

Pacific Northwest National Laboratory

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Retrieval Process Development and Enhancements Project Fiscal year 1995 Simulant Development Technology Task Progress Report

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Prepared for the U. S. Department of Energy
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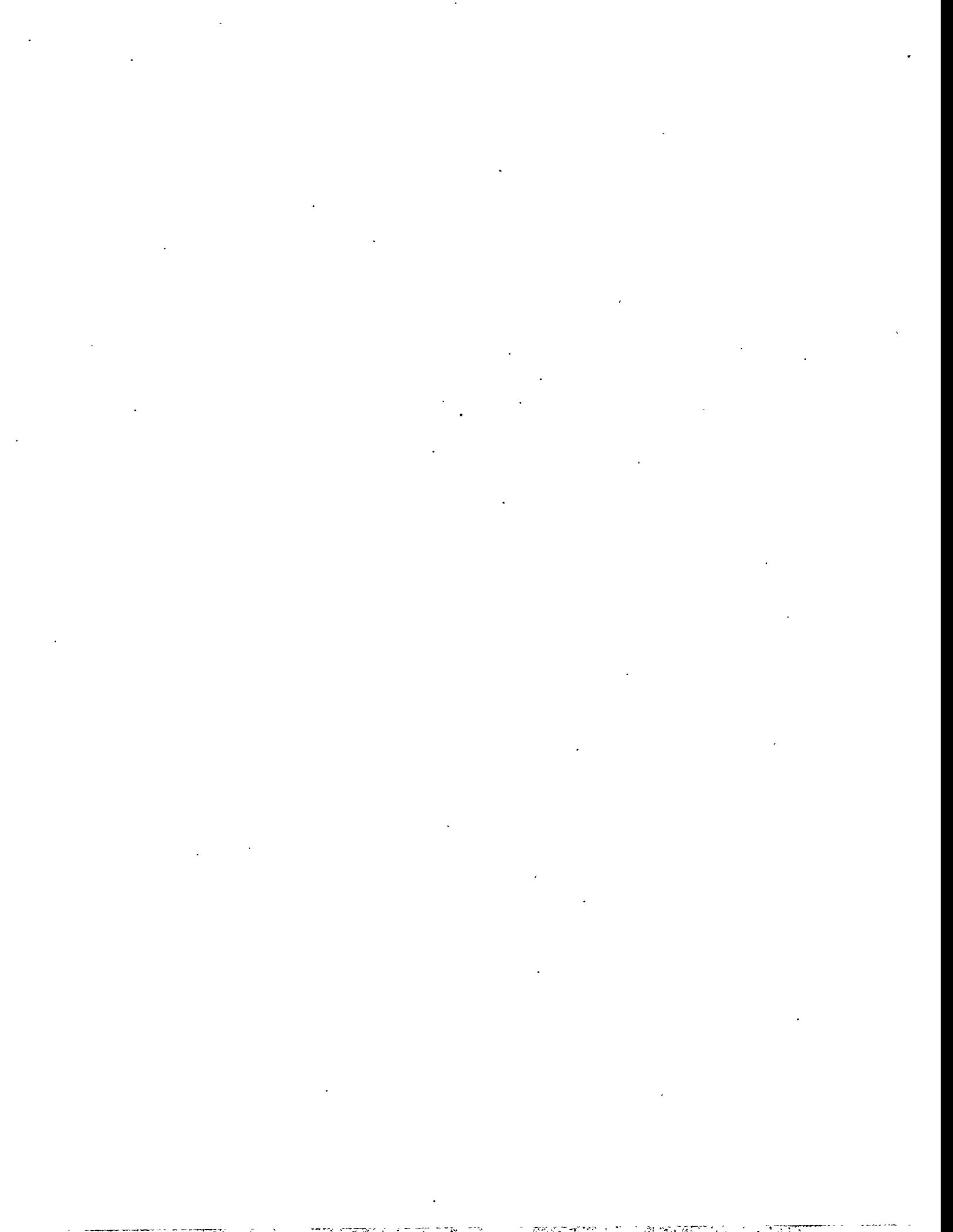
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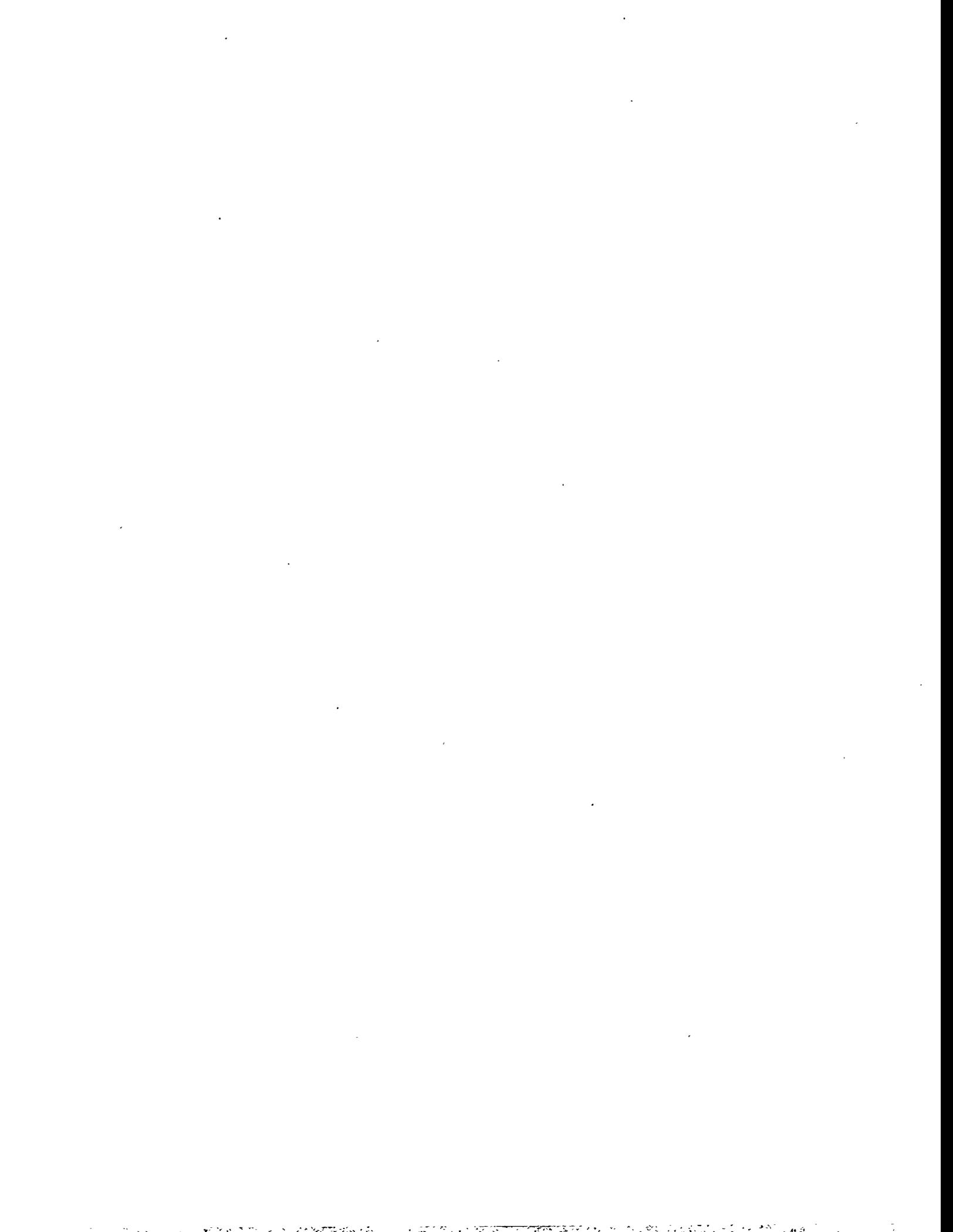
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Summary

The mission of the Retrieval Process Development and Enhancements (RPD&E) project is to develop an understanding of retrieval processes, including emerging and existing technologies, gather data on these technologies, and relate the data to specific tank problems such that end-users have the requisite technical bases to make retrieval and closure decisions. The development of waste simulants is an integral part of this effort. The work of the RPD&E simulant-development task is described in this document. The key FY95 accomplishments of the RPD&E simulant-development task are summarized below.

Development of Saltcake Simulants of Various Porous Media

A number of properties were examined to provide information regarding the correlation between mechanical strength and material structure of the baseline saltcake simulants. This investigation was conducted to obtain a better understanding of the large-scale production of saltcake simulant. The FY95 results of this work are shown in Table S.1.

In general, potassium magnesium sulfate (simulated saltcake) forms a cement-like material via a hydration reaction. Addition of different amounts of water (10 wt% to 30 wt%) changes not only the quantity of reacted starting material but also the material-packing density, which directly affects the pore diameter. The conclusions from this study are as follows:

- Water content controls the quantity of salt reacted in hydration reactions but not the degree of hydration reaction. These results have been confirmed by x-ray diffraction study and thermal analysis.
- Compressive strength of the saltcake simulant varies with water content due to the effect of water content on simulant porosity. During the formation of simulated saltcake, partial dissolution of the starting material affects the particle size and shape, which results in significant changes in porosity, pore diameter, and mechanical strength.
- Beyond a water content of about 14 to 16 wt%, even though the total reacted water content is not changing according to the thermal analysis, the compressive strength decreases because the porosity gradually increases while the pore size remains relatively unchanged.

Progress in GAAT-TS Sludge Simulant Development for RPD&E Testing

A preliminary qualitative assessment of the physical properties of GAAT tank sludge was made based on the videotaped extrusion and testing of samples W07H302 through W07H304 from tank W-7. Two qualitatively different types of sludge were visible in these samples. In the lower regions of the tank, apparently there was a brown, cohesive sludge. Above the brown sludge was a yellow/orange sludge layer with noticeably different physical properties. Relevant physical and rheological data are not currently available for these wastes; thus, simulated ORNL wastes cannot be developed based on quantitative waste property data. Rheological measurements are needed to help develop simulants to support the development of mining path and end-effector orientation strategies. Also, operational

Table S.1. Material Structure and Mechanical Strength of Simulated Saltcake

Water Composition (Wt%)	Apparent Density (g/ml)	Bulk Density (g/ml)	Porosity (%)	Compressive Strength
10	2.51	2.08	17.2	1420
12	2.40	1.94	18.9	2620
14	2.48	2.22	10.5	4140
16	2.61	2.25	13.7	2750
18	2.57	2.19	14.8	2190
20	2.44	2.27	6.8	2220
25	2.92	2.56	12.5	1840
30	2.42	2.33	4.0	1720

problems could be encountered during final tank cleaning when the jets have reached the tank floor. Accurate waste simulants are needed to improve our understanding of these potential problems.

A range of sludge simulants of varying rheological properties was developed. The objective of the

The simulant/waste property that determines dilute-phase pneumatic-transport behavior is principally particle-settling velocity, which is a function of particle size, shape, and density. It is expected that these same waste properties also affect jet-pump conveyance, but comparatively little literature data are available to verify this. The simulants recommended for developing conveyance rate and power requirement data are sand (nominal particle size of 0.2 mm), pea gravel (5 to 10 mm), crushed rock (20 to 30 mm), and crushed potassium-magnesium sulfate fertilizer (also known as "K-Mag") saltcake simulant in a size range consistent with the planned scarifier operation (approximately 1 to 2 cm).

Plugging of the conveyance line represents a credible threat to the selection of either pneumatic- or jet-pump-conveyance systems. If it can be shown, however, that either or both types of conveyance system is (or are) capable of transporting very adhesive/cohesive simulants, then there is confidence that waste will be conveyed successfully. Several types of sludge simulants were selected with the goal of the simulants being at least as likely to plug the conveyance lines as the waste sludge. Only sludge simulants are specified because it is expected that saltcake conveyance is less challenging than sludge conveyance, with respect to line plugging. The sludge simulants developed for this purpose include water-based mixtures of kaolin clay (67 wt% solids), bentonite clay (30 to 35 wt% solids), and a bentonite/kaolin mixture (2.6 wt% bentonite, 61.4 wt% kaolin). It is also recommended that the conveyance of densely packed silica powder (5 to 30 micron) and water mixtures be tested. The silica particles are not adhesive like the clay particles, but silica in this size range tends to form tightly packed cakes, which effectively resist applied mechanical force. Depending on the conveyance line operating conditions, the silica particles may form these dense cakes near bends or in horizontal sections of the conveyance line, thereby restricting the flow.

Consideration was also given to the vulnerability of these conveyance systems (particularly pneumatic conveyance) to erosion by impinging particulate. It is recommended that the K-Mag saltcake simulant be used to provide a preliminary indication of whether or not a full-scale conveyance system would be vulnerable to erosion.

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Nomenclature

A	average specific surface area of particulate
CSEE	confined sluicing end effector
DOE	U.S. Department of Energy
DQO	data quality objective
DTA	differential thermal analysis
EM-50	US Department of Energy Office of Environmental Management - 50
FY95	fiscal year 1995
GAAT	gunitite and associated tanks
G'	viscoelastic storage modulus
G''	viscoelastic loss modulus
G^*	viscoelastic complex modulus
K-Mag	potassium magnesium sulfate fertilizer, used as a saltcake simulant
INEL	Idaho National Engineering Laboratory
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
RPD&E	Retrieval Process Development and Enhancements
TGA	thermogravimetric analysis
TWRS	Tank Waste Remediation System
x	weight fraction
γ	applied strain
γ_0	applied strain amplitude
δ	viscoelastic loss tangent
τ	shear stress

τ_0 stress response
 ω oscillation frequency

1.0 Introduction

The Retrieval Process Development and Enhancements (RPD&E) project, funded by the U.S. Department of Energy Office of Environmental Management (EM-50) through the Tank Focus Area at the Pacific Northwest National Laboratory,^(a) is developing the retrieval processes and technologies necessary for the dislodging, mobilization, and conveyance of radioactive waste stored in underground tanks across the U.S. Department of Energy (DOE) complex. The mission of the RPD&E project is to develop an understanding of retrieval processes, including emerging and existing technologies, gather data on these technologies, and relate the data to specific tank problems such that end-users have the requisite technical bases to make retrieval and closure decisions. Evaluation of RPD&E technologies includes comparisons between waste types and a determination of the sensitivity of candidate technologies to waste properties, as well as evaluations of the applicability of various processes to tank wastes at DOE sites. Due to the hazards and expense of testing RPD&E processes using actual waste, nonhazardous waste simulants are being used. The principal responsibility of the simulant-development task is to develop, qualify, and provide tank waste simulant specifications for use by the RPD&E testing tasks. The simulant-development task assists all of the RPD&E testing tasks by ensuring that appropriately designed waste simulants are used for RPD&E testing.

Many of the physical properties of waste that are important for the development and demonstration of retrieval technologies have not been well measured on waste samples. Fortunately, it is not necessary to develop a simulant that mimics all of the properties of radioactive waste. The development of waste simulants appropriate for the testing of a given process should reflect the specific influence of the waste properties on the process performance. The methodology used to develop simulants focuses on understanding the mechanism of removal and transport for the retrieval technologies being developed. The methodology also includes examining the relation of microscopic factors that affect the macroscopic characteristics of the waste which influence the retrieval-process performance. The goal is to define the key physical and rheological properties that determine the performance of the retrieval technologies being tested. Once the key properties are identified, a range of waste simulants will be available that encompasses the relevant actual waste characteristics (where these data are available).

This report documents the fiscal year 1995 (FY95) technical progress of the RPD&E simulant-development task. The testing and analyses described in this report were performed to understand the effects of and relationships between the selected simulant microscopic properties and the mechanism of brittle failure in saltcake simulants and the rheological properties of concentrated sludge simulants that control waterjet-cutting and conveyance-transport applications. These data will be used to develop a range of saltcake simulants with various shearing and crack-propagation characteristics, as determined by their microstructural grain size and porosity variations. The data also help to develop a range of concentrated sludge simulants of varying cohesiveness, which can be used for the testing of waterjet-based retrieval methods as well as pneumatic- and waterjet-based waste-conveyance methods.

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2.0 Simulant Development Methodology

In FY94, a comprehensive, integrated simulant development strategy was developed for the testing of retrieval and transport technologies.^(a) The strategy describes the methodology used to design and develop waste simulants for the testing of retrieval technologies. The strategy also addresses how these simulants are validated through their interdependencies with waste-characterization activities. This methodology is presented as a logic diagram in Figure 2.1. A critical path based on the most probable outcome of prior steps is outlined. The decision points and rationale for making these conclusions are included as part of the methodology.

Currently, nonhazardous waste simulants are being used to develop and demonstrate waterjet-based waste dislodging, pneumatic conveyance, and jet-pump conveyance technologies because of the hazards and expense of testing these technologies using actual waste. For such tests, the applicability of the data generated to tank waste retrieval depends largely on the capability of the simulants to model the specific types of chemical and/or physical behavior of actual waste. Therefore, it is essential that scientifically defensible and accurate waste simulants be used during testing. It is not practical to develop simulants that duplicate all of the physical and rheological properties that influence each of the steps in the retrieval process. Simulated wastes need to be developed to cover only the expected range of the relevant physical, rheological, and/or chemical properties.

The goal is to develop simulants that bound the specific governing waste properties which influence the performance of critical steps for a particular technology. As waste is retrieved from tanks and transported to treatment facilities, it may undergo changes in phase and will be subjected to various types of force and energy. As fluid jets impinge on sludge, for example, the force of the jet will overcome the attractive forces that give the sludge its strength. The resulting suspension of solids will develop some degree of homogeneity and some solids may settle out. These phenomena depend on the relationship between the physical properties of the waste and the microscopic and macroscopic forces acting on the waste.

The development of simulants must address the specific influence an applied force will have on the waste. Similarly, simulant properties must present the appropriate range of "resistances" to the retrieval and transport systems. The methodology presented here focuses on identifying the critical waste properties that influence the performance of the retrieval system, and then on determining the range of these properties expected in the actual waste.

