Fe}(\text{OH})_3$ suspensions and multicomponent simulants in the basic, high ionic strength regime. Sedimentation experiments are performed by introducing well-mixed slurries

Figure 7.17. Viscosity vs. pH at Two Shear Rates for the 6.5 wt% $\text{Fe}(\text{OH})_3$ Sample with 1 M NaNO_3

into graduated cylinders and observing the cylinders as a function of time. Extensive effort has also gone into development of sedimentation models. A transient sedimentation model has been developed to describe the kinetics of sedimentation and final sediment densities for noninteracting spheres. An alternate model has been developed using Monte Carlo methods to determine density profiles on concentrated colloidal suspensions in sedimentation equilibrium. The latter model has been used to examine sediment compressibility. Some of the modeling results of sedimentation were presented in the previous quarterly report; the rest will be presented in a separate document.

The general characteristics observed during sedimentation are illustrated in Figure 7.19. For samples with a relatively high solids loading (above 1 wt%), a sharp, well-defined interface appears almost immediately between clear supernatant liquid and an opaque region that contains suspended solids. For such suspensions, the sedimentation velocity is monitored by noting the position of the interface as a function of time. With time, the sediment layer becomes thinner as the sediment settles. The average solids loading in the sediment layer increases until the sediment compresses to its equilibrium solids loading. For samples with a low solids loading, the interface between interfacial liquids and sedimenting particles is not immediately apparent. $\text{Fe}(\text{OH})_3$ suspensions exhibit a uniform color associated with suspended colloids. Over time, a layer of material is observed growing up from the bottom of the container. The layer gets thicker with time (in contrast to the behavior of concentrated suspensions) as particles settle to the bottom. Once particle settling is complete, the

Figure 7.18. Viscosity vs. pH at Two Shear Rates for the 13 wt% $\text{Fe}(\text{OH})_3$ Sample with 10^{-2} M NaNO_3

sediment layer attains a constant thickness. For both the concentrated and dilute cases, final sediment densities are estimated by noting the final volume of the discrete sediment layer compared with the initial volume of solids added to the suspension.

For the concentrated $\text{Fe}(\text{OH})_3$ suspensions, sedimentation rates have been monitored as a function of time for two types of suspensions that have different solids loadings. In the first series, the initial 8 wt% (2 vol%) suspension in a pH 12, 1 M NaNO_3 solution was diluted with water to generate the other suspensions. Therefore, for this series, the ionic strength of the suspension is diluted in addition to the solids loading. In the other series, dilutions were performed using the pH 12, 1 M NaNO_3 starting electrolyte. Both series of experiments show the same general trends (Figures 7.20 and 7.21). At the highest solids loading (8 wt%), sedimentation rates are quite slow (0.01 to 0.02 cm/hr). Decreasing the solids loading increases the initial sedimentation rate. However, at intermediate solids loadings, e.g., 2 wt%, unusual sedimentation behavior is observed. As indicated last quarter, "normal" sedimentation behavior is for the rate of sedimentation to decrease as a function of time as solids loadings in the sediment increase. However, the 2 wt% data show that after a few hours of "normal" behavior, sedimentation rates actually increase with time for a short time interval. Sedimentation rates then decrease as expected until the sediment compacts to its equilibrium position.

The "S-shaped" sedimentation curve shown for 2 wt% is apparently associated with the formation of an interconnected network of flocs that initially undergoes hindered settling. However, eventually

Figure 7.19. Dilution of Sludge Simulant Increases Concentration of Nonsedimenting Fines. Behavior is seen for both simple $\text{Fe}(\text{OH})_3$ suspensions and multicomponent sludge simulants

Figure 7.20. Sedimentation of $\text{Fe}(\text{OH})_3$ (pH 12 water)

Figure 7.21. Sedimentation of $\text{Fe}(\text{OH})_3$ (1 M NaNO_3 , pH = 12)

the network is unable to support its own weight, and it collapses, generating the increased sedimentation velocity. The collapsed structure then falls to the bottom and compacts as a normal sediment. More concentrated slurries apparently form denser and more highly interconnected structures (inhibiting collapse), while more dilute slurries are too dilute to form such networks in the first place. The instabilities in the floc network may be related to turbulence in the solution, which in turn is sensitive to the geometry of the sedimentation vessel.

