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Properties Important to Mixing and Simulant Recommendations for WTP Full-Scale Vessel Testing

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EXECUTIVE SUMMARY

Full Scale Vessel Testing (FSVT) is being planned by Bechtel National, Inc., to demonstrate the ability of the standard high solids vessel design (SHSVD) to meet mixing requirements over the range of fluid properties planned for processing in the Pretreatment Facility (PTF) of the Hanford Waste Treatment and Immobilization Plant (WTP). Testing will use simulated waste rather than actual Hanford waste. Therefore, the use of suitable simulants is critical to achieving the goals of the test program. WTP personnel requested the Savannah River National Laboratory (SRNL) to assist with development of simulants for use in FSVT. Among the tasks assigned to SRNL was to develop a list of waste properties that are important to pulse-jet mixer (PJM) performance in WTP vessels with elevated concentrations of solids.

SRNL personnel previously prepared a document describing important properties for simulants for a comparable WTP test program. The purpose of this document is to update the properties that matter based on the current test objectives and information obtained since issuance of the previous document.

The following objectives are the focus of this report.

- Assess physical and chemical properties important to the testing and design verification.
- Identify the governing properties and associated ranges for FSVT to achieve the Newtonian and non-Newtonian slurry test objectives.

The test objectives for FSVT may include the following.
- Determine the operating conditions needed to obtain complete bottom motion and whether the SHSVD can achieve those conditions.
- Determine the extent of solids accumulation following a prototypic pump out and whether this amount of accumulation is acceptable.
- Demonstrate successful transfer of the slurry and select components from the vessel through the pipeline and pump.
- Determine the ability of the PJMs to release gas that has been retained by the vessel contents. This objective is assumed to be out of scope at this time.
- Determine whether a representative sample can be obtained from the vessel.
- Determine the time required to blend miscible liquids in the vessel under prototypic operating conditions.

The slurry properties most important to FSVT depend on the test objective and rheological classification of the slurry (i.e., Newtonian or non-Newtonian).

Review of the existing data on Hanford waste as well as the mixing performance criteria for the vessels indicate that the most important parameters for testing with Newtonian slurries are the particle size, particle density, and the particle concentration (on a slurry basis). Particle size distribution is important and should be considered in simulant development rather than just a median particle size or a maximum particle size. In addition, the particle size and density must be considered together since their influence on mixing is highly correlated and since they are correlated in the waste during processing. They can be combined in a dimensionless parameter such as the Archimedes number or in an engineering metric such as settling velocity or critical suspension velocity. For some test objectives, the settled solids shear strength is important. The density of the bulk liquid by itself does not have a significant effect. However, the density difference between the bulk liquid and added liquid can have a significant effect if the difference

is large enough to cause stratification. Because of particle settling between pulses, liquid viscosity can have a significant effect under some conditions.

The most important properties for testing with non-Newtonian slurries are the slurry yield stress, the slurry consistency, and the slurry shear strength. The solid-liquid density difference and the particle size are also important. The slurry yield stress, solid-liquid density difference, and particle size can be combined in a dimensionless Yield parameter. It is also important to match multiple properties (e.g., yield stress and shear strength) within the same simulant to achieve behavior representative of the waste.

Other properties such as particle shape, concentration, surface charge, and size distribution breadth, slurry cohesiveness and adhesiveness, liquid pH and ionic strength also influence the simulant properties either directly or through other physical properties such as yield stress or particle size. These properties could affect Newtonian slurries or non-Newtonian slurries.

The FSVT will also include limits determination tests. One option for determining limits in meeting mixing requirements is via extending selected properties of the simulants beyond the bounding values discussed in this document.

The recommendations for properties for full-scale vessel testing follow.

- Particle Size

   For Newtonian fluids and non-Newtonian fluids, the recommended range of particle size to be investigated is 1 – 700 micron. The 700 micron particle size is based on the design basis fluid properties (and a particle density of 2.9 g/mL). Limits could be assessed by including a larger particle in the simulant. Since the WTP feed will likely contain particles less than 1 micron, the use of submicron particles should be considered in developing simulants.

- Particle Density

   Particle density should be selected to represent the densities of select particles that exist in Hanford waste. The simulant needs to have particles representative of the largest particles in the feed, the major aluminum compounds in the feed, small dense particles such as PuO_2 or Bi_2O_3, and the fine particles in the feed. Limits are more easily assessed by increasing the particle size rather than the particle density.

- Shear Strength of Settled Layers

   The simulant shear strength to evaluate PJM restart relative to gas retention and release should be 1500 Pa. This limit is based on a single measurement of an actual Hanford waste sample that sat for 72 hours.

- Yield Stress and Consistency for non-Newtonian Simulants

   The slurry yield stress should range between 0 Pa and 30 Pa. The slurry consistency should range between 1 cP and 30 cP. To assess limits, the slurry yield stress should be increased to 40 Pa, and the slurry consistency should be increased to 40 cP. These values are based upon the estimated measurement and sampling uncertainty in yield stress and consistency measurements. Low values of yield stress and consistency (e.g., 0 Pa and 1 cP) may allow fast-settling particles to settle in these fluids, creating a challenge to meeting vessel mixing requirements.

- Solids Concentration

   The recommended insoluble solids concentration for tests with Newtonian fluids is 0 – 20 wt %. To assess limits, the insoluble solids concentration should be increased to 27 wt %. For non-Newtonian fluids, the insoluble solids concentration should be that which is needed to achieve the desired rheology.

- Viscosity

   The recommended viscosity for Newtonian fluids is 1 – 10 cP.

- Physical simulants should be adequate for most or all of the potential test objectives. For the following potential test objectives chemical simulants are recommended: measuring gas retention and release, assessing foaming, assessing aerosol generation, and assessing the impact of aging on slurry rheology. These potential objectives are not part of the current test plan.

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LIST OF ABBREVIATIONS

BNI	Bechtel National, Inc.
CFD	computational fluid dynamics
DNFSB	Defense Nuclear Facilities Safety Board
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
ECR	effective clearing radius
HLP	HLW Lag Storage and Feed Blending Process
HLW	High Level Waste
ICD	Interface Control Document
i.e.p.	Isolelectric Point
IP	Implementation Plan
LAW	Low Activity Waste
FSVT	full-scale vessel testing
ORP	Office of River Protection
PEP	Pretreatment Engineering Platform
PJM	pulse jet mixer
PNNL	Pacific Northwest National Laboratory
PSD	particle size distribution
PSDD	particle size and density distribution
PTF	Pretreatment Facility
SHSVD	Standatd High Solids Vessel Design
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
UDS	undissolved solids
UFP	Ultrafiltration Process
V&V	verify and validate
WTP	Waste Treatment and Immobilization Plant

LIST OF SYMBOLS

a	longest particle dimension in Corey's shape factor
Ar	particle Archimedes number
b	intermediate particle dimension in Corey's shape factor
c	shortest particle dimension in Corey's shape factor
C	settling regime constant for Re_P to Ar relationship
d_S	particle diameter based on a sphere of equal volume
d_P	particle diameter
g	gravitational acceleration
n	settling regime constant for Re_P to Ar relationship
Re_P	particle Reynolds number
S_F	Corey's shape factor
V_S	terminal settling velocity
$\dot{\gamma}$	shear rate
η	Bingham plastic consistency
ν_L	liquid kinematic viscosity
μ_L	liquid viscosity
ρ	density
ρ_L	liquid density
ρ_S	particle density
τ	shear stress
τ_{YS}	Bingham plastic yield stress

1.0 Introduction

1.1 <u>Hanford WTP Background</u>

Bechtel National Inc., (BNI) is designing and constructing the Waste Treatment and Immobilization Plant (WTP) at the Hanford Site to pretreat and vitrify waste stored in single- and double-shell underground waste storage tanks. The WTP will consist of three primary processing facilities: a Pretreatment Facility (PTF), a Low-Activity Waste (LAW) vitrification facility, and a High-Level Waste (HLW) vitrification facility. The PTF will receive waste feed from the Hanford tank farms (composed of insoluble solids suspended in an aqueous liquid containing dissolved salts and radionuclides) and will separate it into:

- a high-volume, low-activity, liquid process stream stripped of most solids and radioisotopes, and
- a much smaller-volume HLW slurry containing the solids and most of the radioactivity, along with minimal soluble salt (due to the soluble salts being washed out of the HLW).