The methodology used to design and develop waste simulants that are appropriate for the testing of retrieval technologies and to show their interdependencies with characterization activities are presented in Figure 2.1. In this figure, a critical path is outlined that is based on the most probable

^(a) Golcar, GR, and MR Powell. 1994. *Strategy for Development of Accurate Simulants for Waste Retrieval and Transport Testing*. DSTRTP-CY94-004. Letter Report prepared for the U.S. Department of Energy by Pacific Northwest Laboratory, Richland, Washington.

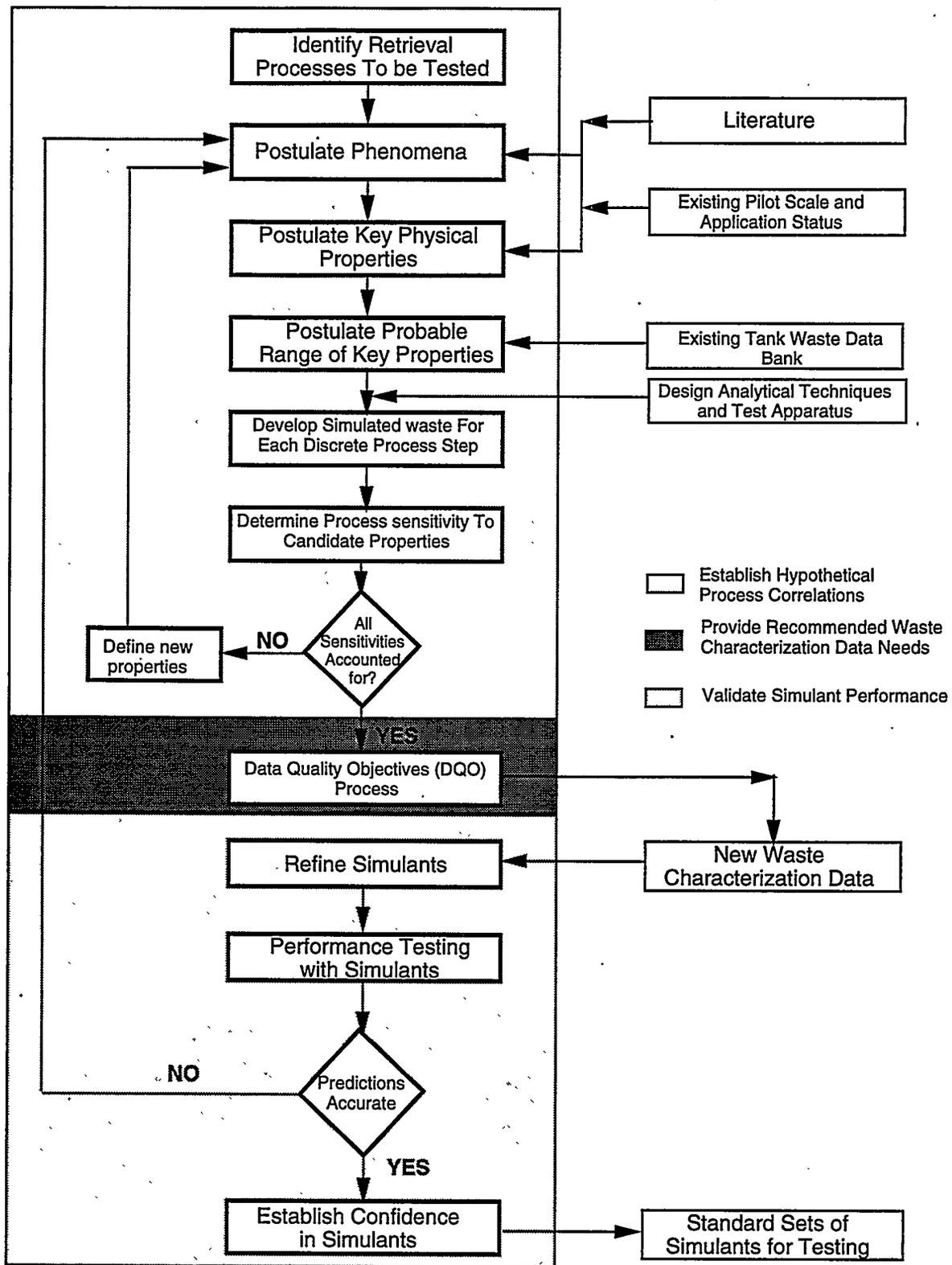


Figure 2.1. Simulant Development Strategy Logic Diagram

outcome of the prior steps. The decision points and rationale for making the decisions are included as part of this strategy. The simulant development strategy in Figure 2.1 consists of three sections:

- (1) Establish hypothetical process correlations. Many of the physical properties of wastes that are important for the development and demonstration of the retrieval technologies have not been well characterized. In addition, it is not necessary to use a simulant that mimics the full range of properties of a radioactive waste. Waste simulants appropriate for the testing of a discrete process only have to reflect the specific influence of the relevant waste properties on the process performance. The most logical way to design simulants with the appropriate range of resistances is to determine the effect of waste properties on process performance and to correlate important process-performance parameters with key waste properties.
- (2) Provide recommended waste characterization data needs. Once the process performance is correlated with key physical properties (in other words, once the process sensitivity is determined), the characterization data needs and the required measurement accuracy are communicated to the waste characterization laboratories through the Data Quality Objectives (DQO) process.
- (3) Validate simulant performance. To establish confidence in the simulant performance, data for the governing waste properties need to be provided. Once the data for the key waste properties have been provided or once a retrieval process is applied to actual waste, simulant performance can be validated.

3.0 Simulant Development for Hydraulic Dislodging

A large part of the FY95 simulant-development effort was focused on the development of sludge and saltcake simulants to support the development of waste-dislodging methods that use waterjets to break up the waste. The development of simulants to support the development of these hydraulic waste-dislodging methods is described in this section.

3.1 Sludge Waste and Sludge Simulants for ORNL

The scope of sludge-simulant development during FY95 includes the development of simulants for the sludge waste stored in Gunitite™ tanks at Oak Ridge National Laboratory (ORNL). These simulants will be used to support the testing of a lightweight confined sluicing end effector (CSEE), which is currently under development at the University of Missouri-Rolla. A preliminary assessment of the physical properties of GAAT tank sludge was made based on the videotaped extrusion and testing of samples W07H302 through W07H304 from tank W-7. Two qualitatively different types of sludge are visible in these samples. In the lower regions of the tank, there apparently is a brown, cohesive sludge. Above the brown sludge is a yellow/orange layer of sludge with noticeably different physical properties.

As is seen in the videotape, the brown sludge layer appears saturated with liquid (i.e., no gaseous voids within the sludge). The sludge sticks to the technician's spatula initially, but becomes more fluid after stirring. It is inferred from this that a portion of the mechanical strength of this sludge is due to the presence of interstitial salt crystals and/or bonding of adjacent sludge particles at their contact points. When sufficient strain is applied to the sludge, these bonds and salt crystals are broken and they do not reform quickly. This behavior is contrasted with that of a pure clay, which very rapidly regains nearly all its initial strength after mixing is stopped. The fact that the brown sludge underwent a plastic deformation in response to applied strain, however, implies that at least a portion of the sludge strength can be attributed to interparticle attractive forces and/or interparticle friction. It is concluded, then, that the strength of the brown sludge layer is probably due to a combination of interparticle attractive and frictional forces along with interparticle bonding and/or interstitial salt crystal formation.

The particle-settling test conducted on sample W07H302 provides some indication of the particle size of the brown sludge. After 159 hours of settling, the slurry had settled to form a loosely packed particulate bed, which poured easily from the sample tube after the supernate was withdrawn. This would be expected from a slurry with particles smaller than about 5 microns. Particles much larger than 5 microns tend to settle into much denser beds, which will not easily pour after extended settling times. This difference in behavior results from the effects of interparticle attractive forces on the smaller particles. This is not to say that all the sludge particles are smaller than 5 microns, but it does appear that the majority of the sludge particles are smaller than 5 microns. This is consistent with the observed plastic deformation of the brown sludge. Particles in this size range (typically less than 1 or 2 microns) are required for interparticle attractive forces to become significant.

The upper, yellow/orange sludge layer was observed to crack and fracture when it was extruded into the collection beaker. This contrasts with the brown sludge, which underwent more of a plastic deformation. The brittle behavior of the yellow/orange sludge is characteristic of sludges where the mechanical properties are determined almost entirely by interparticle bonding and interstitial salt crystal

formation. The fracturing of the yellow/orange sludge is very similar to that observed from sludge simulants prepared from a mixture of kaolin clay, water, and plaster of paris. The kaolin clay provides a small amount of strength from cohesive and frictional effects, but the majority of the strength of this simulant comes from the interstitial crystals of hydrated calcium sulfate that form as the plaster of paris cures. The fact that the yellow/orange sludge becomes smooth and creamy when it is stirred is also consistent with the idea that interparticle bonds and interstitial salt crystals are present. It is very difficult to estimate sludge mechanical strength from the data contained in the video. Only order-of-magnitude estimates are possible. Based on the qualitative indications of strength shown in the video and on PNNL's previous experience with sludge simulants, it is estimated that the shear strength of the brown sludge is on the order of 25 kdyn/cm² and that of the yellow/orange sludge is on the order of 100 kdyn/cm². Rheological measurements are required to improve these rough estimates.

Relevant physical and rheological characterization data are not currently available for the waste at ORNL; thus, simulated ORNL wastes cannot be developed based on quantitative waste property data. Rheological measurements are needed to help develop simulants needed for the development of mining path and end-effector orientation strategies. Operational problems could arise during final tank cleaning when the jets have reached the tank floor. In the following sections, the mechanism of sludge-waste erosion and experimental measurements to design sludge-waste simulants of known rheological properties are discussed.

3.1.1 Erosion of Concentrated Sediments by Waterjets

Concentrated sediments such as sludge are composed of fine solid grains surrounded by water or salt solution. Erosion of these sediments by an impinging waterjet is described by the erodability of the sediment and its critical shear stress. The critical shear stress is the minimum applied stress at which erosion occurs. At stresses below the critical shear stress, no significant erosion takes place. Erodability describes the rate at which erosion takes place when the applied stress exceeds the critical shear stress. The magnitude of the erodability is a function of the applied stress, while the critical shear stress is a function only of the sediment properties. Although these two parameters describe erosion reasonably well in macroscopic terms, the fundamental mechanism of sediment and sludge erosion is not well understood.

Deployment of the high-pressure waterjet and medium-pressure CSEE is being investigated as a potential means for the removal of concentrated sludge sediments stored in underground-storage tanks. One of the key aspects of developing waste simulants is the investigation of the erosion mechanisms involved in hydraulic-cutting processes. To understand the erosion mechanisms better, several types of sludge simulants have been formulated to exhibit a wide range of mechanical strengths and cohesiveness.

3.1.2 Rheological Properties

Often, the rheological behavior of sludge sediments cannot be characterized adequately by conventional rheological properties such as yield stress, viscosity, thixotropy, or pseudoplasticity. A sludge sample will deform permanently if the magnitude of an applied stress exceeds the sludge yield strength point. When an applied stress is removed, an ideal viscous material will remain fully deformed and an ideal elastic material will return to its initial shape (assuming the applied strain is small). However, viscoelastic materials behave neither as perfectly elastic solids nor as perfectly viscous liquids. For viscoelastic materials, the stress may depend upon the strain and the rate of strain together, as well as

higher derivatives of the strain. Such time anomalies reflect a combination of solid-like and liquid-like behaviors.

Viscoelastic properties of materials are determined by several experimental approaches, including periodic or dynamic loading. The strain-sweep and the frequency-sweep techniques are the most common experimental procedures. Viscoelastic properties determined by periodic loading patterns are characterized by the storage modulus (G'), the loss modulus (G''), the complex modulus (G^*), and the loss tangent (δ).

The storage modulus G' (in units of Pa) is a measure of the energy stored and recovered per cycle of applied strain. It is defined as the stress in phase with the strain (in a sinusoidal deformation) divided by the strain. In other words, the storage modulus is a measure of the elastic or solid-like property of a sample that is related to its cohesion.

The loss modulus G'' (in units of Pa) is a measure of the energy dissipated or lost as heat per cycle of sinusoidal deformation. It is defined as the stress 90° out of phase with the strain (in a sinusoidal deformation) divided by the strain. The loss modulus is a measure of the viscous or liquid-like property of the sample.

The complex modulus G^* (also in units of Pa) is the vector sum of the storage modulus (G') and the loss modulus (G'').

The loss tangent, which is dimensionless, is a measure of the ratio of the energy lost to the energy stored in a periodic deformation; it quantifies the relative importance of the elastic and viscous characteristics of a sample. When the loss tangent is much greater than 1.0, for example, the sample is more viscous than elastic. When the loss tangent is much less than 1.0, the sample is more elastic than viscous.

3.1.3 Experimental

The objective of the experimental measurements was to examine the changes in the rheological properties of simulants for materials of (1) the same shear strength but varying specific surface area; (2) the same specific surface area but varying shear strength; and (3) the same shear strength but differing pH and ionic strength. The importance of this study is that it could provide information to help develop a wide variety of simulants of varying rheological properties to support CSEE development testing. In this study, two simulant materials (kaolin and bentonite) were chosen, primarily due to the large differences in their viscoelastic properties. Bentonite clay, for example, behaves like a typical Bingham-plastic material, whereas kaolin possesses a combination of elastic and viscous characteristics. The viscoelastic properties of the two materials are strongly dependent upon the water content of the clays. In addition, the specific surface areas of the clays are different; for example, bentonite clay has a specific surface area as high as 800 m²/g, while the kaolin clay surface area is only about 10 m²/g (Lambe and Whitman 1969). Therefore, adding bentonite to kaolin and adjusting the water content yields materials with a wide range of intermediate viscoelastic properties. In addition, these materials are classified as nonregulated and can be used in large-scale testing with minimal waste-disposal concerns. A knowledge of the characteristics of these materials already exists in the literature. The relevant literature has been reviewed and used to design the experimental work described below.

Three types of concentrated sludge simulants (bentonite/water, kaolin/water, and kaolin/bentonite/water) were prepared for these measurements. The measurements made on each of these simulants are discussed below.

Bentonite/Water Mixture

Bentonite clay simulants were prepared by varying the bentonite concentration (20 to 60 wt%), pH, and ionic strength. Changing the bentonite concentration (wt% solids) resulted in sludge simulants with different shear strengths, which were measured and tabulated in previous studies (Powell et al. 1995). At two bentonite loadings (15 and 35 wt% bentonite), the pH was varied from an acidic to a basic solution using hydrochloric acid and sodium hydroxide to investigate the effect of pH on surface charge and the resultant particle interactions, which influence the rheological properties. Similar experiments were carried out in which pH was held constant, but the ionic strength of the interstitial fluid was varied by adding sodium chloride. These tests were conducted at the same two bentonite loadings (15 and 35 wt%).

Kaolin/Water and Kaolin/Bentonite/Water Mixtures

Simulants were prepared from mixtures of kaolin and bentonite clays. The bentonite concentration ranged from 0 to 5 wt% of the dry solids (with the balance being dry kaolin). Increasing the bentonite concentration yielded materials of increasing average specific surface area. The effective average specific surface area of the bentonite/kaolin mixture was computed by a weighted average of the specific surface areas of pure bentonite (about 800 m²/g) and kaolin (10 m²/g) using the following equation:

$$A \text{ (m}^2\text{/g)} = 800x + 10(1 - x) \quad (3.1)$$

where x is the weight fraction of bentonite in the bentonite/kaolin mixture. Note that the specific surface area of kaolin is reported to be on the order of 10 to 20 m²/g (Lambe and Whitman 1969), but in equation 3.1 the specific surface area of kaolin is assumed to be 10 m²/g. In all samples, the solids content was varied to prepare materials of three different shear strengths (10, 30, and 60 kdyn/cm²). The amount of water to be added to the dry clay powders was determined from previously gathered shear strength versus solids loading data (Powell et al. 1995).

All simulant samples were prepared by adding weighed amounts of bentonite, kaolin, and deionized water to a mixer and mixing thoroughly for 10 minutes to ensure the uniformity of the sample. Before rheological property measurements were made, the samples were stored in screw-top containers to prevent water evaporation. Listed in Tables 3.1, 3.2, and 3.3 are the respective amounts of kaolin, bentonite and water used to prepare simulants of 10, 30, and 60 kdyn/cm² shear strength, respectively.

Table 3.1. Sludge Simulant Compositions for 10 kdyn/cm² Shear Strength

Computed Surface Area (m ² /g)	Simulant Composition			Relative wt% of Bentonite in the Mixture
	Kaolin (wt%)	Bentonite (wt%)	Water (wt%)	
10.0	60.00	-	40.00	0.0
14.0	58.93	0.30	40.77	0.5
21.9	56.87	0.87	42.26	1.5
29.8	54.91	1.41	43.68	2.5
37.7	53.05	1.92	45.03	3.5
45.6	51.27	2.42	46.31	4.5

Table 3.2. Sludge Simulant Compositions for 30 kdyn/cm² Shear Strength

Computed Surface Area (m ² /g)	Simulant Composition			Relative wt% of Bentonite in the Mixture
	Kaolin (wt%)	Bentonite (wt%)	Water (wt%)	
10.0	66.50	-	33.50	0.0
14.0	65.53	0.33	34.14	0.5
21.9	63.64	0.97	35.40	1.5
29.8	61.82	1.59	36.60	2.5
37.7	60.06	2.18	37.76	3.5
45.6	58.37	2.75	38.88	4.5

Table 3.3. Sludge Simulant Compositions for 60 kdyn/cm² Shear Strength

Computed Surface Area (m ² /g)	Simulant Composition			Relative wt% of Bentonite in the Mixture
	Kaolin (wt%)	Bentonite (wt%)	Water (wt%)	
10.0	68.00	-	32.00	0.0
14.0	67.25	0.34	32.41	0.5
21.9	65.79	1.00	33.21	1.5
29.8	64.36	1.65	33.99	2.5
37.7	62.96	2.28	34.76	3.5
45.6	61.59	2.90	35.51	4.5

3.1.4 Experimental Apparatus

Strain-sweep and frequency-sweep measurements on the bentonite/water simulants were conducted using a Bohlin VOR Rheometer (Bohlin Instruments) and a CP5/30 cone-and-plate system. The viscoelastic property measurements of the kaolin/bentonite/water simulants were made using two different types of Bohlin VOR Rheometer. The first rheometer, with a torque range of 0.12 to 300 g-cm, was used to measure the viscoelastic properties of samples with yield strength of 10 kdyn/cm² (samples in Table 3.1), while the second rheometer, with a torque range of 300 to 2000 g-cm, was used for the samples with yield strengths of 30 and 60 kdyn/cm² (samples in Tables 3.2 and 3.3). The first rheometer was provided with a water-cooling system, which maintained a constant temperature at 25±2°C. The second rheometer was provided with an air-cooling mechanism, which maintained the temperature between 25° and 30°C. Potentially, there are some temperature effects on the measurement of viscoelastic properties but these were not examined in the present study. For simulant samples in Tables 3.2 and 3.3, the normal stress component was found to be significant. Also, it was observed that the normal stress decreases with time; because of this, no normal stress compensation has been applied. The effect of this on viscoelastic properties was not examined in the present study but should be examined in future.