Researchers at PNL and elsewhere have noticed that, under certain conditions, sedimentation rates are sensitive to the container geometry. Results obtained this quarter suggest that the anomalous sedimentation behavior associated with containers can be attributed to this "instability" regime. For example, Figure 7.22 shows the sedimentation behavior observed this quarter for a 10 wt% (4 vol%) suspension of 1- μm gibbsite particles in 0.1 M NaOH for different liquid levels in graduated cylinders all having the same diameter. All samples exhibit comparable initial sedimentation velocities (1.1 to 1.3 cm/hr); all exhibit the instability at about the same solids loading (12 wt%); and all exhibit similar final sediment densities (18 to 19 wt%). However, the sedimentation distance required to reach the instability concentration of 12 wt% is almost directly proportional to the initial sediment height. The times required to become unstable are roughly 1.3 hr, 2.2 hr, and 3.0 hr for liquid levels of 10 cm, 20 cm, and 30 cm, respectively. Depending on the time interval used to measure the extent of sedimentation, results for each of the three columns could be dramatically different, depending on whether or not the instability region has been reached. Such instabilities clearly need to be accounted for in the design and interpretation of sedimentation experiments.

Assuming that the 2 wt% slurry represents the minimum solids loading for which a network can be formed from the initial $\text{Fe}(\text{OH})_3$ fractal agglomerates present in solution, the solids loading can be used to generalize the effective size of the agglomerates. As stated in the first quarter report, the percolation threshold for forming a space-filling network of hard spheres is 16 vol%. The fact that such a network is formed here at a solids loading of 0.5 vol% (2 wt%) is consistent with the presence of fractal flocs of the 10-nm primary particles with a fractal dimension of 2.25 and an average diameter of from 1 to

Figure 7.22. Sedimentation of 10 wt% Gibbsite in 0.1 M NaOH

2 μm . The inferred agglomerate size is in good agreement with the measured agglomerate size of 1.6 μm for $\text{Fe}(\text{OH})_3$. The gibbsite suspensions depicted in Figure 7.22 exhibit the instability at higher solids loadings (12 wt% or approximately 5 vol%).

However, solids loadings expected for gibbsite agglomerates of micron dimensions are expected to be higher than those seen for $\text{Fe}(\text{OH})_3$ (both at the instability transition and for final sediment packing) because the gibbsite suspension contains larger primary particles [1000 nm for gibbsite compared with 10 nm for $\text{Fe}(\text{OH})_3$]. Assuming a percolation threshold of 16 vol% for packing of "hydrodynamic" spheres, and assuming that gibbsite forms fractal clusters with $n = 2.25$, the instability region for gibbsite is consistent with the formation of a network containing agglomerates that are 0.5 μm in size [smaller than the agglomerate size seen for $\text{Fe}(\text{OH})_3$]. The above example illustrates why it is important to know the dimensions of both the primary particles and the agglomerates in sludge suspensions.

At low solids loadings (below 2 vol%), there is a limited range where a sedimentation front can still be observed, and consequently the sedimentation rates can be estimated in the "nonhindered" regime. As shown in Figure 7.20, sedimentation velocities as high as 25 cm/hr are observed at low solids loadings (0.5 wt% or 0.125 vol%). A pure fractal agglomerate with a fractal dimension of 2.25 does not have a sufficient density to undergo such a high sedimentation rate (see Figure 7.2). For fractal agglomerates, achieving such high sedimentation velocities can only be explained if the settling agglomerates represent a closest-packed array of smaller fractal objects (right side of Figure 7.2). If it