In the PTF, solids and radioisotopes will be removed from the waste received from the tank farms by precipitation, filtration, and ion exchange processes, producing the LAW stream. The washed, concentrated slurry will be blended with the ion exchange eluent streams containing soluble radioisotopes to produce the HLW stream. The HLW and LAW vitrification facilities will receive these streams from the PTF for conversion into molten glass, which will be poured directly into stainless steel canisters for long-term storage.

Numerous vessels are used to process the PTF streams, many of which employ PJM technology for mixing. The vessels may also include air sparging systems. These technologies have been selected for use in black cells in WTP. The black cells will not allow entry after commissioning. Because of the high radiation in the black cells, conventional maintenance of the vessels and components inside the cells is not feasible for the operating life of the WTP. PJM technology was selected for use in the black cells because it lacks moving mechanical parts that would require maintenance within the cell.

PJM technology will be used in the WTP for slurry mixing applications requiring solids suspension and solids mixing, as well as for fluid blending and release of hydrogen gas. The PJMs operate in different modes. The suction phase draws process fluid into the pulse jet tube from the vessel. The drive phase pressurizes the PJM tubes with compressed air, discharging the fluid at high velocity back into the vessel causing mixing to occur. The drive phase is followed by a vent phase, which allows for depressurization of the PJM by venting air into the pulse jet vent system. These three phases (suction, drive, and vent) make up the PJM cycle. The combined suction, drive, and vent cycle time for the major slurry processing vessels occurs over several minutes. In PJM-mixed vessels, solids will tend to settle between PJM drive phases and while the PJMs are idle during some process cycle stages.[1]

In 2014, the U. S. Department of Energy (DOE) – Office of River Protection (ORP) and BNI chose to investigate a standard design for the vessels containing high concentrations of insoluble solids in the WTP (i.e., the most challenging vessels to mix). This standard design is referred to as the standard high solids vessel design (SHSVD).

1.2 Purpose and Scope

As part of the design verification process for the SHSVD, WTP personnel will conduct full-scale vessel testing of the prototypical design. A key aspect of the testing is developing an appropriate and defensible simulant. This document identifies the recommended characteristics for test simulants needed to perform the FSVT. In 2012, SRNL performed an analysis to identify the important properties of simulants for the large scale integrated test program.[2] The purpose of this document is to revise and update the important properties of simulants for the planned standard high solids vessel design testing.

The physical and chemical properties of Hanford waste applicable to FSVT are reviewed in Section 2 of this report. Recommended simulant properties for FSVT testing for both Newtonian and non-Newtonian slurry tests applicable to WTP are summarized in Section 3. The analysis considered the properties and property groupings listed below to address the needs of the test program. Though not all of the following properties are independent, they were considered and evaluated for their relative importance to mixing and related FSVT objectives.

- Particle size
- Particle size distribution (PSD)
- Particle density
- Particle size and density distribution (PSDD)
- Particle shape
- Liquid phase density
- Particle-liquid density difference
- Liquid phase viscosity
- Undissolved solids (UDS) mass and/or volume fraction
- Slurry rheological properties (Bingham yield stress and consistency)
- Slurry thixotropic and rheopectic behavior
- Shear strength of settled waste
- Archimedes number distribution
- Yield parameter
- Critical shear stress for erosion
- Slurry cohesiveness and adhesiveness
- Liquid phase pH
- Liquid phase ionic strength
- Particle isoelectric points (i.e.p.)
- Particle zeta potentials
- Settling velocity
- Critical suspension jet velocity
- Radial jet velocity needed to achieve a certain degree of suspension
- Critical pipeline transport velocity
- Just off bottom suspended impeller speed
- Just suspended jet velocity
- Cloud height

Some of the properties listed above are affected by operating and test parameters such as time and temperature. Some of the properties are not well characterized for Hanford waste, but the fact that data are not available for a property does not alter its significance to mixing. There are methods for preparing simulants with similar properties to actual waste based on first principles.

The basis for deciding which simulants can be physical simulants (i.e., matched to physical properties of the waste streams) and which may need to be chemical simulants (i.e., matched to chemical composition and possessing selected chemical behavior) was also evaluated. The analysis considered conditions both prior to and after the caustic leaching step in PTF operations to address changes in waste properties during processing. This report provides technical justification for a set of simulant properties for full scale vessel testing.

An additional property, particle/slurry abrasiveness, was considered but is excluded from this document because it falls outside of the scope for the FSVT test program.

1.3 Simulant Selection Process

Simulant development, verification, validation, and documentation are governed by a WTP simulant development guide.[3] The guide outlines the following five sequential steps to assure that a simulant is relevant to the test objectives.

1. Define Scope for Simulant Use
2. Specify Simulant Requirements (chemical composition, physical and rheological properties)
3. Design Simulant and Specify Preparation Procedure
4. Verify and Validate Simulant Meets Requirements
5. Finalize Simulant Design Documentation

2.0 Physical Properties that Influence Mixing Behavior

2.1 Mixing Behavior of Interest

In identifying the waste properties important to mixing, one must consider physics and chemistry [The chemistry is described in section 2.3]. In describing the physics, the authors consider five phenomena to be important: particle settling, particle suspension, shear, bubbles rising, and radial wall jets.

One of the key phenomena in the PJM mixed vessels is the settling of solid particles during and between pulses.[4] The settling is due to density differences between the solid particles and the liquid. The settling rate increases with increasing particle size and with increasing solid-liquid density difference. Settling rate decreases with increasing liquid density and viscosity. For dilute slurries, the particle concentration does not affect the settling rate, but when the particle concentration becomes large, the settling rate decreases (i.e., hindered settling).

Another phenomenon is solid particle suspension.[5] The fluid motion produced by the PJMs must overcome gravity and inertia to lift the solid particles off the vessel bottom. Three forces are acting on the solid particles at the bottom of the vessels during PJM mixing: gravity, hydrodynamic lift, and drag. In addition, particle-particle interaction forces can exist between the particles. Gravity causes the particles to settle to the bottom of the vessel. Particle suspension occurs when the lift forces exceed the force of gravity acting on the particle. In some instances, the particle-particle interaction forces lead to a yield stress or shear strength that must also be overcome before the particles begin to move and are lifted off the bottom.

Another phenomenon is shear.[6] All fluids have a resistance to movement. This resistance can be described by physical properties such as viscosity, yield stress, shear strength, and critical shear stress for erosion. Viscosity is a measure of the resistance of a fluid to deformation under shear stress in laminar flow. It applies to Newtonian fluids and any applied shear stress results in fluid motion. For fluids with a yield stress (e.g., Bingham plastic fluids), the applied stress must exceed the yield stress to start movement of a fluid. The term applies to non-Newtonian fluids and is typically used with fluids that are frequently in motion and not stagnant for a significant time. Shear strength is a term used in soil mechanics to describe the shear stress that a soil can sustain before it will move. This term is typically associated with settled solids, originating either from Newtonian or non-Newtonian slurry. The critical shear stress for erosion is the shear stress required to initiate transporting of sediment at rest on a surface. [*These properties will be discussed in greater detail later in the document in sections 2.2.2, 2.2.3, and 2.2.4.]* The force that overcomes this resistance and leads to fluid movement is a shear stress that is produced by a device such as a pump, impeller, pulsed jet mixer, or sparger. The fluid motion caused by the pulsed jet mixers must create a shear stress at the fluid-particle interface that is large enough to overcome the forces holding the particles together and lift them off of the vessel bottom or cause the fluid to begin motion.