In the current study, the viscoelastic properties of materials were determined by the strain-sweep analysis. The strain is varied sinusoidally at a set frequency (ω , radian) and the reaction of the sample to the strain is measured. When the strain (γ) is varied sinusoidally, the reaction of the sample expresses itself with a shear stress (τ) and a phase-displacement angle (δ) between the applied deformation and the observed reaction of the sample. In strain-sweep analysis, τ and δ are measured as a function of the applied strain γ , which is varied sinusoidally with an increasing amplitude at a single frequency. From the amplitudes of the strain (γ_0), stress response (τ_0), and the phase shift or displacement (δ), the viscoelastic properties of the sample can be computed using the following relationships:

$$G^* = \frac{|\tau_0|}{|\gamma_0|} \quad (3.2)$$

$$G' = G^* \cos \delta \quad (3.3)$$

$$G'' = G^* \sin \delta \quad (3.4)$$

$$\delta = \frac{G''}{G'} \quad (3.5)$$

where G^* is the complex modulus, G' is the storage modulus, and G'' is the loss modulus.

3.1.5 Results and Discussion

The results of the viscoelastic characterization of the sludge simulants described in Tables 3.1, 3.2, and 3.3 are presented in this section, along with a discussion of the implications of the data.

Viscoelastic Properties of Bentonite

Figure 3.1 shows the changes in G' and G'' with frequency, for bentonite/water sludge-simulant samples at four different solid loadings, and shear strengths corresponding to approximately 18, 60, 90, and 160 kdyn/cm². The profiles in Figure 3.1 show that the magnitude of loss tangent increases as the bentonite solid loading increases. It appears that the loss-tangent profile for 20 wt% bentonite is higher than that for 30 wt% bentonite. However, this variation is relatively small and is considered to be within the experimental noise level. The loss-tangent profile as a function of solid loading reveals that as the solid concentration increases, there is less spatial freedom for the particles to move within the particulate network. Therefore, as the spatial freedom decreases (by increasing the solid loading), the relative magnitude of frictional effects increases and the magnitude of loss tangent is consequently increased. Also, for each solid loading, the variation in the magnitude of loss tangent is relatively small with respect to changes in frequency.

Viscoelastic Properties of Kaolin

Variations in G' , G'' , and G^* with strain amplitude for kaolin/water (no bentonite added) at three different solid loadings of shear strengths corresponding to 10, 30, and 60 kdyn/cm² are shown in Figures 3.2a to 3.2c. The plots shown in the figures indicate that G' , G'' , and G^* decrease continuously with increasing strain amplitude. Comparing the magnitudes of G' , G'' and G^* at any given strain in Figures 3.2a to 3.2c indicates that the storage, loss, and complex moduli are strong functions of the solids loading and that they increase with decreasing water content. The profiles in the figures indicate that the behavior of kaolin is influenced significantly by both elastic and viscous effects. The relative importance of the viscous and elastic forces is a strong function of the strain amplitude and solid loading. Unlike other viscoelastic materials, which typically exhibit plateau regions in the G' , G'' , and G^* profiles at very low strain amplitudes, the profiles in the figures indicate that the viscoelastic characteristics of kaolin clay are a strong function of strain at low strain. At low strain amplitude, the behavior of kaolin is mostly elastic. For larger strains, however, the viscous effects have a sizeable influence on the behavior of kaolin. The viscoelastic properties of kaolin can be further analyzed from the loss-tangent profiles shown in Figure 3.3. There are three characteristic features of the loss-tangent profiles: (1) at any applied strain amplitude, the loss tangent increases with increasing solids loading; (2) the loss tangent increases with strain amplitude at low strains, appears to plateau at moderate strain amplitudes, and then increases again with further increase in strain amplitude toward loss-tangent value of 1, which is indicative of purely viscous behavior; and (3) the length of the plateau region begins to decrease with increasing solids loading. These observations indicate that frictional interactions become more significant with increasing strain amplitude and solids loading. The exact reason for the plateau behavior of the loss-tangent profiles is not clear at this time. This plateau region is more predominant at lower solid loading, at which particles have relatively more spatial freedom to rearrange and can absorb a greater amount of strain before permanent deformation occurs.