is assumed that the small subunits in the larger flocs consist of the 1.6- μm agglomerates seen via light scattering, the density of the resulting floc would be approximately 1.04 gm/cm³. To achieve the observed sedimentation velocity, the size of the floc would have to be huge--on the order of 0.1 cm. While such a floc is enormous relative to the primary particles present in the system (occupying a volume 10¹⁵ times that of the primary particle), flocs of such a large extent are not ruled out based on visual observations during sedimentation. For example, after the collapse of the 2 wt% sediment, flocs are left in the supernatant liquid that are sufficiently isolated to be seen with the naked eye. Although the flocs are large (approximately 0.01 cm), they do not settle at an appreciable rate, consistent with their fractal nature.

The final sediment packing density has been determined for all but the most concentrated Fe(OH)₃ slurries (which are still settling at a slow rate). Final packing densities in the samples diluted with water is approximately 6.3 wt%, while the more highly agglomerated samples diluted with 1 M NaNO₃ exhibit slightly lower packing densities (5.4 wt%). In terms of volume fraction, the observed solids loadings (1.6 vol% and 1.4 vol%) are close to the 2 vol% calculated for dense packing of fractal agglomerates having a diameter of 1.6 μm and $n = 2.25$. Therefore, sediment density appears to be a property that can be rationalized on the basis of fractal geometry.

The sedimentation results for Fe(OH)₃ reinforce concerns raised in the first quarter report regarding settle-decant operations for sludge. The first major issue is that hindered sedimentation with low (< 0.5 cm/hr) sedimentation velocities is apparent until solids loadings drop below 4 wt% (1 vol%). High levels of sediment dilution will be required in order to meet baseline goals of high sedimentation velocities. (Given reported water contents for actual tank sludges, dilution factors ranging from 2 to 25 are indicated.) Secondly, once settling is complete, most (95 vol%) of the volume of the sediment layer is occupied by interstitial water. For an efficient solid-liquid separations process such as washing or leaching, a desired target might be to have 90% of the total fluids present as removable supernatant liquids and 10% be present as interstitial liquids. Given the poor packing of the sediment, meeting the above target would mean that the total solids loading in the tank would have to be less than approximately 0.5 vol%. In any case, it appears that as many as 200 volumes of liquid per volume of dry sludge will be required to process sludges in proposed washing and leaching operations.

A final concern for settle-decant operations involves particles that do not settle and that are removed with supernatant liquids. In our sedimentation experiments, the fraction of material present in solution as "fines" can be estimated on a qualitative basis by noting the degree of light scattering observed by shining a laser through the supernatant liquids. In general, the supernatant liquids remaining above the sharp sediment boundary seen in concentrated suspensions are almost completely clear, indicating that few fines are present. However, as the initial slurry concentration decreases, the fraction of material that remains in supernatant liquids as fines increases until essentially all of the material added to the suspension stays suspended at short times and leads to highly turbid, colored supernatant liquids (Figure 7.19). As stated above, sedimentation does occur in the dilute suspensions. In some instances, a discrete boundary is eventually observed between the lightly colored zone containing suspended particles and a clearer zone of supernatant liquid above this colored layer. However, sedimentation velocities associated with the colored layer are slow. Even after sedimentation is complete, a significant fraction of fines remains in suspension.

To date, quantitative values for the fraction of material remaining in the fines have been obtained for the most dilute suspensions containing the maximum fraction of fines. Analyses involve removing

samples of the supernatant liquids, acidifying the samples to completely dissolve the $\text{Fe}(\text{OH})_3$, and determining solution concentrations using UV-visible spectroscopy. Results (Figure 7.23) indicate that the fraction of material remaining in suspension as fines decreases as a function of time as slow sedimentation occurs. For the $\text{Fe}(\text{OH})_3$ system, it appears that the fraction of material remaining in the "clear" zone at the top of the column after 1 day of sedimentation is 10^{-3} wt% (2% of the initial solids in the 0.05 wt% suspension remains suspended). [Concentrations in the "yellow" zone in the middle of the supernatant liquid (top point, 30 hr) are 2.5 times higher.] Further clarification occurs over periods of up to a week. The above analysis was performed on samples diluted with water (square data points) and represents a "worst case" scenario; however, similar trends are seen in samples diluted with 1 M NaNO_3 (circle data points).