Another phenomenon is gas rising through a fluid.[7] Mixing approaches such as gas sparging or overblows may be used to provide additional mixing of fluids in the WTP vessels. These mixing approaches create a stream of bubbles that rises through the liquid. Mixing occurs through three mechanisms: gas expansion, kinetic energy transfer, and gas rising through the liquid. Given the expected discharge pressure of the PJMs and gas spargers, as well as the required maximum distance the gas would rise (~ 18.5 ft), the expansion of the gas will not produce appreciable bulk fluid motion in the vessel. Because of the small density of the gas relative to the liquid, no significant energy transfer is expected. The rising gas will cause the surrounding liquid to move, create shear, and entrain minor amounts of the liquid as it rises. As such, rising gas through the liquid is the only mixing mechanism associated with this phenomenon.

A last phenomenon is a radial wall jet.[8] A radial wall jet occurs when a turbulent jet impinges on a planar surface. In the case of the SHSVD, the vessel bottom surface deflects the jet and causes it to spread radially. As the jet spreads radially, it forms a radial wall jet. (The jet will be slightly deformed from a radial jet due to the non-perpendicular angle of impact with the vessel bottom.) The radial wall jet entrains surrounding fluid and can lift settled solids off the vessel bottom. When the radial wall jets meet in the center of the vessel, jet momentum is directed upward to form fountains, commonly termed upwells. (Note that similar upwells exist between adjacent PJMs but these are weaker in nature in that only two jets are colliding.) These upwells are responsible for much of the vertical mixing in the vessels.

2.2 <u>Properties that Influence Mixing Performance</u>

The following subsections discuss properties that can influence PJM-mixed vessel performance. Expected property ranges are described, and the relative impacts of the properties on mixing performance are discussed. A number of the properties considered in this section have well established significance for mixing and transfer operations based on previous analyses and Hanford-related testing. For these properties, the analysis primarily provides an estimation of the relative influence of each property on PJM mixing and defines the expected WTP ranges. The properties are discussed in more or less detail depending on the likelihood of their impact on mixing and transfer operations.

2.2.1 *Particle Size and Particle Density Distribution*

Hanford waste particles come in a wide range of sizes and densities, and this influences how these particles behave when suspended in a liquid or settled on the vessel floor. Both particle size, d_P, and particle density, ρ_S, appear in numerous correlations describing particle suspension and settling behavior. Analytical PSDs have been generated for some waste samples subject to the limitations of the instrumentation and assumptions about the relationship between the shape of a particle and its mean diameter. Additionally, the samples have typically been core samples where the tank contents were not intended to be homogeneous nor were they in a slurry form in many cases when sampled. Therefore, the samples may not be representative of the tank contents upon actual sludge retrieval and preparation operations. Mean particle density can be derived from the ratio of the particle mass fraction and volume fraction. A PSDD can be estimated when assumptions are made to identify the solid phases (i.e., chemical compounds) present in the particles, their inherent density, and the degree of agglomeration. Calculations of this type have been performed for a number of waste samples for different assumed degrees of agglomeration.[9]

Fast settling particles could pose a challenge to PJM-mixed vessels in WTP. The periodic nature of the PJM cycle yields periods when settling can be the dominant phenomenon, especially in vessels containing Newtonian slurries and fast-settling particles. The FSVT simulant needs to include fast settling particles to cover the extreme risks to mixing performance. The particle size distribution impacts particle packing density and thus will influence the settled layer shear strength and critical shear stress for erosion.

Certain particles are of greater interest due to safety related concerns such as criticality. Plutonium compounds containing agglomerates in most of the waste tanks were formed from co-precipitation of plutonium with neutron absorbing isotopes of other elements. This is not the case for wastes from the Plutonium Finishing Plant that are contained in a limited number (16) of tanks.[10,11] However, the bounding fissile particle listed in the design basis is a 10 micron PuO_2 particle.[12]

The washing and caustic leaching operations of PTF are expected to change the PSD and PSDD, as well as other properties such as adhesiveness and cohesiveness. During testing of caustic leaching and washing of actual waste composites, order of magnitude reductions in particle size occurred for two of five feeds.[13] Dissolution and crossflow filtration also tend to break down agglomerates into smaller particles/agglomerates. Caustic leaching tends to dissolve compounds of aluminum preferentially, which are among the lower density species in the waste solids. Thus, there also tends to be an associated change in the average particle density toward denser particles, since the dissolved species are primarily below the average solid density. For example, caustic leaching of high iron solids increased the average particle density from 2.9 g/mL to about 3.8 g/mL.[13]

Salt particles are included in the definition of UDS in the Hanford tank farm. Salt particles may have relatively large sizes and a variety of crystal shapes.[14] The salts tend to be the more soluble components of the waste at the conditions encountered in the PTF. Complete salt dissolution is not expected for some salt components during mobilization in the tank farm. The PSDD analyses used in selection of simulants should include particle information for less-water-soluble UDS.

The following are the recommendations for ranges of particle size and density. The testing should use particles that have behavior similar to the 1- 700 µm particles in the Basis of Design.[15,9,16] The 1 µm minimum particle size is based on the 1st percentile particle size listed in

reference15.   Since the WTP feed will likely contain particles less than 1 µm, the use of submicron particles should be considered in developing simulants. [A revision to ICD-19 lists a maximum particle size of 310 μm and a critical transport velocity of <4 ft/s for particles transferred from the Hanford Tank Farm to the WTP.] The range of particle densities is 2.2 - 11.4 g/mL based on assumed primary particle density.[9] If plutonium metal is present, particle density would be as high as 19 g/mL. These recommendations are consistent with those made for related Tank Operating Contractor simulants.[17] The maximum particle size is important for suspending particles in Newtonian fluids. The maximum particle size, breadth of the PSD and the fraction of fine particles are important for suspension of particles in non-Newtonian fluids.

2.2.2 *Liquid Density and Liquid Viscosity*

Hanford waste particles are transported by the supernatant and interstitial liquid as they move from the tank farm into and through the WTP vessels. This fluid is typically a multi-component salt solution with a pH of 12 to greater than 14. Particle-free salt solutions typically exhibit Newtonian fluid behavior, a linear relationship between shear stress, τ, and shear rate, $\dot{\gamma}$, as $\mu_L = \tau/\dot{\gamma}$. The two liquid-phase properties generally associated with particle settling and suspension are liquid density (ρ_L) and liquid viscosity (μ_L), which often appear together as a ratio, the kinematic viscosity ($\nu_L \equiv \mu_L/\rho_L$). The liquid-phase densities and viscosities of salt wastes are somewhat correlated (i.e., highest viscosities are typically encountered in the highest density liquids).[18]

A system containing a Newtonian liquid plus a dispersion of non-interacting, modest to large-sized solid particles often behaves as a Newtonian fluid under shear. The slurry viscosity of such a solid-liquid system, however, is typically greater than the Newtonian viscosity of the liquid phase. The Newtonian slurry viscosity is typically a function of the particle volume fraction and PSD.

The following are the recommendations for ranges of liquid density and viscosity for Newtonian fluids. A document describing the SHSVD design basis properties and mixing requirements based on vessel operating mode shows the liquid density range to be 1.0 – 1.5 g/mL, and the slurry density range to be 1.0 – 1.7 g/mL.[19] Lower liquid density leads to reduced jet momentum (the driving force for solids suspension and liquid blending) from the PJMs and faster particle settling. In addition, simulant metrics discussed later tend to show mixing to be more challenging with lower liquid density. Testing should focus on lower density liquids. A higher density liquid should be considered in planning the miscible liquid blending tests, because of the possibility of stratification. However, parameters such as particle size, particle density, and rheology have more influence on mixing than liquid density.