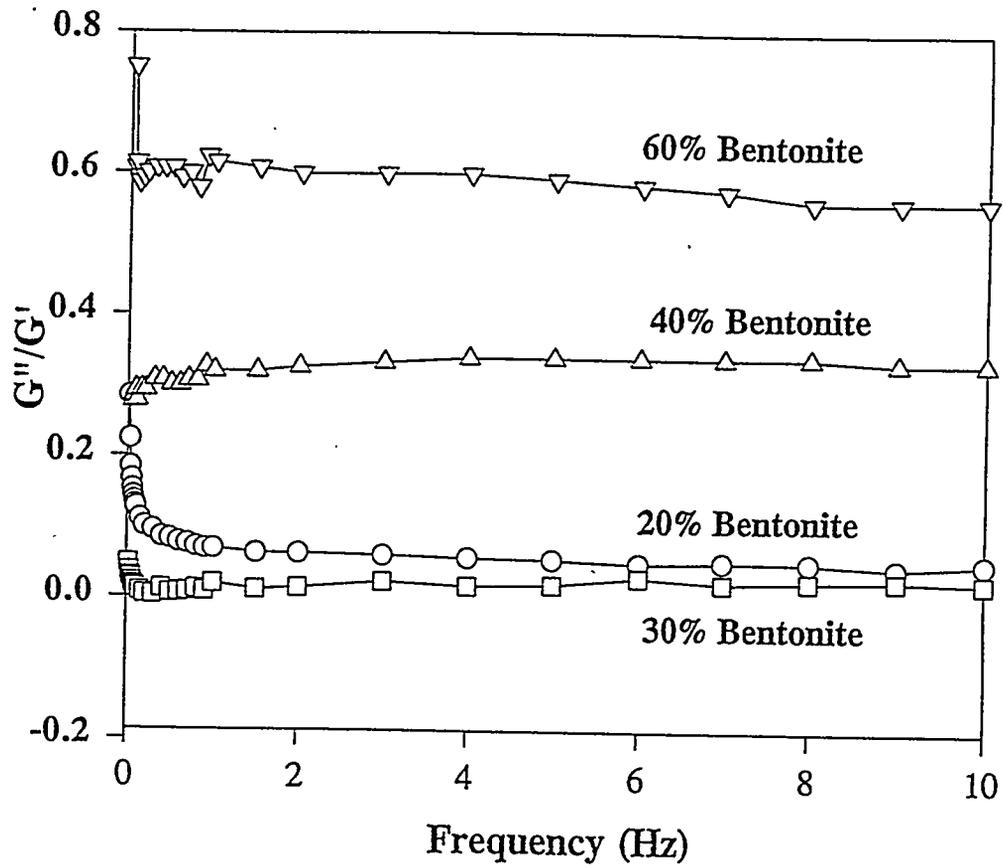


Figure 3.1. Viscoelastic Moduli for Bentonite Clay

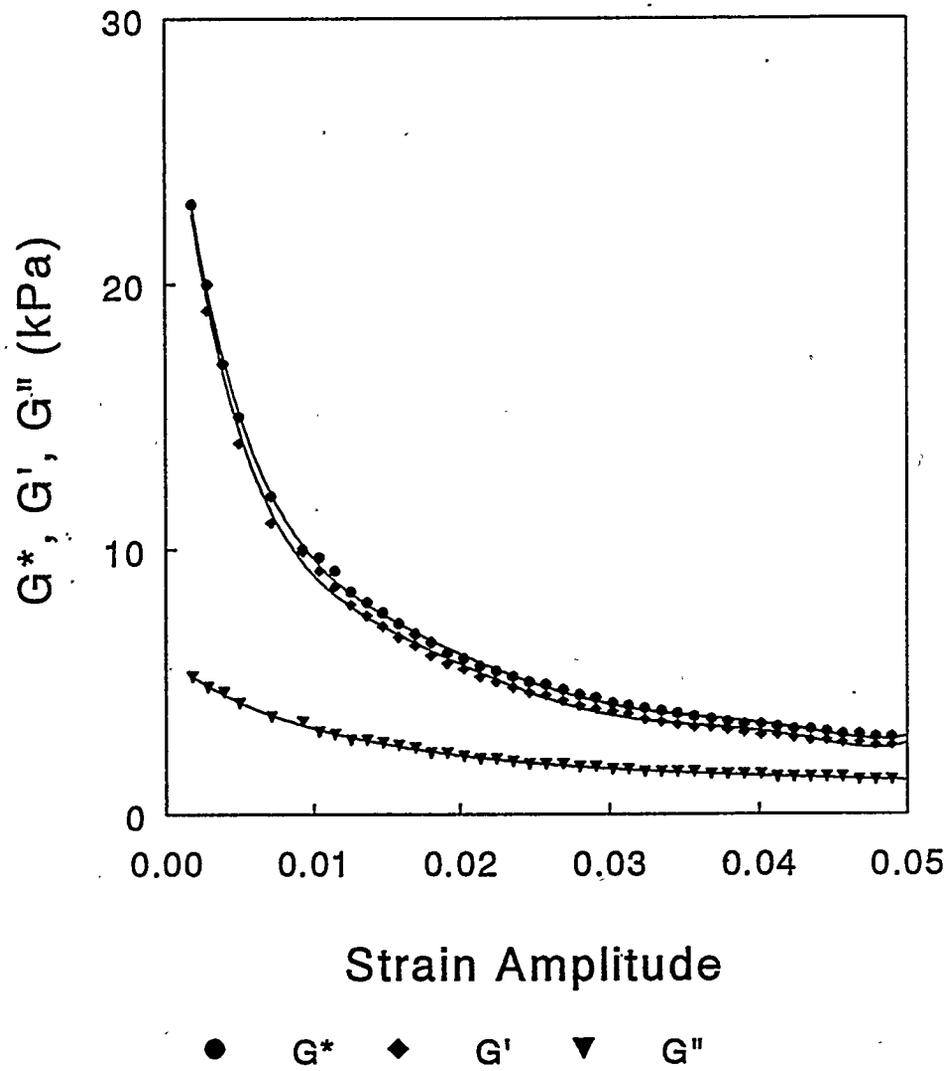


Figure 3.2a. Viscoelastic Moduli vs. Strain for 10 kdyn/cm² Kaolin Clay

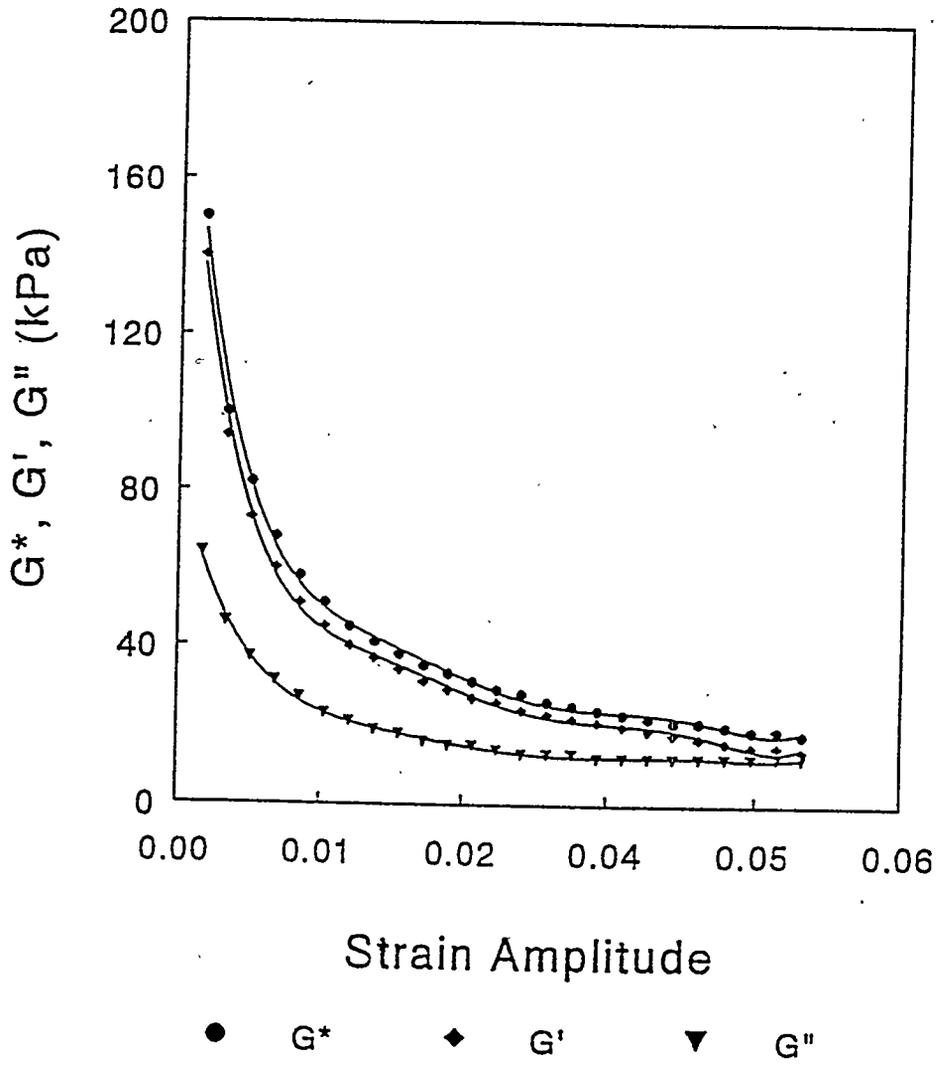


Figure 3.2b. Viscoelastic Moduli vs. Strain for 30 kdyn/cm² Kaolin Clay

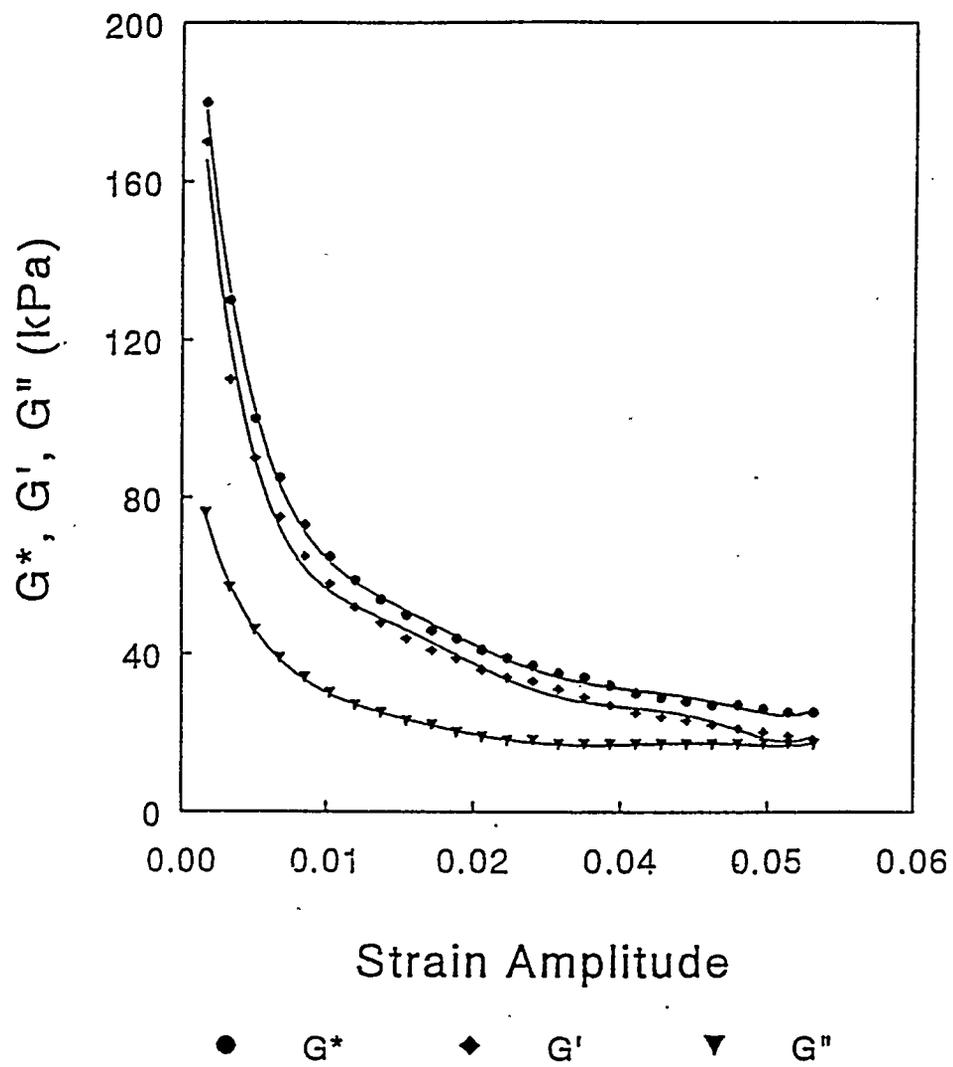


Figure 3.2c. Viscoelastic Moduli vs. Strain for 60 kdyn/cm² Kaolin Clay

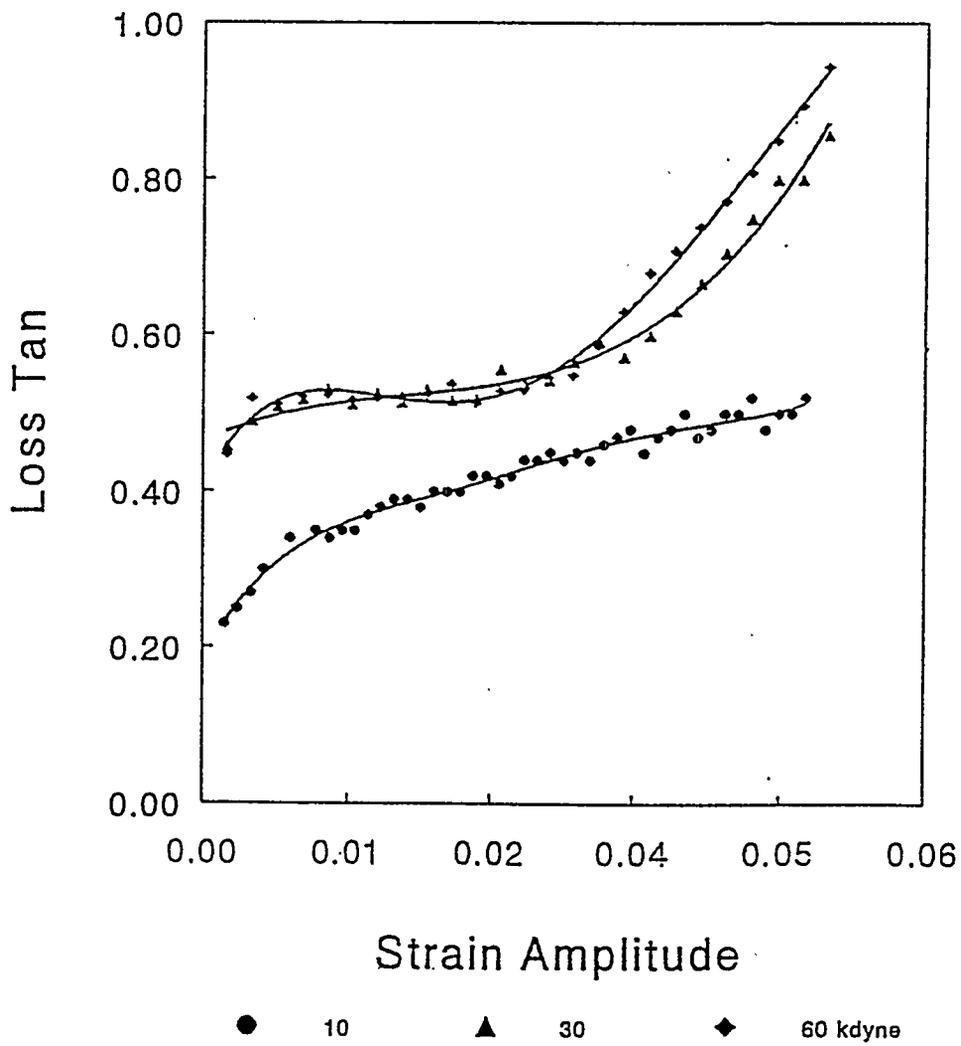


Figure 3.3. Kaolin Clay Loss Tangent vs. Strain and Shear Strength

Effect of Bentonite on the Viscoelastic Properties of Kaolin

The effect of adding bentonite to the kaolin/water samples with a shear strength of 10 kdyn/cm² is shown in terms of the changes in the loss tangent with strain amplitude in Figure 3.4a. The profiles in Figure 3.4a indicate that with increasing bentonite concentration between 0 and 4.5 wt%, which corresponds to an estimated average specific surface area of 10 to 45 m²/g (see Table 3.1), the loss tangent at any fixed-strain amplitude decreases as a sample's specific surface area increases. The same results were observed for samples with shear strengths of 30 and 60 kdyn/cm², which are shown in Figures 3.4b and 3.4c. Also, the plateau regions in the loss tangent become more evident with increasing bentonite concentration. These results indicate that the elastic properties of the sludge simulants tested increases with increasing bentonite concentration. Because the average specific surface area increases with increasing bentonite concentration, it is postulated that these effects are due primarily to the changes in the surface area of the samples. The logic behind this speculation is that the behavior of 100% kaolin (specific surface area of 10 to 20 m²/g) is a function of both inertial and colloidal interactions, while that of pure bentonite (specific surface area of about 800 m²/g) is mostly elastic. Increasing the specific surface area by increasing the bentonite concentration increases the relative contribution of colloidal-type interactions and, consequently, the behavior becomes more elastic. At a constant solid loading, therefore, as the specific surface area of a concentrated sludge mixture increases, there is a net decrease in the energy lost due to frictional forces in response to an applied small strain.

3.2 Saltcake Simulants

Efforts were made to study the crystalline-growth mechanisms that are used to generate saltcake simulants. The goal of these studies is to establish a correlation between the crystalline characteristics (e.g., pore size, crystalline structure) and other selected physical properties. These saltcake simulants will be used in the planned waterjet retrieval sensitivity testing. It is important to test waterjet systems using simulants with a variety of crystalline properties because these properties are likely to have a very significant impact on the efficiency of waterjet cutting. The efforts being made by the simulant-development task will lead to the identification of the physical properties and measurement techniques that are needed to predict the performance of waterjet-based retrieval systems applied to tank waste.

3.2.1 Fracture of Multiphase Brittle Materials by Waterjets

Through consultation with experts in high- and medium-pressure waterjet cutting (experts from the University of Missouri-Rolla and Quest Integrated, Inc.), the mechanisms by which waterjet cutting proceeds were theorized. The key material properties that influence the hydraulic dislodging performance were then postulated.

Waterjet cutting in a brittle, multiphase, granular, or crystalline material, like radioactive saltcake waste, can be described as a sequence of several steps. As water penetrates into cracks or other perturbations on the surface of the material, the flow of water droplets acts to pressurize the fluid in the crack, which tends to cause the crack to grow. Eventually, the cracks grow together, which dislodges the grains or crystals lying between the originally separate cracks. As the material is dislodged,

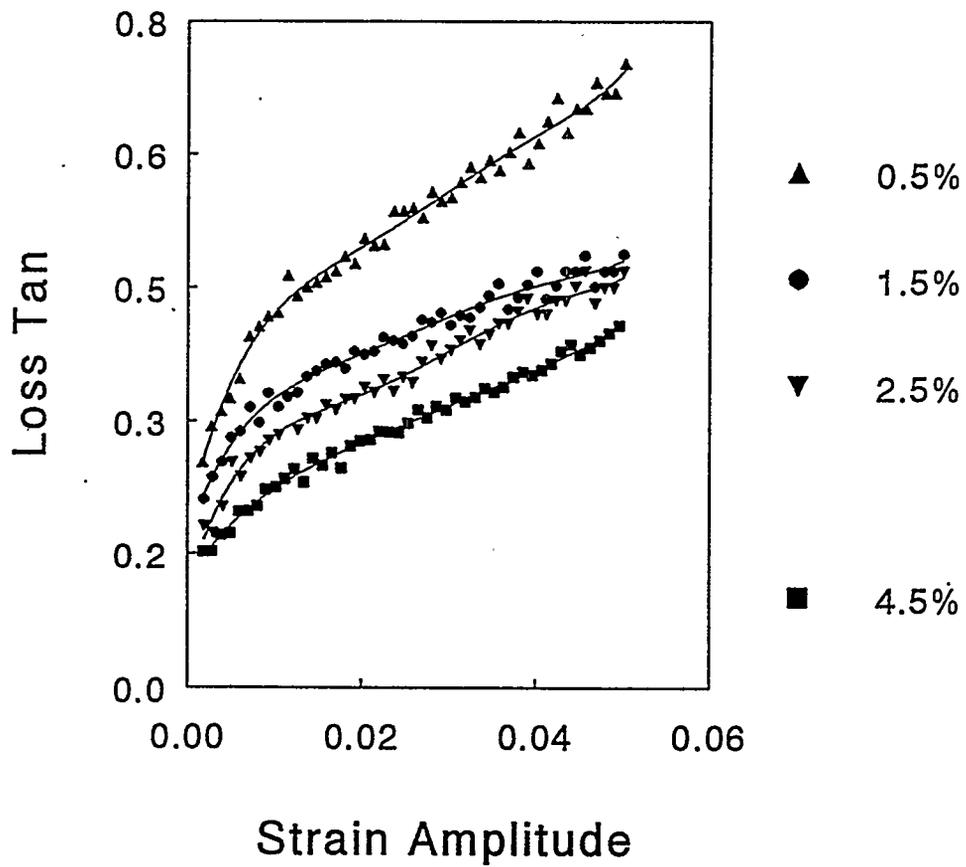


Figure 3.4a. Viscoelastic Loss Tangent vs. Strain for 10 kdyn/cm² Kaolin/Bentonite Mix. Percentages refer to the fraction of total solids that was bentonite.

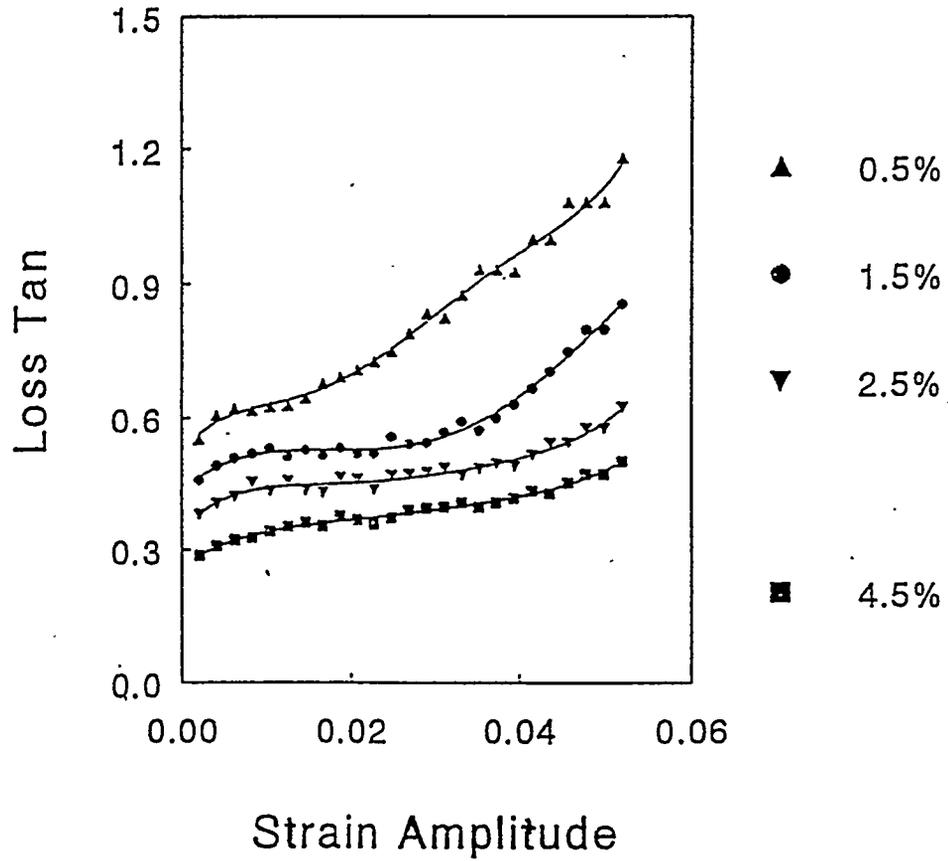


Figure 3.4b. Viscoelastic Loss Tangent vs. Strain for 30 kdyn/cm² Kaolin/Bentonite Mix. Percentages refer to the fraction of total solids that was bentonite.

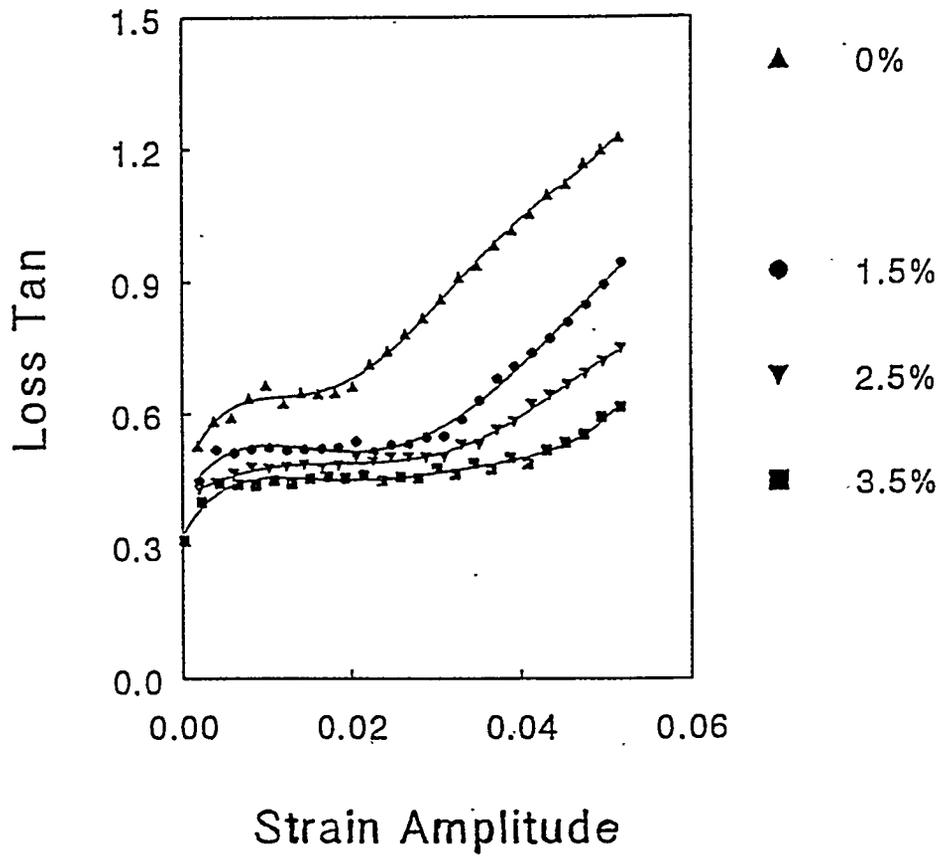


Figure 3.4c. Viscoelastic Loss Tangent vs. Strain for 60 kdyn/cm² Kaolin/Bentonite Mix. Percentages refer to the fraction of total solids that was bentonite.

the cracks grow around the underlying particles or crystals, thus propagating an incipient state of material failure. Although this describes the mechanism of material failure, it is beneficial to discuss the behavior of the waterjet as it strikes the surface of the material.

When the waterjet leaves the nozzle, the slippage of water against air between the nozzle opening and the material surface causes a substantial pressure gradient ranging from zero at the water-air interface to a maximum at the center of the distribution. The radial-pressure distribution typically takes a bell shape, which is significant during the impact of the jet at the surface of the material. The rate of change in this distribution varies with the jet pressure and the jet diameter. Once the full shape is developed, within a short distance the jet will begin to break into segments and form droplets. Droplets quickly break into smaller droplets and lose both velocity and cutting power with additional distance from the nozzle.

The first step in assessing the response of the target material to waterjet attack requires a knowledge of exactly what form the jet is taking as it arrives at the surface. It is known that material failure is likely caused by crack extension from existing surface flaws (Griffith 1920). The applicability of this to material erosion under jet impact has already been demonstrated.

When the jet arrives at the surface, if the pressure profile is flat at the time of impact, then no material across the diameter of the jet-impact will be removed because once the water has impacted the surface, the addition of more water to the surface is hindered by how slowly the previously impacted water escapes. When the impact-pressure differential is increased, however, Hertzian cracks are formed around the impact zone. The formation of these cracks is a result of the stretching of the material, which occurs due to formation of a depression caused by the impact of the waterjet. The stepped nature of the surface at these cracks initiates erosion in the vicinity because of the subsequent flow of water. The controlling factor of the crack depth is the grain size of the saltcake (Brace 1961), and the pressure necessary to cause the crack to grow is controlled by the crack length and the stress in the surrounding area. This implies that the controlling material parameters for waterjet cutting are the crack size and the tensile strength.

3.2.2 Experimental

The experimental techniques and measurements made on the brittle saltcake simulants are described in this section.

Compressive Strength Test

Performance of waterjet cutting is strongly related to material strength properties; therefore, understanding the mechanical properties of hydrated saltcake simulant, potassium-magnesium sulfate ($K_2SO_4 \cdot 2MgSO_4$), is necessary. The profile of compressive strength results over a selected range of water concentration is shown in Figure 3.5. It was anticipated that the addition of a different amount of water could change not only the physical properties of the solid but also the extent of the hydration reaction; thus, by manipulating the amount of water in the sample, the strength properties of the baseline saltcake simulant could be changed. Figure 3.5 indicates the changing pattern of compressive strength as a function of added water. The compressive strength increases with increasing water loading up to 14 to 16 wt% and decreases again with further increase in water content. These water-content-dependent compressive

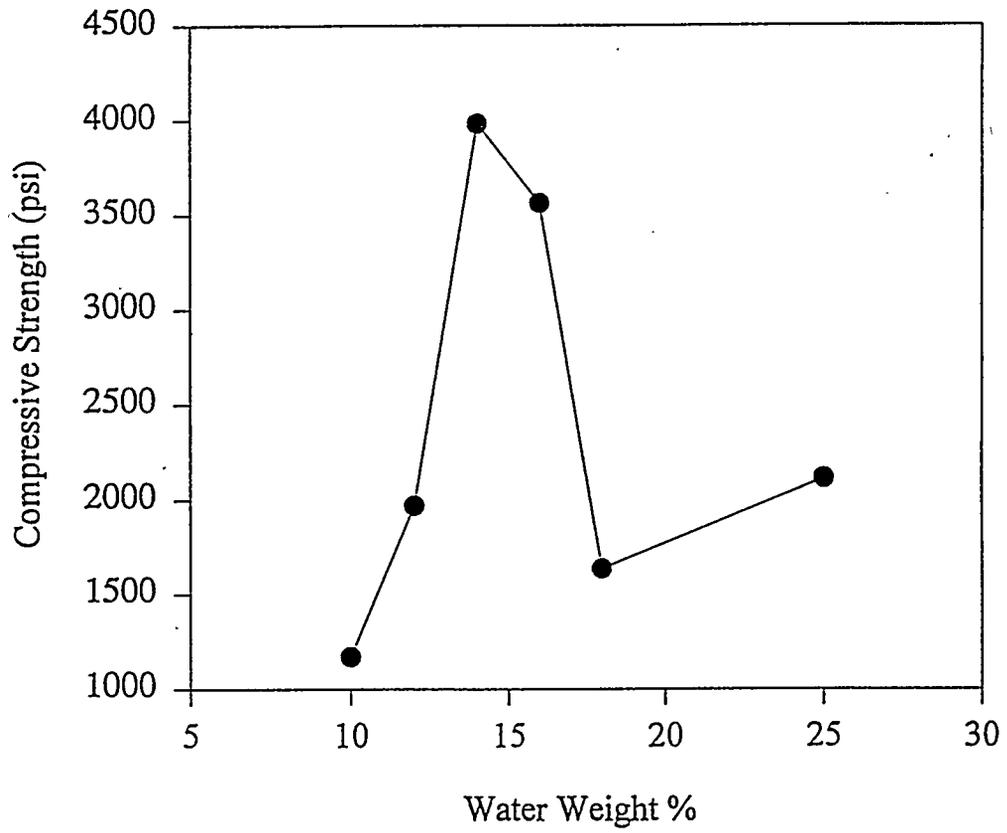


Figure 3.5. Compressive Strength versus Water Content

strength changes suggest that somehow the material physical and chemical behaviors are changed due to water-induced solubilization, precipitation, and hydration reactions.