The above "fines" analysis is important to tank processing and to current TWRS testing programs for several reasons. First, ever since TEM images were obtained showing that most of the primary particles in sludge are of submicron dimensions, concerns had been raised regarding the extent to which nonsedimenting fines might be present. Fortunately, under the highly agglomerating conditions found in the high pH, high-salt-content regime expected for sludge processing and examined to date, the population of fines appears to be low. However, the presence of organics can inhibit agglomeration even in basic salt solutions, as will be discussed in subsequent reports. Secondly, the fraction of solids expected in supernatant liquids is low, at least for the case of aged $\text{Fe}(\text{OH})_3$ that contains "hard"

Figure 7.23. Percent Unsettled $\text{Fe}(\text{OH})_3$ vs. Time (Total Solid Loading = 0.05 wt%, pH = 12)

agglomerates. However, although a solids loading in the supernatant liquid of 10^{-3} wt% seems negligible, the filtration studies described below demonstrate that this loading is actually quite significant.

The final set of sedimentation experiments performed this quarter involve the four- and five-component simulants for Tank C-103 sludge. The results for the C-103 simulants are in qualitative agreement with results obtained for $\text{Fe}(\text{OH})_3$. Sedimentation rates vs. solids loadings for samples diluted with water (Figure 7.24) show that at 8 wt % (approximately 3 vol%), the slurry represents the "hindered" settling regime with an initial sedimentation velocity of less than 0.5 cm/hr. The "instability" regime where collapse of the sediment leads to an "S-shaped" sedimentation curve is not observed. If present, this regime probably occurs between 8 wt% and 4 wt%. The maximum initial sedimentation velocity of 16 cm/hr measured (for 1 wt%) is nearly equal to the value measured for a 1 wt% $\text{Fe}(\text{OH})_3$ suspension (14.5 cm/hr), and slightly greater than the 10 cm/hr estimate for an $\text{Fe}(\text{OH})_3$ slurry having the same vol% solids. Final sediment densities of 13 wt% (4 vol%) are over twice as high as the 1.5 vol% seen for $\text{Fe}(\text{OH})_3$ alone. The higher solids loading is probably a consequence of the fact that the C-103 simulant contains a mixture of primary particle sizes that can pack more effectively than the $1.6\text{-}\mu\text{m}$ hard agglomerates in $\text{Fe}(\text{OH})_3$.

It is interesting to note that the shape of the curve for initial sedimentation velocity vs. initial solids loading for the four-component system (Figure 7.25) exhibits exactly the same shape calculated (as shown in the first quarterly) for hindered settling of noninteracting spheres. The only difference between the real system and the hard sphere model appears to be the scale of the volume axis. While sedimentation rates drop to 10% of the free-fall value at 30 vol% in the hard sphere case, a similar decrease in velocity is attained by approximately 4 vol% for the C-103 simulant. It appears that, once again, the difference between the hard sphere and the agglomerate case can be rationalized on the basis of the fractal nature of the agglomerates. It may be that many of the hard sphere models developed early in the program have direct applicability to actual sludges if the primary particle sizes, agglomerate sizes, and fractal dimensions can be determined.