The document also shows the liquid viscosity to range from 1.0 – 10 cP, and the slurry viscosity to range from 1.0 – 10 cP.[19]   Based on the expected density and viscosity, the expected range of the kinematic viscosity is $1.0 \times 10^{-6} – 6.7 \times 10^{-6}$ m^2/s for vessels with Newtonian fluids (i.e., vessels with low concentrations of solids or vessels with non-cohesive solids). Particles settle faster in lower viscosity (or kinematic viscosity) liquids, making solids suspension and liquid blending[20] more challenging. Simulant metrics discussed later show conflicting results on whether low viscosity or high viscosity is more challenging [see section 2.2.7]. Testing should use high and low viscosity simulants. In addition, most of the metrics show a weak dependence on viscosity.

Because of the small change in liquid density, the relative effect of liquid density on mixing, and the difficulty in obtaining a simulant with density less than 1 g/mL, the benefits of testing at lower density are small and not recommended. Liquid viscosity has less impact on PJM mixing than particle size, particle density, yield stress, and shear strength. [21] For Newtonian fluids, testing at < 1 g/mL or < 1 cP is not recommended.

2.2.3 *Yield Stress and Consistency*

At sufficiently low solids concentrations, slurries of cohesive solids act like Newtonian fluids. Cohesive solids are those small enough to possess behaviors affected by interparticle forces. At moderate and high solids concentrations, slurries of cohesive solids can exhibit non-Newtonian behavior (i.e., shear-thinning). Slurries of larger particles tend to be heterogeneous suspensions that are not well modeled as pseudo-homogeneous media. Figure 1 shows a comparison of the response of a Newtonian fluid and an idealized Bingham plastic fluid to an applied shear stress.
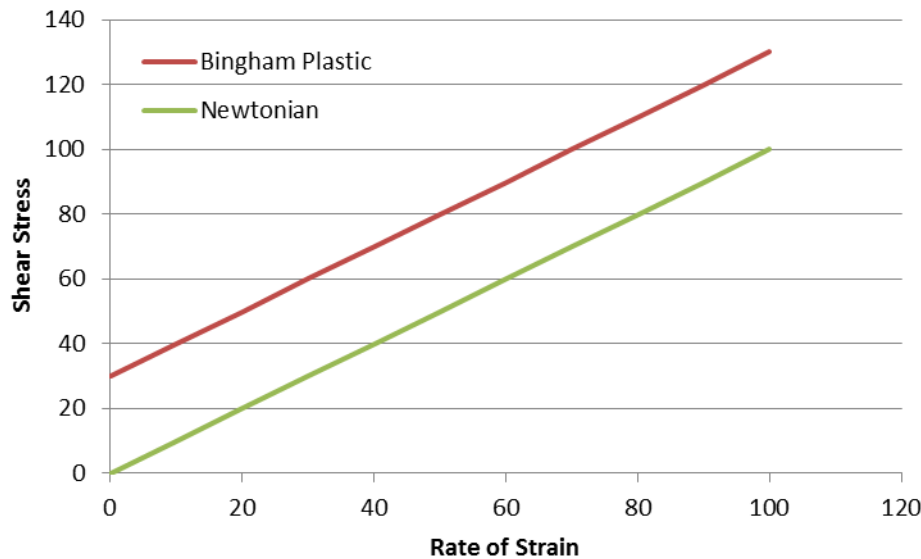
Figure 1. Comparison of Newtonian Fluid and Bingham Plastic

The two-parameter Bingham plastic equation is generally sufficient for *steady*, non-Newtonian shear flow applications and has been the primary method employed to characterize HLW slurries to date. The two parameters in the model are the Bingham yield stress (τ_Y) and consistency (η), which are fit respectively to the intercept and slope of the flow curve data (a graph of shear stress as a function of shear rate).

$$\tau = \tau_Y + \eta\,\dot{\gamma} \qquad\qquad [1]$$

The basis of design for yield stress and consistency in WTP non-Newtonian vessels is 0 Pa and 1 cP to 30 Pa and 30 cP.[16] This range is more appropriate for FSVT testing than the actual range of yield stress and consistency measured on waste tank core samples. The as-received HLW slurry is currently limited to a yield stress of less than 1 Pa, and this serves as the upper limit for yield stress in the vessels containing Newtonian fluids.[22]

While the Bingham plastic model can be used to describe some steady non-Newtonian flow systems, pulse jet mixing of slurries in the WTP is not a steady shear application. The Bingham plastic model has no parameters for time-dependent phenomena, and thus has some limitations.[23] Consequently, matching the two Bingham parameters in a simulant to those for a waste sample does not guarantee identical mixing behavior in a PJM vessel. This possibility is mentioned here because it introduces uncertainty in the simulant development. Anecdotal evidence from Hanford and SRS discussed situations in which waste samples with similar rheology had vastly different behavior. The fluid motion and shear stress produced by the PJMs during the drive phase may overcome the attractive forces between the particles changing the yield stress and consistency. When the drive phase stops, the attractive forces between particles may reestablish changing the yield stress and consistency. However, the Bingham plastic yield stress is a measurable property for which a large data set exists on Hanford tank wastes and has been used in WTP design. In addition, Bingham plastic yield stress and consistency were used to size transfer pumps, mixer pumps, and impellers for the SRS Tank Farm and the Defense Waste Processing Facility (DWPF).

Testing will need to be performed at and above the upper bounding process values for yield stress and consistency, as well as at lower values. Lower values may allow faster settling of large, dense particles and potentially be more challenging to some test objectives than the design limit values. The testing needs to evaluate lower values of yield stress and consistency (at or near 0 Pa and 1 cP) and higher values of yield stress and consistency (greater than 30 Pa and 30 cP).

SRS experience measuring rheology of chemical simulants and actual waste suggests an uncertainty of $\pm 5\%$ for simulants and $\pm 10\%$ for actual waste samples. Experience measuring the solids (total, dissolved, and insoluble) concentration of actual waste samples suggests an uncertainty of $\pm 5\%$. Rheology is generally an exponential or power function of insoluble solids concentration[24], so the impact of a 5% uncertainty in the insoluble solids concentration could have a small effect or a large effect on the uncertainty in the rheology, depending on where the sample is on the rheology versus insoluble solids curve. An investigation of the sampling uncertainty for the SRS DWPF found the sampling uncertainty for solids measurements to be less than $\pm 10\%$.[25] Taking the square root of the sum of the squares for these uncertainties (rheology of actual waste, solids concentration, and sampling) gives an uncertainty of $\pm 15\%$. The 95% confidence limit would be $\pm 30\%$, and the recommended upper limit of yield stress and consistency to be tested is 40 Pa and 40 cP.

Plots of rheology of Hanford samples from the same tank, at the same temperature and undissolved solids concentration show the measured yield stress can vary by as much as a factor of 2X.[9] Using this uncertainty, the upper bound on yield stress and consistency would be much higher (~ 60 Pa and 60 cP.) However, the data with the large variance was from samples with low (< 5 Pa) yield stress. Uncertainty of yield stress measurements can become very large at low values, especially as the material approaches becoming a Newtonian fluid.

The SRNL experience is likely more useful post startup of the WTP since the bulk of the analyses reflect qualification samples obtained freshly for that purpose. The Hanford uncertainty may be less reliable given a larger number of waste samples that required reconstitution for measurement.

One approach to selecting a lower bound on the yield stress is to compare the yield stress with the buoyancy force. Previous work has used this ratio to determine a criterion for whether particles will settle in Bingham plastic fluids. According to the criterion, particles will settle if $\tau_y/g\ d_p\ \Delta\rho$ $< 0.2 - 0.4$.[26] Based on this criterion, a 700 micron particle with a solid-liquid density difference of 1.9 g/mL will settle if the fluid yield stress is less than $2.6 - 5.2$ Pa. Testing should evaluate non-Newtonian fluids with yield stress in this range, and possibly lower.