Pore Size and Porosity Measurements

The saltcake simulant mechanical properties are related to the material structure and the processing conditions. To explore the changes in compressive strength with changing water content, pore-size distribution and porosity measurements were performed on several samples. Typically, for a sample with smaller pore size and lower porosity, it is expected that material strength would be higher than that with larger pore size and higher porosity. From the pore-size and porosity measurements, therefore, it can be predicted how addition of water into the sample affects the pore-size distribution and how the variation in pore size is related to compressive strength. Figure 3.6a shows the porosity versus water content, and Figure 3.6b shows the average pore size versus water content. Figures 3.6a and 3.6b suggest that the porosity of the hydrated material decreases with increasing water content up to about 14 wt%, and further increases in the water content result in some increases in porosity. Similarly, the average pore size varies with addition of water in a way that at a lower water loading (12 wt%), the large pores increase the average pore size. As more water is incorporated into the sample, the pore-size distribution shifts towards the smaller sizes, leading to a decrease in the average pore size. The average pore diameter does not change as the water loading is increased beyond 14 wt%.

From the above discussion, it may be concluded that the increased dissolution of solid with increasing water content significantly changes the particle size and shape, leading to more effective particle contact and smaller pore sizes. Obviously, the pore size plays a key role in determining compressive strength when water loading is below 14 wt%. A continuous increase in compressive strength and a continuous decrease in the pore diameter were observed as the water loading was increased to 14 wt%. Above 14 wt% water loading, dissolution/precipitation dominated the material pore properties and there was a more homogeneous pore-size distribution in the hydrated material.

Structure and Phase Composition by X-Ray Diffraction

In addition to the mechanical-strength testing and pore-size characterization, efforts were made to gain more insight into how the degree of hydration affects the composition of the final hydrated products. X-ray diffraction was used for this. X-ray diffraction is a very useful technique for the quantitative determination of structure and phases because the intensities of the diffraction peaks of a given compound in a mixture are related to the fraction of the material in the mixture. Direct comparison of the diffraction peak intensities, however, is fraught with difficulties. In this instance, x-ray diffraction was used to gain qualitative information on the composition of phases. A series of x-ray diffraction analyses was made on samples with different amounts of water ranging from 10 to 30 wt%. From water-content-dependent studies, one can gain more understanding of whether adding different amounts of water changes the extent of the hydration reaction.

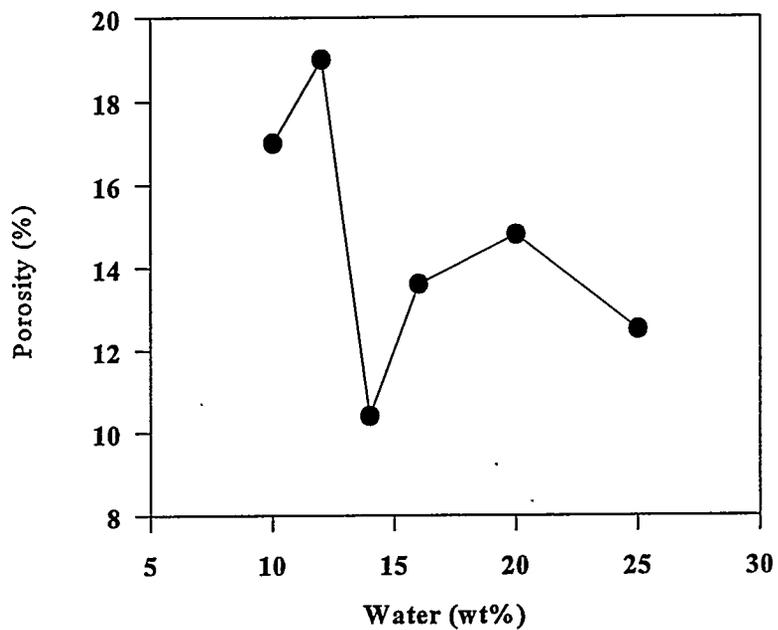


Figure 3.6a. Porosity vs. Water Content

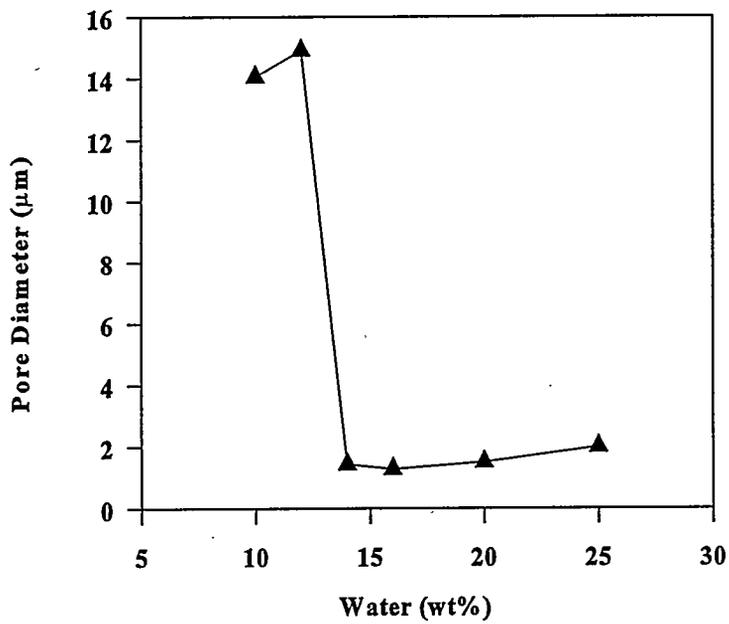
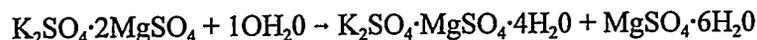


Figure 3.6b. Average Pore Diameter vs. Water Content

X-ray diffraction studies show that the hydration of potassium-magnesium sulfate follows this reaction:



In all cases, three major products, $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ (starting phase), $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ (product phases), were identified. A small quantity of an additional trace phase ($\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), however, was detected in some samples and is likely attributable to the sensitivity of the measurement method and small variations amongst the samples. The presence of this phase ($\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) was neglected because of its small contribution (1 to 2 wt%) and its absence in most samples.

X-ray diffraction studies demonstrated that the amount of water (10 to 30 wt%) does not change the hydration-reaction mechanism. To reveal the effects of temperature on this reaction, samples prepared at a higher temperature (100°C) and water loading (66.7 wt%) were examined. At this higher water loading and temperature, K-Mag has a higher solubility. Under these experimental conditions, a sample contains two phases: an undissolved solid phase and a supersaturated salt solution. The final cured sample has two different apparent phases, the major solid phase (about 98 wt%) from the undissolved sample hydration reaction and the small amount of crystal phase (2 wt%) recrystallized from the supersaturated solution.

X-ray analysis of these two phases gave very different diffraction patterns. Surprisingly, the bulk solid phase also contains three phases, the same as samples prepared at room temperature. The crystal phase from the supersaturation, however, is completely due to formation of a new phase, that is, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ (shown in Figure 3.7).

If the solid growth follows a dissolution/precipitation mechanism, the degree of hydration reaction is not very dependent on water loading and temperature. X-ray diffraction studies showed the same phase compositions and structure in all samples regardless of initial water content. The hydrated compound can be different, however, if the reaction mechanism occurs through crystallization because crystal growth from a supersaturated ionic solution occurs by a series of consecutive steps: bulk diffusion, surface adsorption, surface diffusion, surface reaction, and integration of ions or molecules into the crystal lattice, leading to formation of a different solid phase.

Thermal Treatment and Analysis

From the above discussion, it can be concluded that compressive strength, porosity, and phase composition are affected by changes in the initial simulant water content. We were also interested in knowing if there is any correlation between the saltcake simulant compressive strength and its chemistry. A thermal-analysis technique was used to investigate how the bonding interaction between water and substrate correlates with the material compressive strength.

Observations were made on the effects of water loading and temperature on the degree of hydration. Qualitative analysis from x-ray diffraction revealed the number of phases produced by the hydration reaction. However, a lack of knowledge on how these water molecules bond to the substrate and the strength of these bonding interactions needed to be considered.

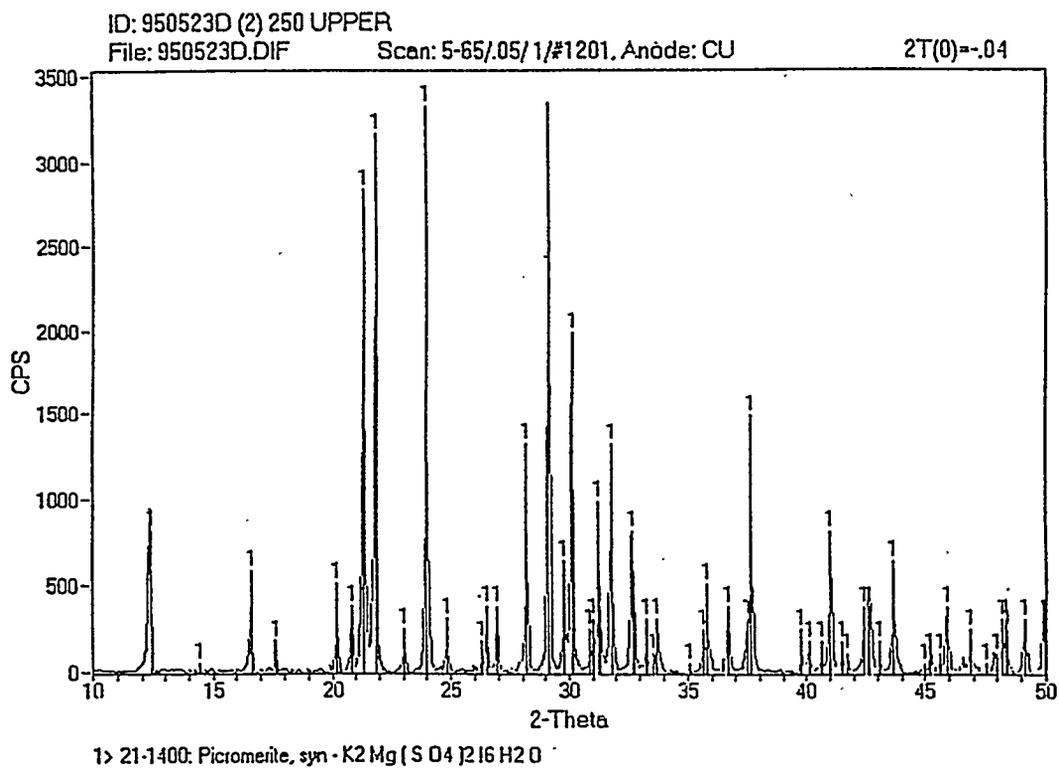


Figure 3.7. X-Ray Diffraction Pattern of $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ from Supersaturation

Typical plots of weight loss vs. temperature as a function of initial water content up to 30 wt% water are shown in Figure 3.8. Interestingly, there are three water-desorption reactions over the temperature range of 80° to 200°C in all samples with water of 10 to 30 wt%. The three peaks were attributed to three different types of water bonds within the simulant. The difference in the dehydration temperatures can be due to either the difference in water environment, such as the different rigidity caused by the pore sizes, or the different bonding interactions between water molecules and the substrate (e.g., different degree of hydrogen bonding). There are also some changes in the peak position and magnitude of the weight loss of these three peaks as a function of water (Figure 3.8). Generally, endothermic reactions include phase transitions, dehydration, reduction, and some decomposition reactions. Similarly, endothermic reactions were observed in all cases for these dehydration reactions. The differential thermal analysis results as a function of furnace temperature at 10 wt% water are given in Figure 3.9.

Figure 3.10 summarizes the total weight loss (panel a) and the fractional contribution of each weight loss process to the total (panel b) as a function of water content. Because of the saturation of water in the hydrated compound, the total weight loss is unchanged with further addition of water beyond 16 wt%. Figure 3.10 (panel b) indicates that the predominant contribution to the dehydration process is from first and second peaks. The fractional contributions of peaks 1 and 2 are invariant with water addition over the entire water-loading range (10 to 30 wt%), indicating that the partitioning of water into each domain is unchanged.

The ratios of peaks 1, 2, and 3 in Figure 3.10b are 2:2:1 and did not change with water content between 10 and 30 wt%. This raises two possibilities: Are these three peaks due to differences in chemical bonding (e.g., different degrees of hydrogen bonding) or due to differences in physical environments (such as different pore size)? If the temperature-dependent dehydration reaction is due to differences in hydrogen bonding in the hydrated compounds, we then can reasonably assign the first peak (80° to 90°C) to the liberation of the least-bonded water, for example, from $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$. The second and third peaks are from the more strongly bonded water ($MgSO_4 \cdot 6H_2O$). To clarify our hypothesis, samples with initial water loadings of 20% and 30% were thermally treated at 130°C and 170°C, respectively. X-ray diffraction analyses were then applied to these samples. In contrast to the previous results, x-ray diffraction analyses from these samples show that the phase compositions ($K_2SO_4 \cdot 2MgSO_4$, $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$, $MgSO_4 \cdot 6H_2O$) at both water contents and temperatures remain the same as those samples without thermal treatments. Thus, the thermally treated samples show us that the thermally induced water liberation is not attributed to a difference in chemical bonding. Instead, different physical environments around the water within the sample play a key role in determining the thermally dependent dehydration reactions.

The peak temperatures as a function of initial wt% water are shown in Figure 3.11. All three peaks shift slightly toward higher temperatures with increasing water content. The largest shift was observed for the first peak (80° to 88°C), which is a relative change of about 10%. The second peak (145° to 150°C) has a smaller shift (about 4%). The third peak (184° to 188°C) has the smallest shift (only about 2%). Based on our thermal analyses, we postulate that a water-content-dependent microporosity change is responsible for the observed peak shifts. The rigidity of water within the pores of the simulant is controlled by the pore size. At lower water contents, large pore size facilitates the water release, which results in a lower dehydration temperature. At high water content, the initial dissolution and subsequent reprecipitation

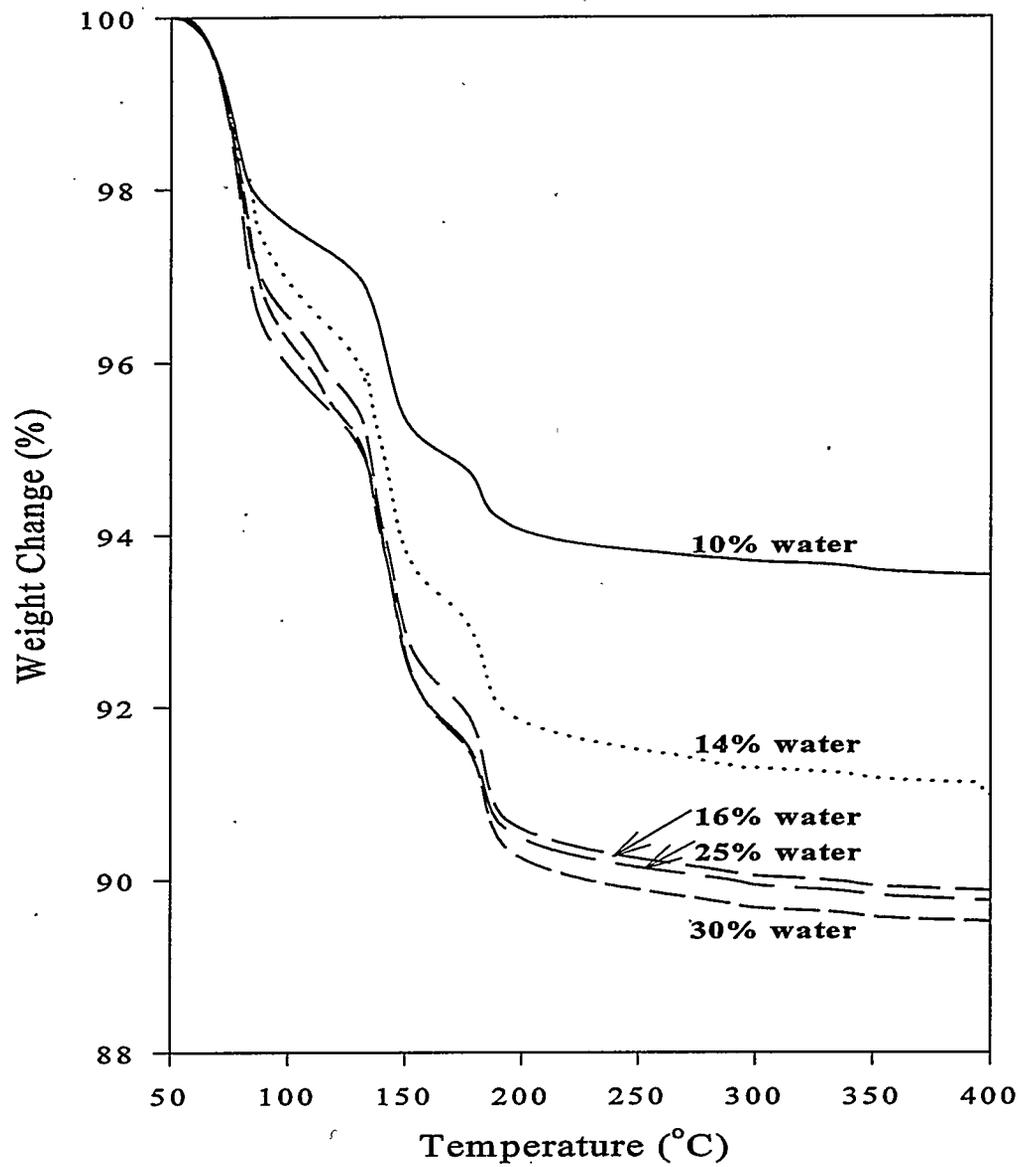


Figure 3.8. Weight Loss as a Function of Water Content (TGA)