Figure 7.24. Sedimentation of C-103 Simulant

Figure 7.25. Sedimentation Rate vs. Initial Solids Loading C-103 Simulant

A final observation of interest with regard to C-103 simulant involves a comparison of the behavior of fines with and without the presence of the calcium phosphate mineral apatite. In the absence of apatite, fines are present in supernatant liquids after sedimentation, especially in the more dilute suspensions. The fines are still present after 1 month of settling, indicating that the particles do not settle. TEM analysis of the supernatant liquid indicates that most of the fines are present in the form of colloidal silica. The observation of interest is that in suspensions containing apatite, the supernatant liquids are clear. No light scattering is observed in supernatant liquids after only a few days of settling, even for the most dilute suspensions. The results suggest that apatite is capable of scavenging fines from basic supernatant liquids by a heterocoagulation process. Protons and hydroxide ions are not potential determining ions for apatite. Apparently, the surface charge on apatite is low enough, even at high pH, so that there is negligible electrostatic repulsion between apatite and other oxide and hydroxide particles present such as silica. Under certain conditions, it appears that heterocoagulation may provide a mechanism for minimizing the production of fines during sludge processing. In addition, the above result suggests that it may be possible to deliberately remove fines from supernatant liquids by addition of certain types of particles. Coagulation via particle addition may be preferable to adding conventional organic flocculating agents.

Filtration

For filtration, major issues of concern include 1) whether filtration media are capable of trapping fines, 2) the rate at which liquids can be processed through a filter, and 3) the extent to which trapped fines foul filtration media. In the previous quarter, pressure filtration studies on boehmite using filtration membranes with pore diameters of $0.2 \mu\text{m}$ suggested that, although a few fines can pass through the medium initially, no particles pass through the filter once a finite filter cake begins to build up on the membrane surface. Almost immediately, the porosity and permeability of the filter are

controlled by the pore structure of the filter cake. For the case of boehmite, consisting of 5×50 -nm primary particles, it was found that the filter cake can exhibit permeabilities as low as 10^{-21} m^2 . To put this low permeability in perspective, the permeability is equivalent to that expected for a 1-mm-thick filtration membrane that has pores approximately 0.5 nm in diameter. In terms of processing, if desired filtration rates involve a drop in liquid levels above the filtration membrane of 1 cm/hr, membranes could be fouled by a boehmite layer only $0.1 \text{ }\mu\text{m}$ thick. If the desire is to filter a column of water 1 m high, particle concentrations in the water column would have to be kept below $10^{-5} \text{ vol}\%$ to prevent fouling. The measured concentration of fines in $\text{Fe}(\text{OH})_3$ suspensions of $10^{-3} \text{ vol}\%$ exceeds this level by a factor of 100. Therefore, the boehmite results indicate that the submicron particles expected to be present in supernatant liquids might represent a significant fouling problem for filtration media.

The filtration studies conducted on boehmite could represent a worst case scenario with regard to filtration for several reasons, including 1) the submicron platelets of boehmite might exemplify the most difficult particle type to filter; 2) the pressures used in the pressure filtration study might compress the filter cake and produce artificially low permeabilities; and 3) the dead-end filter geometry used might accentuate aspects of filter cake properties not found using alternate filtration technologies such as cross-flow filtration. Experiments conducted this quarter address the first two points above by examining the filtration characteristics of a different particle type [$\text{Fe}(\text{OH})_3$] and by examining filtration as a function of pressure.

As reported in the first quarter, filter cake permeabilities have been determined by measuring the rate of fluid flow through a filter cake, measuring the thickness of the filter cake, and solving for the permeability using Darcy's Law:

$$dV/dt = KAP\eta L$$

where dV/dt is the filtration rate (volume/hr), K is the permeability, A is the surface area of the filter, P is the applied pressure, η is the solution viscosity, and L is the thickness of the filter cake. As stated last quarter, pressures as high as 6000 psi are used in the system to provide measurable filtration rates through the relatively impermeable filter cake.