Other rheology models could be equally valid for describing the rheology of the WTP slurries (e.g., Ostwald, Herschel-Bulkley). However, a large database of Hanford and Savannah River Site rheology exists that used the Bingham plastic model and the Bingham plastic model was used in the design and startup of the Savannah River Site Defense Waste Processing Facility. In addition, comparison of the Bingham plastic, Ostwald, and Herschel-Bulkley models fitting Hanford rheology data shows the Ostwald and Herschel-Bulkley models under predicting flow resistance at high shear rates and the Bingham plastic model providing a conservative upper bound at high shear rates.[27]

2.2.4 *Shear Strength and Critical Shear Stress*

Shear strength (measured by vane rheometry) is the point at which a fluid ceases to deform like a solid and begins to flow like a liquid. The critical shear stress for erosion is the applied stress above which particles are removed from a surface or body. These are both related properties for beds of settled particles. These waste properties should be simulated for tests that represent conditions in which regions of settled solids can accumulate. The critical shear stress for erosion is conceptually similar to the shear strength of a bed of settled solids. However, the relationship between these two properties will differ for different systems.

The shear strength of a settled bed that is held quiescent and allowed to become more consolidated, by continued settling or packing of the particles, tends to increase as a function of time. This increase is due to continuation of the packing of the solid particles, interparticle forces, and/or chemical reactions. Vane measurements of the settled layers are quantitative lab-scale measures of the shear strength and are dependent on material history. The shear strength is dependent on the particle shape, interparticle forces and microstructure.[28] Shear strength is influenced by compaction time, weight under which compaction occurs, bed depth, and degree of saturation of the pore space.

Critical shear stress is typically measured in an engineering test bed or fume rather than using a laboratory instrument. No measured critical shear stress measurements on actual waste have been conducted at Hanford or SRS. Historically, Hanford has measured shear strength for actual waste samples, and a large database of shear strength measurements exists.

The critical shear stress for erosion has been calculated with equation [15], which is described in section 2.2.7.[29] The paper that develops equation [15] provides upper and lower bounds on the critical shear stress data, which correspond to an uncertainty of approximately ± 50%.[30] This large uncertainty complicates the development of simulants based on this property. In addition, the data used to develop the correlation had a uniform particle size and a solid particle density of 2.49 – 2.68 g/mL. WTP feed slurries and simulants will likely contain particles with densities larger than 2.68 g/mL, as well as non-uniform particle sizes and densities.

Shear strength and critical shear stress for erosion are most applicable to the FSVT program where resuspension of zones of settled particles from the vessel floor is important, including the PJM restart following a Design Basis Event. These properties apply to Newtonian and non-Newtonian slurries.

The advantages of the shear strength measurement are that it is an established technique at Hanford and SRS, the large database of shear strength measurements for Hanford waste and the reasonable sample size (~ 50 – 100 mL) needed to perform a measurement with actual waste.

The advantage of the critical shear stress for erosion is that it better describes the physics of the suspension of solid particles by PJMs. The disadvantages of the critical shear stress for erosion property are no measurements have been performed with Hanford or SRS actual waste, the large uncertainty in calculations of critical shear stress for erosion, the limited particle density range (2.49 – 2.71 g/mL) used to develop the correlation, the uniform particle size and density used to develop the correlation, and the large sample that would be needed to measure this property.

At this time, shear strength is the recommended property for developing simulants for PJM tests with settled beds of solid particles. If a reliable and practical method could be developed to measure the critical shear stress for erosion of actual Hanford waste, that property should be reconsidered for developing test simulants.

The expected maximum shear strength is 1500 Pa based on the shear strength of samples that settled for up to 72 hours.[19,31] Testing conducted by SRNL for the actinide removal process showed samples of simulated sludge and MST that sat for up to 6 weeks showed dramatic increases in slurry shear strength (up to 16X).[32] Given that the shear strength has a strong dependence on settling time and that the sample results analyzed previously had a wide range of settling times, setting an upper bound or limit for shear strength is not possible at this time.

2.2.5 *Undissolved Solids Concentration*

The UDS concentration, either as a volume or weight fraction, is not constant during WTP processing. Several WTP processes, including caustic and oxidative leaching, washing, and filtration, will change the UDS concentration of the waste. UDS concentration influences the flow behavior of the jet produced by the PJMs as well as the slurry viscosity and density (tanks with Newtonian fluids) or Bingham plastic yield stress and consistency (tanks with non-Newtonian fluids). UDS concentration is also a variable that impacts the settling regime, with lower solids concentration favoring free settling over hindered settling. For beds of settled solids, the solid particle concentration influences the settled solids bed depth, shear strength, and critical shear stress for erosion.

UDS concentration of selected simulants should represent the range of waste properties throughout the WTP PTF. The UDS concentration can be expressed as a mass fraction or a volume fraction. Solids volume fraction influences the depth of settled solids that can form when mixing is lost for an extended period. Having a representative UDS leads to a more representative simulant. If the UDS is significantly different from that of actual waste, there is a possibility that the mixing problem being studied by FSVT is not the same as what will occur during actual WTP operations. Two concentrations of undissolved solids should be considered: the bulk concentration and the centrifuged concentration. The bulk concentration is important for suspending the solids, while the centrifuged concentration provides an indication of how tightly the solids pack, which influences the shear strength and critical shear stress for erosion. The bulk UDS is a contributor in a number of the metrics discussed in section 2.2.7. The centrifuged solids concentration may be useful in developing simulants, but the important properties for suspending settled solids are the shear strength and critical shear stress for erosion. Centrifuged UDS should be evaluated as a possible measurement during sample qualification.

For Newtonian simulants, the bulk UDS concentration should range from nearly 0 to 20 wt %.[a] Testing at higher UDS is expected to be more challenging. Examining the effect of insoluble solids concentration in equations [11], [12], [14], [16], [17], and [18] in section 2.8 shows that

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[a] The undissolved solids concentration could be as high as 27 wt % for UFP-02 to achieve the target rheology.

increasing the insoluble solids concentration by 2X (i.e., from 10% to 20%) increases the metrics of critical suspension jet velocity, radial jet velocity to achieve a certain degree of suspension, critical transport velocity, just suspended impeller speed, and just suspended jet velocity by 7 – 20%, indicating that UDS has a weak influence on PJM mixing. The recommended insoluble solids concentration should be increased to 27 wt % for limits testing.

For non-Newtonian simulants, the solids concentration will be varied to impact the yield stress and consistency. The maximum concentration of UDS will be that needed to achieve a yield stress of 40 Pa, a consistency of 40 cP, or a shear strength of 1500 Pa as needed for testing. Ideally, the UDS concentration for the simulant should be within the range required to achieve similar rheology in actual waste.

2.2.6 *Dimensionless Numbers (Archimedes Number and Yield Parameter)*

The properties discussed above need to be evaluated together. The most challenging values of each parameter may not occur with the same feed. Selecting a feed that uses the most challenging value for each property would be overly conservative and may be unrealistic for testing. One method to evaluate the properties together is with dimensionless groups. Two groups which should be considered when selecting simulants are the Archimedes number and the Yield Parameter. Other dimensionless numbers were considered, but determined to be either redundant or less important for developing simulants for full-scale vessel testing. Those additional dimensionless numbers are discussed in Appendix A.