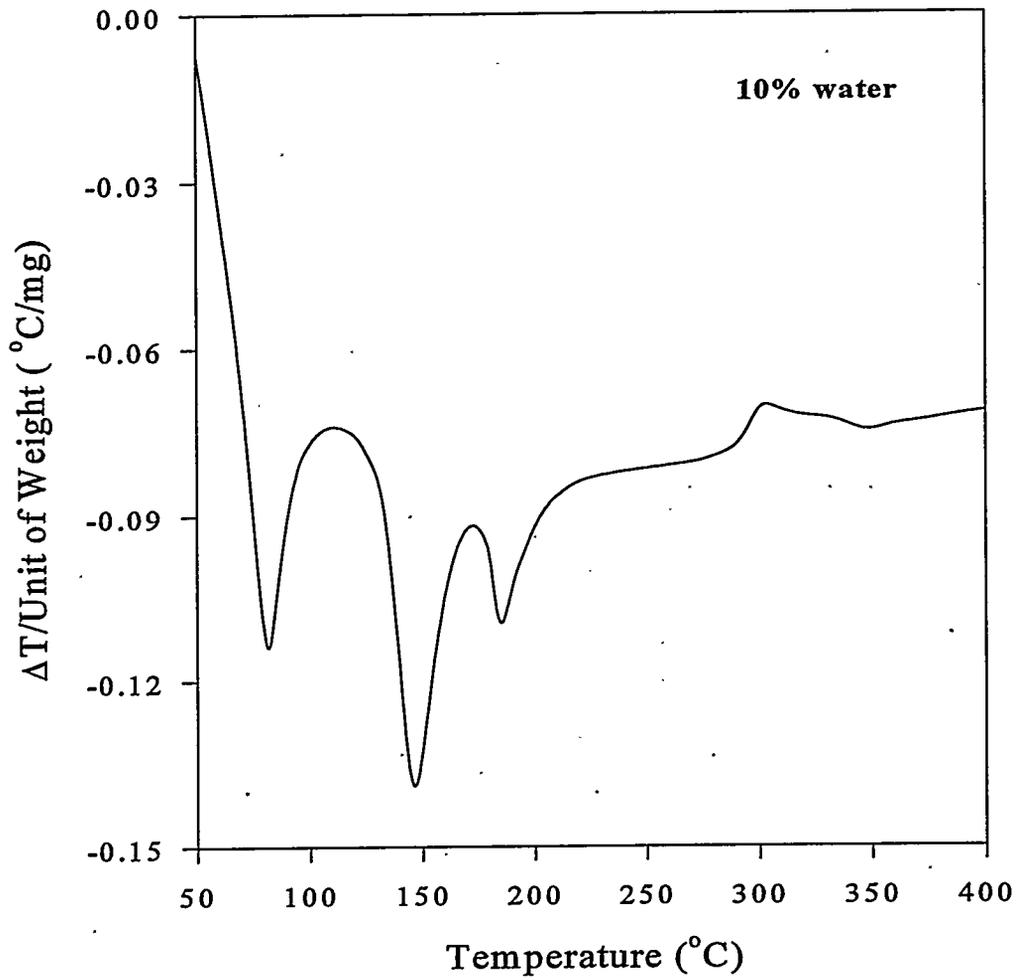


Figure 3.9. Differential Thermal Analysis for 10 wt% Water Loading

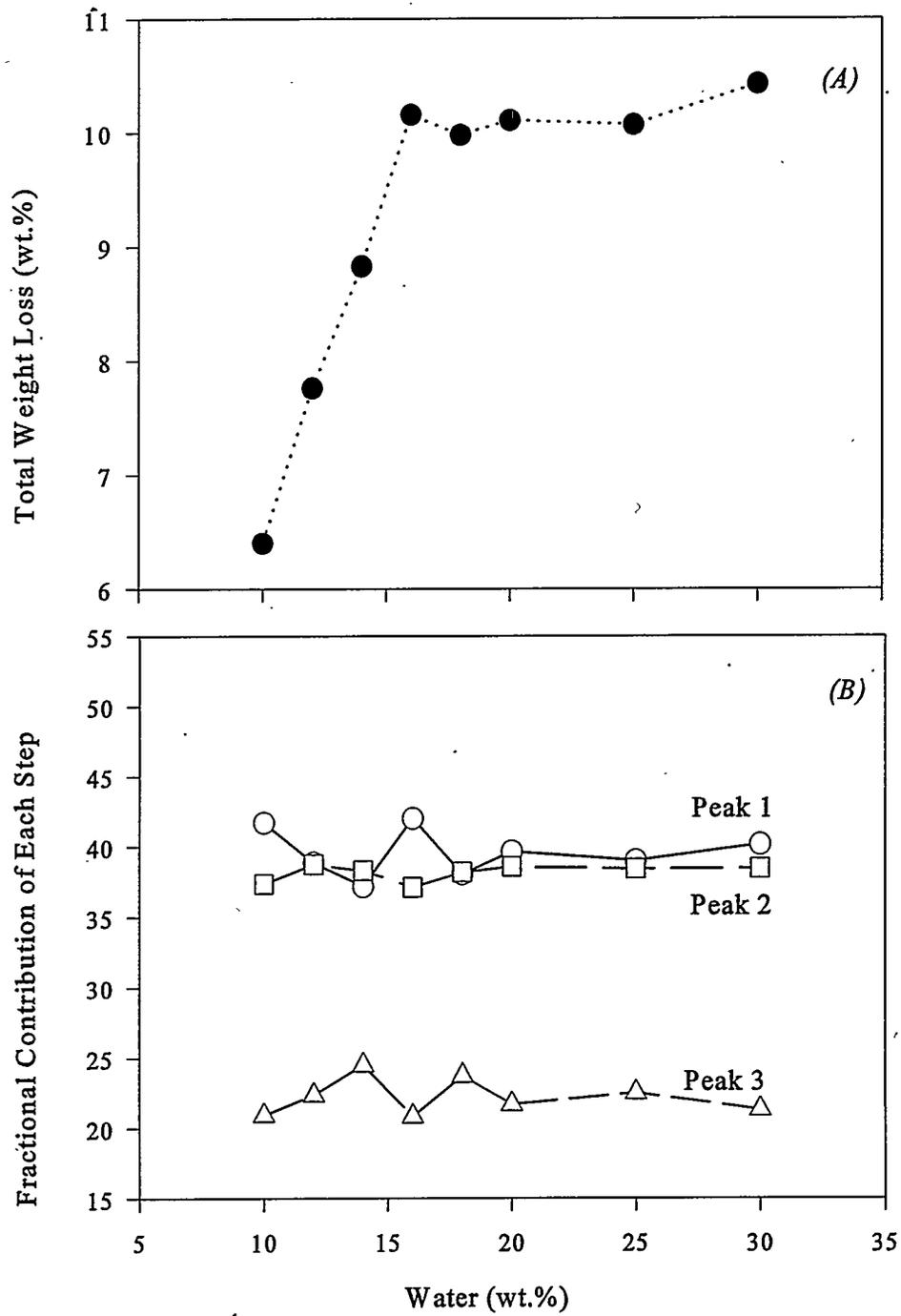


Figure 3.10. Total Weight Loss (a) and Fraction of Each Peak (b) vs. Water Content

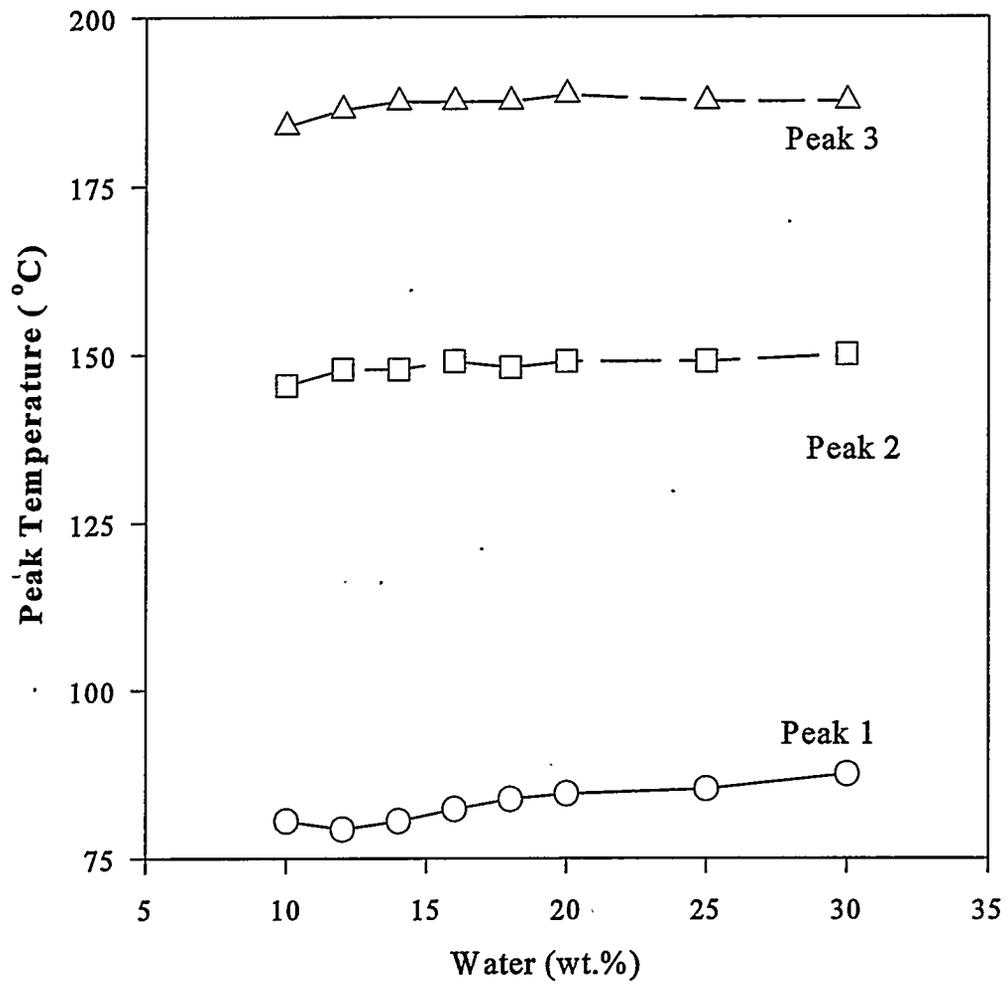


Figure 3.11. Peak Shift as a Function of Water Content

results in a smaller particle size and ultimately a smaller pore size in the sample. As a result, the water within the simulants will be retained more strongly with increasing water content. This leads to the observed small shift in the thermal peak positions.

The effects of temperature on the degree of hydration were also studied. Temperature is a very important factor in controlling physical and chemical reactions. From a kinetics standpoint, increasing temperature increases the reaction rate. As a result, the hydration reactions are expected to proceed to completion more quickly at higher temperatures. Another goal of the temperature effects testing was to change the solubility of the simulants so that the degree of hydration, particle size, and packing density can be manipulated. Changes in these physicochemical properties significantly affect the simulant mechanical strength. Unfortunately, there was not sufficient time to measure the hydrated simulant mechanical strength after temperature treatment.

Temperature and concentration gradients are both important in the determination of crystal phases and structure. We prepared one sample with a high water loading (66.7 wt%) and mixed it with $K_2SO_4 \cdot 2MgSO_4$ at $100^\circ C$. At this temperature, more solid dissolves in the aqueous phase, and supersaturation is reached when temperature is subsequently lowered to room temperature. The sample was allowed to cure at room temperature over three weeks and then subjected to thermal analysis.

Two solid phases were observed visually: a transparent phase on the surface and a light-pink phase in the bulk. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) tests were conducted on both phases. The differences in thermal reactions were significant (Figure 3.12a and 3.12b). In Figure 3.12a, a single-step reaction from the transparent surface phase was observed, whilst multiple-step reactions for the bulk light-pink phase were resolved that are very similar to those samples prepared at room temperature. X-ray diffraction analysis suggests that the single-phase compound from the transparent surface was $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. Quantitative thermal analysis agrees well with the postulated presence of only $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ because the total weight loss due to a complete dehydration of $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ should be

$$\frac{6 MW_{H_2O}}{MW_{K_2SO_4 \cdot MgSO_4 \cdot 6H_2O}} \times 100\% = \frac{108}{402.7} \times 100\% = 27\% \quad (3.6)$$

if all six waters dehydrate at once. The lower bulk solid phase, however, maintains the same features as those prepared at room temperature, although a small peak split takes place in the second peak. Figure 3.8b depicts more clearly the differential thermal behavior of these two samples.

Some further comments about these plots are in order. First, the thermal behavior of the lower bulk solid phase resembles that of the samples prepared at room temperature. This suggests that the phase composition of the samples prepared at different conditions (water % and temperature) are similar. Second, three significant dehydration steps with intensity ratios of 2:2:1 from the lower solid phase are identified by the loss of 40% of the hydrated water in the first temperature region, 40% in the second, and the remaining 20% in the third. The second peak was split into two peaks, which may indicate similarity

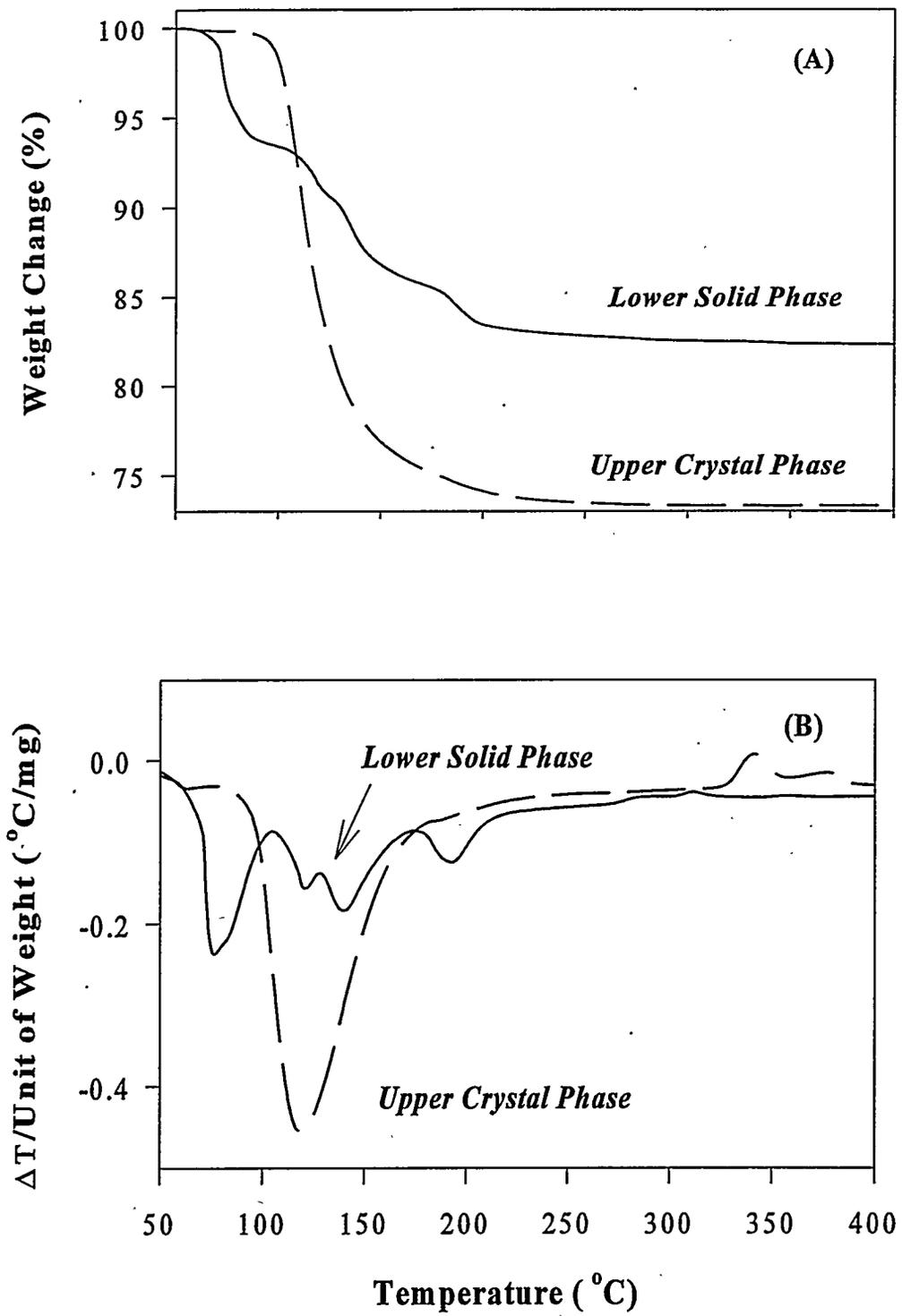


Figure 3.12. TGA (a) and DTA (b) Results for the Temperature-Treated Sample

of the water environments. Third, and finally, a single-step weight loss for the transparent-surface phase obtained from the supersaturated solution reflects not only the homogeneity of the hydrated material but also the degree of hydration in the $K_2SO_4 \cdot MgSO_4$ (i.e., six waters of hydration).