Participants at the Solid-Liquid Separations seminar reported that, while fresh $\text{Fe}(\text{OH})_3$ suspensions clog filtration media, aged $\text{Fe}(\text{OH})_3$ suspensions are relatively easy to filter. The change in filtration behavior with aging may be related to the presence of the hard agglomerates such as the $1.6\text{-}\mu\text{m}$ particles observed in the current study. In any case, existing filtration beliefs suggest aged $\text{Fe}(\text{OH})_3$ should certainly be easier to filter than boehmite. Measured permeabilities support the industry experience. The permeabilities for $\text{Fe}(\text{OH})_3$ range from approximately $2 \times 10^{-19} \text{ m}^2$ to $2 \times 10^{-18} \text{ m}^2$, depending on solution pH (Figure 7.26) compared with values as low as 3×10^{-21} for filter cakes of dispersed boehmite. As for boehmite, permeabilities are highest for the most agglomerated systems (near the isoelectric point) and lowest for the most dispersed slurries. However, permeabilities are still so low that fouling of filtration media is likely. The maximum $\text{Fe}(\text{OH})_3$ permeability would result in a filtration rate of around 10^{-3} L/day through a 1-m^2 , 1-mm-thick filter cake when the pressure drop across the cake is 1 atmosphere. The equivalent pore diameter for the filter cake is calculated to be approximately 10 nm, which is comparable to the primary particle size of the $\text{Fe}(\text{OH})_3$. Therefore, while $\text{Fe}(\text{OH})_3$ is easier to filter than boehmite, providing filter cakes that are as much as 1000 times more permeable, $\text{Fe}(\text{OH})_3$ is still capable of fouling filtration media. To achieve a desired filtration rate of 1 cm/hr (as described above for boehmite), filter cake thicknesses need to be kept below $1 \text{ }\mu\text{m}$.

Figure 7.26. Filter Cake Permeability for Pressure Filtration of $\text{Fe}(\text{OH})_3$ as a Function of pH

To filter a 1-m column of solution, $\text{Fe}(\text{OH})_3$ concentrations need to be kept below 10^{-4} vol%. Therefore, the concentration of fines seen in the $\text{Fe}(\text{OH})_3$ sedimentation experiments of 10^{-3} wt% could actually be significant in terms of subsequent filtration.

As stated above, while high pressures are needed to measure the permeabilities of impermeable filter cakes, the pressure can cause rearrangement of the filter cake, changing its porosity and biasing the results. To check this possibility, permeability measurements have been made on 1 vol% boehmite (1 M NaNO_3 , pH 12) suspensions as a function of applied pressure. Filter cake thicknesses were also measured to obtain appropriate estimates for the permeability. The filter cake thickness decreases with increasing pressure (Figure 7.27), indicating that the applied pressures are indeed sufficient to compress and densify the filter cake. Permeabilities for boehmite filter cakes (calculated using the measured solids fractions for the cake) show that, as the solids loading increases, the porosity of the cake decreases, and the permeability also decreases (Figure 7.28). In lowering the pressure from over 5000 psi to 1000 psi (the lower limit for the current apparatus), the permeability increases from approximately $1 \times 10^{-18} \text{ m}^2$ to over $6 \times 10^{-18} \text{ m}^2$. Over the pressure range studied, the data can be fit using an empirical relationship of the form $K = K_0 P^x$, where $K_0 = 7.8 \times 10^{-14} \text{ m}^2$ and $x = -1.32$. Extrapolation of the empirical curve to pressures of 1 atmosphere might suggest that permeabilities as high as $7.8 \times 10^{-14} \text{ m}^2$ could be possible for boehmite. However, extrapolation of filter cake densities to low pressures (with the aid of centrifugation data) suggests that the minimum filter cake density expected during filtration is 9 vol%. Extrapolation of the permeability data to a filter cake density of

Figure 7.27. Solids Fraction in Cake with Pressure (1% boehmite, 1 M NaNO₃; calculated from cake height)

9 vol% suggests that the maximum permeability to be expected for boehmite is closer to $3 \times 10^{-17} \text{ m}^2$. This extrapolation will be checked next quarter using a new pressure filtration system capable of operating at lower pressuring than the existing unit. However, until further results are available, most suspensions containing submicron particles (either as primary particles or agglomerates) do not appear easy to filter.