The Archimedes number combines the properties of particle size, particle density, liquid density, and liquid viscosity into a dimensionless parameter. The Archimedes number, Ar, which is a measure of the ratio of buoyancy forces to viscous forces and is indicative of particle settling, is defined as

$$\text{Ar} = d_P{}^3 \, g \, (\rho_S/\rho_L - 1)/\nu_L{}^2 \qquad [2]$$

where g is the gravitational acceleration constant. Viscous forces dominate at small Ar, while buoyancy forces dominate at large Ar.[6]

The Archimedes number has a distribution of values for a waste slurry (analogous to a PSD or PSDD). It can be determined from a PSDD calculation with knowledge of the liquid viscosity and liquid density.

Three properties are evident in the Archimedes number. The most significant property is the particle size, which is present to the third power. Waste slurries span many orders of magnitude in Archimedes number through the particle size alone. The second significant property grouping is the buoyancy, $\rho_S/\rho_L - 1$, also called the dimensionless solid-liquid density difference. The buoyancy can vary from about 0.5 to greater than 10 for primary particles and can approach neutral buoyancy ($\rho_S/\rho_L \approx 1$) for waste agglomerates leading to order of magnitude ranges in Archimedes number. The third property is the kinematic viscosity, which varies by about a factor of 100 as the liquid viscosity chances from 10 to 1 cP.

Assuming a maximum particle size of 700 micron, a particle density of 2.9 g/mL, a liquid density of 1 g/mL, and a liquid viscosity of 1 cP, the calculated Archimedes number is 6400 (see Table 1).[16] Assuming a minimum particle size of 1 micron, a particle density of 2.9 g/mL, a liquid density of 1 g/mL, and a liquid viscosity of 1 cP, the calculated Archimedes number is 2 x 10^{-5}.

A 100 micron PuO_2 particle (density = 11.4 g/mL) would have an Archimedes number of 102, and a 100 micron Pu metal particle (density = 19 g/mL) would have an Archimedes number of 176. [The 100 micron PuO_2 and Pu metal are based on documents by Isom et al. and King et al.[11,33]] Reference 12 is not clear on the shape of the PuO_2 or Pu metal particles.

Table 1. Archimedes Number as a Function of Particle Properties

d_p (μm)	ρ_s (g/mL)	ρ_l (g/mL)	μ (cP)	Ar
700	2.9	1.0	1.0	6400
100	11.4	1.0	1.0	102
100	19	1.0	1.0	176
1	2.9	1.0	1.0	0.00002

A second dimensionless number is the yield parameter described by equation [8]

$$Y = \tau_y/d_p(\rho_s-\rho_l)g \qquad [8]$$

where τ_y is slurry yield stress, d_p is particle size, ρ_s is solid particle density, ρ_l is fluid density, and g is gravitational acceleration.[34] This parameter is the ratio of yield stress to gravitational forces or negative buoyancy. In other words, this number can be considered an indication of whether particles will settle in a stagnant (i.e., between PJM pulses) non-Newtonian slurry. In this parameter, yield stress, particle size, and solid-liquid density difference have equal weighting. With large values of the yield parameter, solid particles are less likely to settle. The parameter can also be used to help select a lower bound on yield stress for testing non-Newtonian simulants. This parameter would be important for selecting solid particles to investigate particle suspension and settling in non-Newtonian fluids. [If the yield stress in equation [8] is replaced with the critical shear stress for erosion, Y becomes the Shields parameter, and describes the ratio of the critical shear stress for erosion to gravitational forces or negative buoyancy.[30]]

The discussion in section 2.2.3 indicates that particles will settle if Y < 0.2 – 0.4. Table 2 shows the value of the yield parameter for selected values of particle size, particle density, liquid density, and yield stress. If the Yield parameter is less than 0.2 – 0.4, the particles are likely to settle.

Table 2. Yield Parameter as a Function of Fluid Properties

d_p (μm)	ρ_s (g/mL)	ρ_l (g/mL)	τ_y (Pa)	Y
700	2.9	1.0	30	2.3
700	2.9	1.0	6	0.46
100	19	1.0	30	1.7
100	19	1.0	6	0.34
100	11.4	1.0	30	2.9
100	11.4	1.0	6	0.59
10	19	1.0	30	17
10	19	1.0	6	3.4
10	11.4	1.0	30	29
10	11.4	1.0	6	5.9
Critical value for particles to settle				< 0.2 – 0.4

The yield parameter can be used to determine the range of fluid rheological properties and particle properties that will produce a simulant that is likely to have settling particles, to compare simulants to determine which is most likely to have settling particles, or to compare results from tests with different simulants.

2.2.7 *Engineering Metrics*

In addition to the dimensionless numbers described in section 2.2.6, metrics have been developed to provide a means to compare (rate) aspects of mixing performance as a function of measureable properties of the waste. These properties include particle size, particle density, liquid density, liquid viscosity, and solid particle concentration. The metrics described below have different relative influences of particle size, particle density, liquid density, liquid viscosity, and solid particle concentration. For some of the metrics, particle size is the most important parameter. For others, solid-liquid density difference is the most important parameter.

The metrics include the unhindered settling velocity, the critical jet suspension velocity, the radial jet velocity needed to achieve a certain degree of suspension, the critical shear stress for particle erosion, the critical transport velocity, the just off bottom suspended impeller speed, the just suspended jet velocity, and the cloud height. The equations used to describe the metrics were taken from the FSVT Vessel Group 5 Simulant 90% document, where possible.[33] An additional metric, the just suspended jet velocity, and an alternative equation for unhindered settling velocity have been added. For many of the metrics, alternative equations are available.

The **steady-state unhindered settling velocity** of the particle is described by equation [9].[35]

$$U_T = \frac{\mu}{\rho_L d_p}\left[\sqrt{15 + \sqrt{\frac{Ar}{0.3}}} - \sqrt{15}\right]^2 \qquad [9]$$

An alternative equation which describes the unhindered settling velocity in the intermediate flow regime (the regime which would be applicable to the fastest settling particles expected in the PTF vessels) is equation [10]

$$U_T = 0.13[g(S-1)]^{0.72}d_p^{1.18}\left(\frac{\mu}{\rho_l}\right)^{-0.45} \text{ (for } 1.4 < Re_p < 500) \qquad [10]$$

where S is the ratio of solid particle density to liquid density.[4] In equation [10], the ratio of the exponents for particle size and density difference is 1.18/0.72 = 1.64. Therefore, the ratio of the density difference exponent to the particle size exponent is 1:1.64.

The **critical suspension jet velocity** (U_{CS}) is described by equations [11] – [13]

$$U_{cs} = 2.302 U_{TH}\left[\frac{D^*}{Ar^{0.673}}\right]^{0.261} \qquad [11]$$

$$U_{TH} = U_T\left[1 - \frac{\varphi_s}{0.6}\right]^6 \qquad [12]$$

$$D^* = \frac{D(S-1)g\varphi_s}{(DC)U_{TH}^2\varphi_p^{0.898}\varphi_j^{1.958}} \qquad [13]$$

where U_{TH} is the hindered settling velocity, ϕ_s is the solids volume fraction, DC is the duty cycle, ϕ_p is the pulse volume fraction, and ϕ_j is jet density.[36] In equations [11] – [13], the effects of particle size and density difference are observed in the Archimedes number, the settling velocity, and the hindered settling velocity. Combining the equations and comparing the exponents for particle size and density difference shows the influence of density difference to be significantly larger than the influence of particle size, with the ratio being 12:1.

The **radial jet velocity needed to achieve a certain degree of suspension** is described by equation [14]

$$U_n = \frac{\mu}{\rho d_p}\left[0.13 X^{0.22} Ar^{0.38}\left(\frac{D}{D_j}\right)\left(1 + 0.25\left(\frac{z}{D_j}\right)\right)^{-0.25}\left(1 + 0.25\left(\frac{z}{D}\right)\right)\right] \qquad [14]$$

where X is the volume fraction of solids, D is tank diameter, D_j is jet diameter, and z is distance between the jet discharge and tank bottom.[37] Combining equation [2] with equation [14] shows the radial jet velocity to be proportional to $\Delta\rho^{0.38}d_p^{0.14}$. Therefore, the ratio of the density difference exponent to the particle size exponent is 0.38/0.14 = 2.71.