This study revealed how simulant-processing conditions affect the material phase compositions, chemical properties, and most importantly, the simulant mechanical properties. At elevated temperatures, if the homogeneity of the hydrated products can be varied by changing the processing temperature, we then can control the hydrated material mechanical strength by changing the processing temperature. We hope to perform more experiments by manipulating the processing conditions to control the material strength.

Conclusions Based on Thermal Analyses

Initially, water-dependent dehydration reactions using DTA/TGA were investigated because it was anticipated the saltcake simulant strength was somehow related to the extent of water-substrate interactions. If this relation could be determined, we would be better able to understand how the material chemistry affects its mechanical strength, which directly affects the waterjet-cutting performance.

Thermal analysis gave three water-evolution peaks, which are believed due to physisorbed water (in the lowest temperature region), less-bonded hydrated water (in the intermediate temperature region), and strongly bonded hydrated water. In all cases (10 to 30 wt% water loadings), these three peaks exist no matter how the porosity and pore-size change as a function of water loading. At this time, we are still investigating the correlation between thermally induced dehydration reactions and material pore-size distribution and strength properties. We expect to get better understanding by extending the experimental temperature regime to higher temperatures.

The other interesting result is the total weight loss as a function of water content obtained from TGA measurements. The total weight loss (Figure 3.10a) indicates that more water is liberated from the sample as water content increases. However, the total weight loss no longer changes appreciably once the water loading exceeds 16 wt%. Although this result seems to be inconsistent with the compressive strength and porosity data, it is likely that more water can be liberated at higher temperatures where some structural water will be removed.

3.2.3 Conclusions

Hydrated compounds from potassium-magnesium sulfate fertilizer (K-Mag) were characterized with respect to compressive strength, pore size, and porosity, and by x-ray diffraction and thermal analysis. We observed a continuous change in compressive strength as a function of water content. This water-content-dependent compressive-strength change was affected by pore size, porosity, phase composition, and the thermal behavior of the hydrated products. X-ray diffraction tests indicate that the degree of K-Mag hydration reaction at room temperature is not a strong function of water content. The fraction of raw material participating in the hydration reactions, however, varies with the amount of water added. We conclude that the continuous increase in compressive strength with increasing water content (for samples with less than 16 wt% water) is due to a decrease in pore size and porosity. This is supported by TGA measurements.

The continuous decrease in compressive strength with increasing water content for samples with greater than 16 wt% water follows a different mechanism. At water contents higher than 16 wt%, for instance, more complete dissolution and precipitation results in more effective particle contact and more homogeneous pore environments. Therefore, the pore size is no longer changing, and porosity decreases. Decreases in compressive strength with increasing water content likely are due to the hydration reaction. More water associated with the material weakens the material strength; however, the total weight loss from TGA in this water-loading range did not show a continuous increase in the weight loss with increasing initial water content. This is possibly because some structural water can be observed at very high temperature but our experiment did not extend to that high-temperature region.

Thermal analysis of the hydrated compounds gives more insight into the hydration mechanisms. If we changed the processing conditions, we obtained a different product; for instance, supersaturation of potassium-magnesium sulfate leads to the formation of a homogeneous, single phase of $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. In addition, by changing the temperature, finer particles can be formed and more homogeneous hydrated product can be obtained. It will be interesting to examine the effects of cure temperature on the mechanical properties of the hydrated saltcake simulants.

4.0 Simulant Development for Conveyance

It is postulated that water-scavenging conveyance systems may be needed as part of waste-retrieval operations where only small amounts of water may be added to the tank (e.g., if the tank is known to leak). The waste-dislodging concepts include devices that employ high- and medium-pressure waterjets for cutting and slurring the waste solids. To convey the cuttings from the waste dislodging unit out of the tank, a pneumatic- or jet-pump-based conveyance system will be evaluated. These two conveyance-system concepts are briefly described below.

Pneumatic-conveyance systems are typically used to transport particulate solids. Compressed air or a downstream-vacuum source is used to entrain the solids and transport them through a pipeline. The system envisioned for tank-waste retrieval will use a vacuum source (located outside the tank) rather than compressed air. Compressed-air systems require special equipment to feed the solids into the conveyance line; this equipment would be impractical for use in tank-waste conveyance.

Pneumatic-conveyance systems used in industry are operated in either dense-phase or dilute-phase modes. Dense-phase conveyance, where possible, is generally preferred because of the relatively low power requirements and minimized conveyance-line wear. Dilute-phase conveyance uses much higher air-flow rates and much lower solids concentrations (mass of solids per unit volume of air). Dilute-phase transport must be used for tank-waste conveyance because of the high vertical lift required and the need to avoid plugging the conveyance line with cohesive solids.

In industry, pneumatic-conveyance systems are usually used to transport dry particulates such as agricultural grains or concrete mix. Using pneumatic conveyance to transport wet, sticky solids like tank waste is rarely attempted in industry (Stringfield 1994). Testing at Hanford indicates that wet, sticky solids can be transported using pneumatic-conveyance systems provided that some additional water is injected into the inlet of the conveyance line to provide a lubricating water film, which reduces sticking (Wellner 1993).

An alternative waste-conveyance system uses a waterjet pump located near the suction of a conveyance line, which is coupled with the waste-dislodging equipment. The waterjet pump uses high-pressure fluid jets focused near the throat of the jet pump to impart axial momentum to the fluids being pumped. The jet-pump suction draws in liquids, gases, and solids, thereby potentially creating a three-phase flow through the remainder of the conveyance pipe.

Jet-pump-conveyance systems are expected to be less vulnerable to plugging and/or slugging (movement of large chunks up the conveyance line which impart considerable dynamic forces on conveyance line supports). Any large pieces of dislodged waste drawn into the jet pump will be cut into much smaller pieces by the focused waterjet. The problem of large pieces of waste moving through pneumatic conveyance systems may be avoided by using a large-mesh screen to cover the entrance to the conveyance line. Plugging may be less of a problem for waterjet-pump conveyance because a greater amount of water is used to transport the waste up the conveyance line. There is, however, the potential for plugging the jet pump with a piece of very hard material (e.g., rock or steel), which would require that the jet pump be back-flushed to remove the obstruction.

4.1 Relevant Simulant Properties for Conveyance Testing

There are three aspects of conveyance-system performance that are to be evaluated through testing using simulants: steady operating capabilities; plugging, choking, or slugging; and erosion of system components. Simulants have been formulated to specifically investigate conveyance-system performance in each of these areas. The simulant properties that influence each aspect of system performance are described in this section.

4.1.1 Steady Operating Capabilities

The steady operating performance of a conveyance system is measured most directly by the maximum waste flow rate obtained for a given system design. The pressure drop versus flow characteristics of pneumatic-conveyance systems are affected by the properties of the conveyed media as well as the system design. With respect to waste conveyance-system performance, the most important waste properties are expected to be particle size, particle density, and particle shape (Bamberger et al. 1993). These three properties determine the effective particle-settling velocity.

For particles of similar density and shape, larger particles will have faster settling velocities and will, in general, be more difficult to convey. In pneumatic-conveyance systems, faster settling rates mean that higher gas velocities are required to maintain a given waste-transfer rate. In jet-pump-conveyance systems, the effect of particle size is expected to be similar. Increasing the particle density or sphericity also increases the settling velocity.

4.1.2 Plugging, Choking, and Slugging

The second aspect of conveyance-system performance for which simulants are needed is the vulnerability of the system to problems like plugging, choking, or slugging. Plugging of the conveyance line is to be avoided for the obvious reason that a plugged conveyance line is useless. Choking refers to the flow restriction caused by the buildup of solids on the conveyance line walls. Even if the choking does not continue until the line is plugged, the reduction in available waste transport flow rate may be cause for concern. Slugging occurs when a relatively large piece of waste or other solid material passes through the conveyance line. As the large piece travels through the line, considerable dynamic forces can be imparted to the conveyance line and its support structure. This is particularly problematic for air-conveyance systems due to the high velocities involved. The lower transport velocities used in jet-pump conveyance make the jet-pump system more immune to slugging problems. Slugging could occur when a large piece of solid is fed to the conveyance system or when some accumulations on the conveyance line wall suddenly detach.

The waste properties that influence a conveyance system's tendency for plugging, choking, and/or slugging are different than those that establish system flow rate performance. All three of these problems stem from the tendency of the transported material to adhere to itself and to the conveyance line. This

cohesive/adhesive behavior is typical of materials composed of very fine particulate.^(a) Much of the tank-waste sludge consists of very small particles; thus, the sludge tends to be sticky as has been observed while handling hot-cell samples.^(b) Saltcake particles are expected to consist of comparatively larger pieces (larger than about 5 microns). Particles in this size range are not expected to be adhesive.

Particles in the sub-micron-size range have very high surface-area-to-volume ratios and surface-chemistry effects tend to dictate their behavior. Particles of all sizes are attracted to each other in response to van der Waals and London dispersion forces (Hiemenz 1986). These attractive forces decay rapidly with distance, so, in effect, it is only the material near the surface of each particle that is close enough to the adjacent particle to participate in the mutual attraction. When particles are very small, their high surface area makes these surface-induced attractive forces much more important in determining particle behavior than for larger particles. As a general rule, the behavior of particles with a specific surface area^(c) of greater than about 25 m²/g is dominated by interfacial forces (Lambe and Whitman 1969). For this reason, concentrated particle systems (like tank sludge) with high specific surface areas tend to be cohesive.^(d) Particulate systems with smaller surface areas are usually more influenced by body-type forces (such as inertia and friction) and tend to be noncohesive.

Measurements of specific surface area on samples of tank sludge would probably establish which types of tank sludge have specific surface areas greater than or equal to about 25 m²/g and are, therefore, likely to be cohesive. However, such measurements might not be required to make this determination. There are indications from the handling of hot-cell samples^(e) and from electron microscopy

^(a) Some materials are adhesive for different reasons, but these reasons are of reduced importance for tank waste. Some materials are sticky as the result of interfacial tension or high viscosity effects. Honey, for example, is sticky because of its extremely high viscosity and not because of interparticle attractive forces (as is the case for some tank sludge).

^(b) Tingey, JM, RD Scheele, ME Peterson, and MR Elmore. 1990. *Characterization of Double-Shell Tank 103-AW*, letter report for Westinghouse Hanford Company prepared by Pacific Northwest Laboratory, Richland, Washington.

^(c) Specific surface area is defined as the particulate surface area per unit mass of particulate and is usually reported in units of square meters per gram of solid. Specific surface area can be measured through a variety of gas- and surfactant-absorption techniques.

^(d) Sludge-like materials will be cohesive provided that the repulsive effects of particle electrostatic charges are overcome by the interparticle attractive forces. This is generally the case when the ionic strength of the interstitial fluid is high. High ionic strength is characteristic of most tank sludge. If ionic strength is low, the sludge will be less cohesive and, therefore, easier to dislodge and transport. The assumption of high ionic strength for all sludge is conservative.

^(e) Tingey, JM, RD Scheele, ME Peterson, and MR Elmore. 1990. *Characterization of Double-Shell Tank 103-AW*, letter report for Westinghouse Hanford Company prepared by Pacific Northwest Laboratory, Richland, Washington.

examinations^(a) that at least some of the tank sludge has a high specific surface area and is also highly cohesive and sticky.

As mentioned earlier, saltcake waste is not expected to exhibit sticking behavior to the same extent as will tank sludge. The particles that will be generated through the dislodging and cutting of the saltcake will likely be in the 0.0005- to 5-cm-size range. Particles smaller than 0.0001 cm (1 micron) are needed to form highly cohesive pastes. Mechanical cutting and crushing operations typically generate few particles in the sub-micron range (Perry and Green 1984), so it is not expected that the saltcake cuttings from the waste-dislodging unit will contain enough sub-micron particles to create a cohesive, sludge-like paste.

It is possible for saltcake particles to bind together through a chemical cementation process, but it is unlikely that this would occur within the waste-conveyance line. At the points where saltcake particles touch each other, a surface-curvature effect reduces the local solubility of salts. Salts present in the interstitial liquid will be driven to precipitate near the particle-to-particle contact points until the curvature of the solid/liquid interface is sufficiently reduced. These precipitating salts form the bonds between adjacent particles. Given enough time, this effect will increase the bulk strength characteristics of the bed of saltcake particles. The time-scale for the formation of these bonds, however, is diffusion-controlled and probably on the order of minutes or hours. The residence time of saltcake particles inside the conveyance line is on the order of a few seconds, and the particles are kept in constant motion by the turbulent flow; thus, it is highly unlikely that this effect could play a role in waste conveyance under normal circumstances.

If saltcake particles are able to accumulate within the conveyance line, however, this interparticle-cementing effect could result in the initially loose accumulation of particles consolidating into a very hard mass. This could result in a progressive choking of the conveyance line and/or slugging when large chunks of consolidated saltcake break free. This effect may also apply to the collected saltcake cuttings in the retrieval system receiver tank. If the saltcake cuttings are allowed to settle and remain unmixed for sufficient time, they may bind together and form a difficult-to-retrieve mass.

Problems associated with waste cuttings sticking and accumulating within the conveyance lines will be avoided, it is planned, by surrounding the cuttings with enough water (or another liquid such as tank supernate) to minimize sticking. Pneumatic-conveyance systems have been tested at Hanford using this approach and very sticky, clay-based sludge simulants were conveyed at high rates for short periods (Wellner 1993). It has not yet been established whether the addition of a "lubricating film" of water at the air-conveyance line inlet will prevent the accumulation of sticky sludge simulants indefinitely.

Waterjet-pump-conveyance systems use the jet-pump fluid to both size-reduce the cuttings and to reduce the potential for sticking. The jet-pump water-to-waste ratio employed in a jet-pump-based system is likely to be considerably greater than that in a pneumatic-conveyance system. This higher ratio makes it less likely that waste cuttings will accumulate on the walls of the conveyance line. There is some concern over whether the waste volume increase that results from this increased dilution ratio is

^(a) Virden, JW, J Liu, BC Bunker, VS Stenkamp, and L Song. 1994. *Solids Formation and Sludge Dissolution: Final Report for FY1994*. TWRSP-94-092, letter report prepared for Westinghouse Hanford Company by Pacific Northwest Laboratory, Richland, Washington.

acceptable, but some waste dilution will be required to transport the retrieved-waste slurries through the existing transfer pipelines, so the jet-pump dilution might not be a significant issue.

The lubricating film water used in the pneumatic-conveyance system and the jet-pump fluid used for jet-pump conveyance may affect the chemical and rheological properties of the waste. In general, these effects will be favorable in the sense that conveyance will be facilitated. It seems unlikely that adverse dilution effects will be encountered. Several possible dilution effects are considered below.

If the diluting fluid is water or a lower concentration salt solution, then dilution will decrease the ionic strength of the fluid surrounding the waste cuttings. Some fraction of the saltcake cuttings would be expected to dissolve in response to this dilution. Saltcake dissolution would continue until the interstitial fluid reaches saturation. This process might not occur fast enough to be of any significance for conveyance, but its effect is expected to be favorable. The smallest saltcake particles would be expected to dissolve most rapidly thereby leaving a slightly larger saltcake cuttings particle-size distribution. This should not affect the conveyance significantly. Despite the fact that the relative fraction of larger particles increases somewhat, there are still the same number of larger particles to convey.

Decreasing the ionic strength (by dilution) of sludge-like waste is expected to result in favorable effects on conveyance as well. Decreases in ionic strength usually result in greater electrostatic repulsion between particles due to double-layer expansion effects (Hiemenz 1986). Increases in repulsive forces result in a net decrease in the strength of interparticle attraction and, thus, a decrease in cohesiveness. Decreasing the ionic strength of the sludge interstitial fluid will make the sludge less likely to adhere both to itself and to the conveyance-line walls.

Dilution may also bring about some chemical-phase changes that may affect conveyance. Any additional solids dissolution is expected to be favorable (whether it be sludge solids or saltcake) because it results in a net decrease in solids loading of the conveyed slurry. However, there is the potential for dilution to induce the precipitation of new solids from the interstitial fluid. Some tank sludges contain large amounts of aluminum, some of which is in the form of dissolved aluminum hydroxide ($\text{Al}(\text{OH})_4^-$ ion). At high pH (i.e., above about 12.0), aluminum hydroxide is readily soluble, but at lower pH, the chemical equilibrium shifts toward the insoluble form ($\text{Al}(\text{OH})_3(s)$). Dilution of the waste slurries could cause the precipitation of significant quantities of aluminum hydroxide if the dilution causes a sufficiently large decrease in pH. The solubility of aluminum hydroxide is shown as a function of pH at 25°C in Figure 4.1. Depending upon the initial pH of the waste solution, the amount of aluminum hydroxide dissolved, and the chemical characteristics of the diluent, precipitation of some aluminum hydroxide might occur. The data shown in Figure 4.1 imply that dilution with water will not induce aluminum hydroxide precipitation because the decrease in solubility as pH is decreased (from water dilution) is less than the decrease in aluminum hydroxide concentration. Diluting with an acidic liquid, or one laden with aluminum ions, could result in precipitate formation. This effect should be considered when selecting the lubricating film liquid and/or the jet-pump fluid.