7.2 Hot Colloids Laboratory

A Hot Colloids Laboratory is being established to provide a level of characterization for actual sludge samples that approaches the level currently attained in cold facilities. A plan has been developed for consolidating existing equipment that is dedicated to examining "hot" samples and supplementing the equipment with new instruments purchased.

Purchase requisitions have been prepared for most of the major new items planned for the Hot Colloids Laboratory. These items include particle size analyzers, surface charge measurement equipment, and a BET surface area analyzer. Components are being selected for the gamma or x-ray densitometer to be used in sedimentation studies. The above equipment will supplement equipment already in place, i.e., viscometers, an electrobalance system for quantifying sedimentation rates, a

Figure 7.28. Permeability vs. Pressure Drop (1% boehmite, 1 M NaNO₃, pH 12; calculated using measured solid fraction)

particle size analyzer, and a DCS/TGA and a tensiometer for analyzing organics. Raman facilities may also be incorporated for determining vibrational spectra of both organic and inorganic species.

7.3 Summary

Work has continued on studying the fundamental principles governing the nature of colloidal slurries relevant to sludge processing. The major conclusions to be drawn from work performed this quarter include:

- General conclusions inferred from studies of the viscosity, sedimentation, and filtration behavior of boehmite and gibbsite have been confirmed this quarter on studies involving Fe(OH)₃ and a multicomponent sludge simulant. The results reported last quarter describe general phenomena, and are not peculiarities associated with a specific particle type.
- In terms of a general understanding of sludge behavior, it appears that the concepts of fractal geometry as applied to agglomeration phenomena are of central importance. The fractal analysis indicates that properties such as viscosity, sedimentation, and distributions of particle types in fines can be predicted if we can determine primary particle size distributions, agglomerate distributions, and the fractal dimensions of the agglomerates. Several of the above

parameters are strongly influenced by both chemical and physical phenomena that include the interaction potential between the particles and fluid movement (shear forces and Brownian motion.)

- In terms of a direct analysis of processing conditions for the baseline process, the conclusion last quarter was that the presence of small primary particles could compromise many of the central baseline assumptions with regard to viscosities, sedimentation rates, and fines. This quarter, we can be more specific regarding the nature of the challenge. If low viscosity (< 100 cp) suspensions are desired that can yield rapid sedimentation velocities (> 3 cm/hr), existing tank solutions may represent the best possible processing environment because the high ionic strength of tank waste promotes agglomeration. However, even under ideal conditions, i.e., no organics), the desired viscosities and sedimentation rates can only be achieved if slurries are dilute enough to minimize contact between the agglomerates in the solution. Current indications are that the maximum solids loadings that can be tolerated are approximately 1 vol%. If much of the sludge consists of submicron particles, the dilution levels required, and the volumes of liquid waste that will be generated during processing will be significantly larger than the factors of 3 to 4 posed in the baseline process. A potential danger associated with extensive slurry dilution is that the required dilution levels will result in increased concentrations of nonsedimenting fines that will have to be removed downstream. Filtration results suggest that such fines will tend to clog most filtration media.

7.4 Focus for Next Quarter

In the next quarter, we will focus on an increased understanding of agglomeration, which is central to all solid-liquid separation processes. We will also begin to explore processing options (such as the addition of particles to scavenge fines) to either improve or offer options to current baseline processing schemes. Examinations of actual waste samples will also begin.

7.5 Reference

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J. N. Appel
H. Babad
G. R. Bloom
A. L. Boldt
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56 **Pacific Northwest Laboratory**

G. S. Anderson
E. G. Baker
D.L. Blanchard
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J. L. Cox
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A. R. Felmy
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E. A. Jenne
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M. M. Lamoureux
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