The **critical shear stress for particle erosion** is described by equation [15].[30]

$$\tau_c = \frac{0.273(\rho_s - \rho_L)g d_p}{1 + 1.2 Ar^{1/3}} + 0.046(\rho_s - \rho_l)g d_p\left(1 - 0.57 exp\left(-0.02 Ar^{1/3}\right)\right) \qquad [15]$$

Selecting a particle size of 700 micron, a particle density of 2.9 g/mL, a liquid density of 1 g/mL, and a liquid viscosity of 1 cP, a 10% increase in particle size produces a 9% increase in critical shear stress, and a 10% increase in density difference produces a 9.6% increase in critical shear stress. The effects of particle size and density difference are about the same under these conditions.

The **critical pipeline transport velocity** is described by equation [16]

$$U_C = 1.85\sqrt{gd(S-1)}\,C_V^{0.1536}\left(1 - C_V\right)^{0.3564}\left(\frac{d}{D_P}\right)^{-0.378}\left[\frac{D_P\rho_L\sqrt{gd(S-1)}}{\mu}\right]^{0.09}\chi^{0.30} \qquad [16]$$

where S is ρ_S/ρ_L, C_V is the solids volume fraction, D_P is the pipe diameter, and χ is the fraction of eddies having velocities equal to or greater than the settling velocity. χ is set to 0.96.[38] In equation [16], the critical pipeline transport velocity is proportional to $\Delta\rho^{0.545}d_p^{0.167}$. Therefore, the ratio of the density difference exponent to the particle size exponent is 0.545/0.167 = 3.26.

The **just off bottom suspended impeller speed** is described by equation [17]

$$N_{js} = S_z v^{0.1}\left[\frac{g(\rho_S - \rho_L)}{\rho_L}\right]^{0.45} X^{0.13} d^{0.2} D^{-0.85} \qquad [17]$$

where S_z is a geometric constant of the mixing system (e.g. impeller, impeller off-set, baffles, etc.).[39] In equation [17], the just off bottom impeller speed is proportional to $\Delta\rho^{0.45}d_p^{0.2}$. Therefore, the ratio of the density difference exponent to the particle size exponent is 0.45/0.2 = 2.25.

The **just suspended jet velocity** is described by equation [18].[40]

$$V_{js} = \frac{\left(\frac{\mu}{\rho}\right)^{0.16}\left(\frac{\Delta\rho}{\rho_L}\right)^{0.28} g^{0.42} D^{1.16} d_p^{0.1} X^{0.24}}{D_j} \qquad [18]$$

In equation [18], the just suspended jet velocity is proportional to $\Delta\rho^{0.28}d_p^{0.1}$. Therefore, the ratio of the density difference exponent to the particle size exponent is 0.28/0.1 = 2.8.

Fort et al. developed a model to calculate the **cloud height** (H_c) of the solids using PJMs.[36] Equations [19] and [20] describe the model.

$$ln[H_C^* Re^{-0.143}] = 8.223\left(\frac{U}{U_{TH}}\right)^{0.1364} \qquad [19]$$

$$H_c^* = \frac{H_c(s-1)g\varphi_s N^{0.658}}{DCU_{TH}^2 \varphi_p^{0.898} \varphi_j^{1.662}}$$ [20]

Equations [19] and [20] can be combined and simplified to remove parameters that do not change with changing viscosity to produce equation [21].

$$H_c \propto \frac{U_{TH}^2}{\mu^{0.143}} exp\left[8.223\left(\frac{U}{U_{TH}}\right)^{0.1364}\right]$$ [21]

In this metric, the ratio of the density difference exponent to the particle size exponent is 1:1.64.

The metrics described in this section show the relative effects of particle size, solid-liquid density difference, liquid viscosity, and particle concentration on particle settling and suspension. The metrics show a stronger dependence on particle size than density difference for settling and cloud height, and a stronger dependence on density difference than on particle size for suspension metrics. With a particle size of 700 micron, a particle density of 2.9 g/mL, a liquid density of 1 g/mL, and a liquid viscosity of 1 cP, the effects of particle size and density difference on the critical shear stress for erosion are about the same. A review of the metrics shows that settling velocity and cloud height have the largest ratio of particle size exponent to solid-liquid density difference exponent and critical suspension velocity has the largest ratio of solid-liquid density difference exponent to particle size exponent. Because these metrics bound the relative effects of particle size and solid-liquid density difference, they should be considered in developing Newtonian simulants.

2.2.8 Particle Shape

Particle shape potentially influences two main physical behaviors within PJM-mixed vessels during FSVT: 1) the settling of solid particles, and thus the ability to keep the large and dense particles suspended; and 2) the remobilization of settled particles or beds of particles. The particle shape influences these two behaviors differently, and thus they are addressed separately. Particle shape and surface roughness also impact particle adhesion to surfaces. This section reviews what is known about particle shape in Hanford wastes, the influence of particle shape on settling, and the influence of particle shape on suspension and bed erosion.

Particle shape influences settling rate, with spherical particles providing the maximum settling rate. Particle shape may influence the ability to suspend particles off the bottom of a tank, where some evidence exists that nonspherical particles require an increased velocity for off-bottom suspension. Particle shape is one of several factors that influence the remobilization of solids through its influence on the shear strength of beds.

2.2.8.1 Shape impacts on particle settling

Fluid mechanics relationships developed for the drag coefficient often consider the influence of particle shape.[41,42,43] The drag coefficient and terminal velocity of a nonspherical particle have been related empirically to its equal volume sphere diameter (d_S) and its sphericity.[44,45,46] Most of these analyses are for the free fall of individual particles. Much less information is available for the influence of particle shape on settling in the hindered settling regime.

The influence of particle shape on the drag coefficient is dependent on the settling regime. Based on expected WTP process conditions, the majority of individual particles are in the Stokes settling regime. Towards the higher end of particle size and density expected in WTP waste, the particles will be in the Intermediate settling regime. It is not expected that the Newton settling

regime will be encountered since the hypothesized case of a large dense particle (d_P = 1 mm, ρ_S = 11.4 g/mL) settling in water is still in the Intermediate settling regime ($Re_P \approx$ 500).

Particle orientation during free fall is a function of the particle Reynolds number, $Re_p = U_T d_p / \nu_L$.[43] In the low Re_p Stokes regime, all settling orientations are stable. As Re_p increases, settling is stable in the orientation of maximum drag. At higher Re_p, the particle orientation during settling becomes unpredictable, with wobbling and rotation possible. At high Re_p, particles rotate about the axis of least inertia.

With some minor exceptions, spheres are the fastest settling particles when compared to non-spherical particles of the same volume. For spheroids and ellipsoids with shapes ranging from disks to needles, the minimum drag shape for a given particle volume when averaging over all orientations is a sphere.[47] When considering specific orientations of such shapes with respect to the flow direction, some objects have a very slight (<5%) drag reduction from that of a sphere of the same volume.[47] Because this occurs for orientations only stable in the Stokes settling regime, enhanced drag is not applicable to the most bounding or challenging situations for FSVT. The influence of this slight reduction in the free settling velocity from that of a sphere is well within the other uncertainties involved with PSDD, and thus free falling spheres can be considered to provide the practical maximum settling velocity during testing.