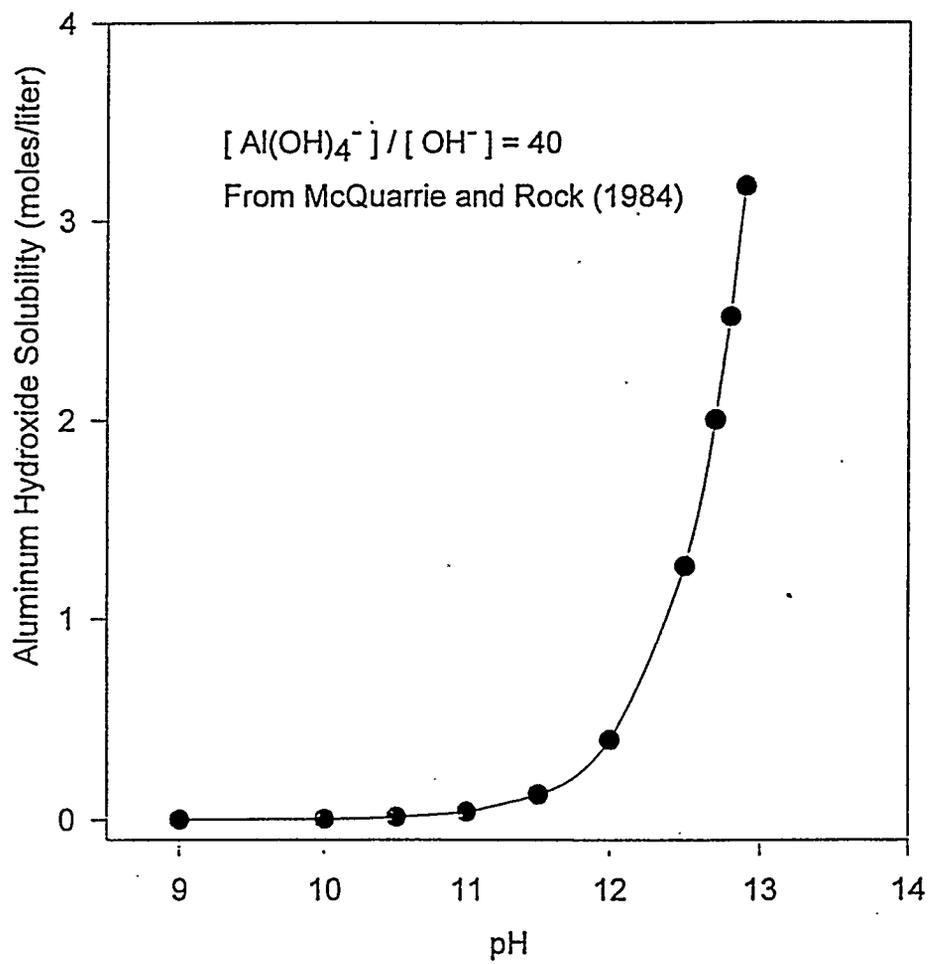


Figure 4.1. Aluminum Hydroxide Solubility vs. pH

4.1.3 Conveyance-Line Erosion

The third, and final, aspect of conveyance system operation to be considered is the erosion of the conveyance line and associated equipment by the moving waste solids. A review of the available literature reveals that erosion of pneumatic-conveyance system components due to particulate impact and abrasion is a common problem, but there are no accurate means for predicting erosion based on the properties of the conveyed material and the operating characteristics of the conveyance system (Burnett 1993). Erosion of the conveyance line in jet-pump-conveyance systems is expected to be less problematic, but relatively little data are available to evaluate erosion of the jet-pump surfaces. It is expected, however, that jet-pump erosion problems can be avoided through the judicious choice of pump materials. Erosion in pneumatic-conveyance systems, by contrast, may require careful attention to avoid premature failure of the conveyance line. Special materials and equipment designs have been proven effective for controlling wear in pneumatic conveyance systems (Wypych and Arnold 1993).

The waste and simulant properties that influence pneumatic-conveyance line erosion rates have not been determined. The erosive effects of particle size, shape, and hardness do not follow consistent trends (Burnett 1993). Therefore, to study the effects of particulate erosion on the planned waste-conveyance systems, it is necessary to select waste simulants that match many of the expected waste physical properties.^(a) A consideration of the nature of erosion in pneumatic-conveyance systems leads to the conclusion that particle size, shape, density, and mechanical strength should largely determine erosion rates. The appropriate measure of mechanical strength is not known, but as a first approximation will be taken as shear and compressive strengths. Fracture toughness and saltcake granule strength may also have a significant effect on conveyance line erosion.

Testing is required to identify the properties that determine erosion in conveyance systems. The strategy used to develop simulants for testing uses an iterative process that includes postulating key simulant properties, testing, and waste characterization (see Section 2.0). The simulant-development strategy is used to identify key simulant properties needed to develop process performance correlations or to evaluate various process operation scenarios. For the problem of conveyance-system erosion, however, performance correlations are of reduced interest. The principal desire at this point is to determine whether erosion is a problem. If testing indicates that it is, then testing with additional simulants may be required to determine whether the selection of robust materials and specially designed components can extend the conveyance-line lifetime to an acceptable length. To address the near-term question of whether erosion is likely to be a problem, testing should be done using near-prototypic conveyance-system components (in terms of materials used) and simulants designed to match the postulated waste key physical properties.

^(a) Waste and simulant chemical properties are unlikely to be relevant to the study of conveyance-system erosion other than in terms of how chemistry affects physical properties. This assumes that conveyance-system materials are selected such that chemical-corrosion effects are minimal.

4.2 Recommended Waste Simulants for Conveyance Testing

The simulants that should be used for conveyance-system testing are described in this section. For each of the conveyance-system testing needs, the recipe(s) for a simulant or set of simulants is given along with a description of the justification for selecting each of the recommended simulants. Simulants are specified for each of the aspects of conveyance-system operation described earlier: steady operating capabilities; plugging, choking, and slugging; and erosion of the conveyance system.

4.2.1 Steady Operating Capabilities

The goal of this aspect of conveyance-system testing is to develop correlations that allow the prediction of conveyance rates, power requirements, and equipment size based on the properties of the conveyed materials and the operational parameters of the system (e.g., lubrication water flow rate and volume fraction of waste being conveyed). As described earlier, it is expected that the key waste/simulant properties for these correlations are particle size, density, and shape, which taken together determine the aerodynamic settling velocity of the particles.

To examine the effects of these key properties on process performance, the following simulants should be tested:

- Simulant #1: Crushed Rock. Shape is angular and random. Size ranges from 1 to 3 cm with an average of about 2 cm. Density is determined by mineralogy, but ranges from 2.6 to 3.0 g/cm³.
- Simulant #2: Pea Gravel. Shape ranges from elliptical to spherical but is generally smooth. Size ranges from 0.5 cm to 1.5 cm with a mean of approximately 1 cm. Density is determined by mineralogy, but ranges from 2.6 to 3.0 g/cm³.
- Simulant #3: Sand. Particle shape ranges from cubic to spherical. Size range is from 0.1 cm to 0.3 cm with a mean of approximately 0.2 cm. Density is determined by mineralogy, but ranges from 2.6 to 3.0 g/cm³.
- Simulant #4: Course-grained potassium-magnesium sulfate fertilizer (K-Mag). Particle size and shape should be similar to that expected from the action of a waste dislodging tool on saltcake waste. These data will be obtained from dislodging tool testing.

The densities of all four simulants are slightly higher than, but comparable to that expected from the saltcake tank waste.^(a) The primary variable is the particle diameter. By correlating conveyance system performance to particle diameter, it may be possible to optimize the cuttings size produced by the waste dislodger such that the performance of the integrated system is near optimal.

^(a) Tank saltcake is composed primarily of sodium nitrate, nitrite, carbonate, and sulfate. The densities of these salts range from 2.2 g/cm³ to 2.7 g/cm³ (Weast 1982). Density data for actual tank saltcake samples are not available.

4.2.2 Plugging, Choking, and Slugging

As described earlier, the tendency of saltcake and sludge cuttings to adhere to the conveyance system components is expected to be determined by the waste's cohesiveness. Previous work has demonstrated that in some dense particulate systems (e.g., sludge), cohesion is a function both of the volume fraction solids and the specific surface area of the solids (Powell et al. 1995).

If it was desired that a correlation be developed between conveyance-line plugging and waste properties, then it would be necessary to test the conveyance systems of interest using a wide variety of waste simulants. These simulants would differ widely in cohesiveness as well as any other postulated key properties. While this type of approach is valuable in many applications, it is probably not warranted here. There are indications from previous testing that the conveyance of sticky materials is not problematic for either pneumatic- or jet-pump-conveyance systems, provided that sufficient "lubricating" water is injected at the entrance to the pneumatic-conveyance line (Wellner 1993). If this can be verified for long-term conveyance system operation using conservatively sticky simulants and an acceptably small rate of lubricating water flow, then the concerns with plugging, choking, and slugging (in most cases) can be dismissed.

It is recommended that conveyance-system tests be conducted using conservatively sticky sludge simulants in an effort to establish whether sludge is likely to adhere to the conveyance line. As discussed earlier, saltcake cuttings are not expected to present problems to the same degree as the more sticky sludge. The sludge simulants specified below should be tested using the maximum allowable lubricating water flow (for pneumatic conveyance) to determine whether sludge simulant accumulates within the conveyance line. If simulant accumulations are minimal, further testing should be done using a low lubricating water flow rate.^(a)

If the conveyance system being tested can successfully transport (without accumulation) all the simulants given below at both the high and low lubricating water flow rates, then confidence is high that adhesion of waste cuttings to the conveyance line will not be a problem during retrieval. Because the jet-pump-conveyance system does not require additional lubricating water, it will be sufficient to demonstrate successful long-term conveyance of these simulants only once using the jet pump. The conveyance systems being tested should be fed waste simulant in the form expected to be produced by the candidate waste-dislodging units.

Both candidate conveyance systems, of course, must be tested in vertical, horizontal, and diagonal orientations to ensure that successful conveyance in the test system can be extrapolated to the full-scale system. Consideration should also be given to whether the test conveyance system is constructed from the same materials as is intended for the full-scale system. System scale-up, orientation, and materials effects should be considered and addressed in the conveyance testing plans.

^(a) The actual flow rate used should be low enough that it is essentially insignificant; that is, the flow rate should be low enough such that making the flow rate lower has a negligible negative impact on the overall retrieval operation. The flow rate should, however, be high enough such that a higher flow rate *would* have adverse effects on the overall retrieval operation.

The simulants recommended for testing to investigate potential plugging, choking, and slugging problems are:

- Simulant #1: 67 wt% EPK Pulverized Kaolin Clay in Water. Suggested manufacturer is Feldspar Corp. (Edgar, FL)
- Simulant #2: 30-35 wt% Custom Sealant-50 (CS-50) Bentonite Clay in Water. Suggested manufacturer is American Colloid Company (Arlington Heights, IL)
- Simulant #3: 61.4 wt% EPK Pulverized Kaolin Clay, 2.6 wt% CS-50 Bentonite Clay in Water
- Simulant #4: Min-U-Sil 30 silica powder. Suggested manufacturer is Pennsylvania Glass Sand Corp. (Berkeley Springs, WV).

The clays and silica may be obtained from alternate manufacturers, but tests will be required to ensure that the properties of the resulting simulants do not differ significantly from those of simulants prepared using the manufacturers specified above.

Simulants 1 through 3 are very sticky sludge simulants and are expected to be as or more adhesive than tank sludge, based on the expected sludge-particle sizes. Simulant 4 is a non-cohesive powder, which may accumulate within the conveyance line but by a different mechanism than the sticky materials. The justification for each of these simulants is given below.

As described earlier, the stickiness of a sludge or sludge simulant is a function of the specific surface area of the sludge particulate. In general, the behavior of particles with a specific surface area of greater than 25 m²/g is dominated by colloidal forces. Under the right conditions, the interparticle attractive forces overcome repulsive forces and the net attractions give rise to cohesiveness. Particulate systems with specific surface areas of less than about 25 m²/g exhibit cohesion to a lesser extent.

Kaolin clay has a specific surface area of about 10 m²/g and that of bentonite is about 800 m²/g (Lambe and Whitman 1969). Bentonite is highly cohesive and its behavior is dominated by colloidal forces. Kaolin, however, is influenced by a combination of colloidal and body-type (e.g., inertial and frictional) forces (Powell et al. 1995).

Direct measurements of the specific surface area of tank-waste sludge have not been made. Particle-size analyses, however, indicate that tank sludge specific surface areas likely range from below 10 m²/g to as high as 200-300 m²/g (see footnotes b and c on page 4.3). The range of specific surface areas for the sludge simulants specified above adequately encompasses the range expected from tank sludge. Thus, it is expected that the specified sludge simulants are conservative in the sense that they bracket the expected tank-sludge adhesiveness and cohesiveness.

Despite the high specific surface area of bentonite clay, it is not certain whether bentonite will provide a greater challenge to conveyance systems with respect to plugging, choking, and slugging. This is because bentonite exhibits a behavior known as osmotic swelling, which is likely to reduce the tendency of pieces of bentonite-based sludge simulant to adhere to the conveyance system components. When a bentonite sludge simulant is exposed to water at its surface, the water is drawn into the bentonite gel structure. This occurs rapidly enough that the resulting weakening of the simulant near its surface is

expected to reduce, greatly, the tendency of chunks of wetted bentonite simulant to adhere to conveyance-system components.

The kaolin clay simulant does not exhibit any significant osmotic swelling (Powell et al. 1995) and, for this reason, the kaolin may present a greater challenge to the conveyance systems with respect to sludge stickiness.

The osmotic swelling of the bentonite clay is due to the double-layer repulsion between the surfaces of the bentonite particles. Due to impurities in the crystal lattice of clay minerals, the surface of clay particles are negatively charged under most conditions. This negative surface charge electrostatically attracts a cloud of cations that tend to diminish the electric field of the negative particles. When two bentonite particles are close enough, their respective cation clouds will overlap. This creates a repulsive force because the positively-charged cations electrostatically repel each other. The swelling of the bentonite clay is termed osmotic swelling because the water outside the clay permeates into the region between particles in an effort to equalize the local high cation concentration with that of the water far away from the particles. This influx of water tends to push the particles apart until double-layer overlap is no longer significant (van Olphen 1977).

The degree to which a clay will imbibe water due to osmotic swelling depends on the average double-layer thickness compared to the distance between adjacent clay particles. Double-layer thickness is determined by the clay's surface-charge density, which is a function of its mineralogical composition, and by the ionic strength of the fluid surrounding the clay. The distance between clay particles is a function of the weight fraction of clay in the clay/fluid mixture. White and Pichler (1959) studied the rate of water absorption of several different clay types. Beyond the liquid limit of each clay, osmotic swelling was small or non-existent for illite clay, kaolin clay, and calcium-bentonite clay. Sodium-bentonite, however, showed continuing osmotic swelling even when the concentration of clay had fallen to about 12 wt%. The swelling of sodium-bentonite is expected to cease when the particles are so far apart that double-layer repulsions are balanced by the attractive van der Waals and edge-to-face cross-linking forces (van Olphen 1977). Calcium-bentonite does not show the same continuous swelling as the sodium-bentonite due to the capability of the calcium cations to compress the double-layers. In calcium-bentonite, the wt% clay at which the double-layers cease to overlap is higher than for sodium-bentonite. The bentonite specified above is a sodium-bentonite clay.

Osmotic swelling up to about the liquid limit is commonly observed in concentrated dispersions like clay pastes when the behavior of the particles is principally governed by colloidal effects. Osmotic swelling is not observed in dispersions of large particles like sand because colloidal effects do not affect sand particles significantly.

The kaolin/bentonite mixture (Simulant #3) is formulated to provide a highly cohesive sludge simulant that is also nonswelling. By mixing a small amount of bentonite clay with the kaolin, the average specific surface area of the mixture is sufficiently elevated such that the simulant behavior is colloidally dominated. The tendency of the bentonite clay to imbibe water is greatly reduced by the presence of the kaolin (Powell et al. 1995). It is expected that the kaolin/bentonite mixture simulant will present the greatest challenge to conveyance in terms of combined stickiness and immunity to the "lubricating" effects of water.

Simulant #4 is a noncohesive simulant composed simply of crushed-silica particles in the size range of roughly 1 to 40 microns. Particles in this size range have a tendency to form tightly-packed cakes when mixed with a small amount of water. The apparent mechanical strength of a wet particulate cake varies considerably depending on the particle-size distribution, moisture content, and how the cake was prepared. Experience has shown that the specified material (Min-U-Sil 30 silica) forms moderately strong cakes when mixed with a small amount of water or when allowed to settle out from a dilute slurry.

The strength of wet, tightly packed particulate beds is due to the effects of dilatancy. In response to an applied strain, the bed volume must increase slightly to enable the particles (which are initially tightly packed) to slide past each other. The bed expansion and particle movement are resisted by the viscosity of the interstitial liquid.

The formation of a dilatant bed of particles within a conveyance line is a different mechanism for line plugging than postulated earlier for sticky sludge-like materials. Particles in the size range of Simulant #4 do not possess significant interparticle attractive forces and are, therefore, not very adhesive or cohesive. Because of the lack of significant attractive forces, however, these particles can pack to a very high volume-fraction of solids, which exhibit dilatancy when a strain is applied.

It is postulated that particulate in the 1- to 40-micron-size range could accumulate near conveyance system bends or in horizontal sections and form a densely packed cake. Simulant #4 has been proposed to investigate this possibility. Considering the fluid velocities involved in both pneumatic and waterjet conveyance, it seems unlikely that such cakes would form, but the possibility cannot be eliminated at this time. Demonstration of successful, long-term conveyance using the Min-U-Sil 30 simulant should be sufficient to resolve this concern.

4.2.3 Conveyance-Line Erosion

As mentioned earlier, the waste properties expected to determine the erosion rates for conveyance system components are not well understood. Thus, it is not possible to specify waste simulants with enough certainty to allow the accurate prediction of full-scale system-erosion rates based on measurements using simulants. The goal of the recommended testing at this point must be limited to determining whether or not conveyance system erosion is likely to be a problem. If testing with the simulant specified indicates that erosion may be a problem, then a more exhaustive examination will be warranted, based both on literature data and on the results of testing.

It is recommended that conveyance testing be completed using the same K-Mag saltcake simulant that has been used to test candidate waste-dislodging systems. The particle size and shape of the saltcake simulant fed to the conveyance system should be representative of that produced by the waste dislodging tools of interest. This saltcake simulant has been formulated to possess mechanical-strength properties (i.e., shear and compressive strengths) similar to or stronger than those expected from saltcake waste.

The results of conveyance-system erosion testing using the K-Mag simulant will be evaluated to determine whether further testing and simulant development are required. If there is no evidence of conveyance-system erosion using the K-Mag simulant, then there is reasonable confidence that system erosion will not be of great concern for the full-scale conveyance systems.

5.0 References

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