For settling, particle surface roughness (small length scale roughness) does not strongly influence settling until Re_p is in the high Newton range that will not be encountered in WTP tanks.[47]

2.2.8.2 Shape impacts on particle suspension and bed erosion

Particle shape can influence the behavior of particles during suspension. Testing on suspension by gas streams revealed that spherical particles start their motion by rolling and large non-spherical particles start their motion by sliding.[48] This change in mechanism in turn changes the amount of particle-surface friction, thus leading to higher velocities required to initiate motion of large non-spherical particles than for analogous spherical particles.[48] This incipient motion is usually the precursor to particle pickup and entrainment in the liquid. Pickup, or critical, velocity studies of spherical and non-spherical particles proposed adjustments to the Archimedes number to compensate for the higher velocities needed for the suspension of non-spherical particles.[49]

For specific systems, particle shape influences removal of particles from a stationary bed by a liquid.[50] For some systems, the effect of particle shape on particle suspension can be less pronounced for higher solids (i.e., 10 wt % UDS) loadings than for low solids loadings (isolated particles).[50]

Particle shape is one of the factors that influence the shear strength of a settled layer.[28] This influence can be due to factors such as surface forces, friction, and solids packing. While spheres contact each other at a single point, non-spherical particles can contact each other at one or more points, lines, or planes. For small nonspherical particles, surface forces can act over larger particle contact areas than for spheres.[51] This can lead to large deviations (but similar average values) for critical suspension velocities of nonspherical particles relative to those for spheres.[51] Nonspherical material can potentially have higher pickup velocity than spherical material due to particle-particle interlocking that occurs for nonspherical particles.[51]

2.2.8.3 Recommendations for particle shape

Because of the absence of information on the particle shape distribution in Hanford waste, the baseline simulant need not be matched to any specific range of particle shape distributions. For Newtonian and non-Newtonian simulants, FSVT should use a mixture of particle shapes, including spherical and non-spherical particles.

In testing settling of large dense particles, spherically shaped particles would provide the maximum settling rate and thus would be conservative. In testing of the remobilization of beds of solids, non-spherical particle shapes may contribute to an increased velocity needed for off-bottom suspension.

Previous M3 and LOAM testing used simulants that contained dense nonspherical components, including irregularly shaped tungsten carbide alloy and rod shaped bismuth oxide.[52,53] As spheres give the fastest settling rate, spheres should be considered for use for at least a portion of the particles at the high end of the particle size distribution.

2.2.9 Time Dependent (Thixotropic/Rheopectic) Rheological Phenomena

Flow curve data from the M-12 program were examined, some of which showed hysteresis between the up and down portions of the curves.[54,55,56,57] This hysteresis has been cited as potential evidence for time-dependent rheological behavior of Hanford wastes.[55,56,57] Time-dependent rheological properties are not the only possible explanation for the small amounts of hysteresis noted on certain flow curves in the discussion that follows. This is particularly true when the sample matrix is heterogeneous (liquid-solid or gas-liquid-solid) and the rheometer uses the concentric cylinder geometry with rotating inner cylinder. As acknowledged by the authors of the M-12 reports, plausible explanations for the observed hysteresis include the following:
- solids settling out of the measurement gap,
- breaking of the structure of the slurry from the shearing,
- evaporation of water during measurements,
- sample degassing during measurements, or
- uncertainty in rheology measurements. [Plots of rheology of samples from the same tank, at the same temperature and undissolved solids concentration show the measured yield stress can vary by as much as a factor of 2X.[9]]

As time-dependent rheological properties are not the only possible explanation for the hysteresis and the magnitude of the potential time-dependent rheology impacts does not appear to be significant in comparison to the WTP non-Newtonian operating range, it is not recommended that simulants of the Hanford wastes be formulated to exhibit time-dependent rheological behavior.

2.3 <u>Waste and Simulant Chemistry</u>

The effects of the chemical composition of Hanford waste slurries need consideration in the test program, and in developing simulants. Waste chemistry is significant in the testing of unit operations such as washing or leaching. These unit operations are not part of the FSVT program, but the effect of chemistry on the physical properties needs to be considered when developing simulants.

In describing the chemistry, the authors consider four phenomena to be important: solubility, interparticle forces, cohesion/adhesion, and hydrophilicity of the particles.

Solubility is important within the PTF during blending of different process streams, washing, and leaching. When blending waste streams of different composition, changes in pH, ionic strength, and chemical composition can cause compounds to precipitate or dissolve, resulting in changes in the undissolved solids concentration. These changes in undissolved solids concentration may change the PJM velocity needed to suspend particles in Newtonian fluids or change the rheology of non-Newtonian fluids. In some instances, the precipitation may occur slowly and not manifest until downstream (e.g., post filtration precipitation). Washing causes a decrease in the pH, which could lead to aluminum precipitation, and decreases in ionic strength that could increase the solubility of many compounds. Leaching dissolves compounds such as aluminum and chromium. These chemical phenomena need not occur within the planned FSVT since simulation of the chemical processes is not a test objective. Matching of chemical behavior for the simulants is not necessary for most FSVT test objectives. Simulants that undergo such chemical changes during the mixing tests could convolute mixing and chemical behavior, making data interpretation more difficult. The dynamic nature of such chemical changes could unnecessarily complicate and extend the testing program. Rather, simulant selection should focus on stable simulants that capture the mixing challenges (e.g., when the chemical changes yield extremes in the rheological properties of interest to mixing) that exist throughout the chemical process and the key physical properties.

Interparticle forces are important when particles are small (on the order of 1 μm)[58]. These interparticle forces influence properties such as particle size, liquid viscosity, yield stress, consistency, shear strength, and critical shear stress for erosion. However, 99% of the particles are larger than 1 μm.[16]

Cohesiveness and adhesiveness are properties of the solids that make them "tacky" or "sticky". These properties can influence the rheology of the slurries. Slurries that are cohesive or adhesive could be more difficult to suspend, more likely to accumulate on vessel internals, and retain gas more effectively than non-cohesive or non-adhesive slurries. Particles that are cohesive or adhesive may be more difficult to suspend and mobilize than non-cohesive/adhesive particles with similar rheology. Cohesiveness and adhesiveness could be important in testing to evaluate accumulation, transfer and pump outs, and gas retention and release. Cohesiveness and adhesiveness of solid particles could lead to pockets of material not being mobilized in the vessels or to particles accumulating in transfer pipelines.

Hydrophilicity describes a material's affinity for water. Hydrophilic particles like to be around water, while hydrophobic particles do not. Biphylic partles have hydrophilic and hydrophobic characteristics. The biphylic nature of particles has an impact on their propensity to foam and retain gas or gas bubbles. The project has invested heavily in studying foaming behavior at lab and bench-scale.[59,60] The mixing test objectives do not currently include testing for aerosols, foaming, and similar behavior. Hence, matching these properties is not required for the proposed testing objectives.

The importance of chemistry of simulants for evaluating gas retention and release in PJM-mixed vessels depends on the requirements of the test. If the demonstration of complete motion is sufficient to show that gas will be released from PJM-mixed vessels, the chemistry of the actual waste does not need to be matched in the simulant. Matching the rheology of the actual waste is sufficient. However, if it is necessary to measure gas retention and release in the testing, the chemistry of the actual waste must be considered in developing the simulant. Measuring gas retention and release is assumed to be out of scope for FSVT.

The effect of chemistry on simulants is discussed in more detail in Appendix B.

3.0 Recommendations for Simulant Properties to Meet Test Objectives

This section examines potential test objectives and assesses the simulant properties that are important in testing different objectives. The potential test objectives follow.
- Determine the operating conditions needed to obtain complete bottom motion and determine whether the SHSVD can achieve those conditions. [MR10]
- Determine the extent of solids accumulation following a prototypic pump out and whether this amount of accumulation is acceptable. [MR10]
- Demonstrate successful transfer of the slurry and select components from the vessel through the pipeline and pump. [MR2]
- Determine the time required to blend miscible liquids in the vessel under prototypic operating conditions.   [MR3]
- Determine the ability of the PJMs to release gas that has been retained by the vessel contents. [MR8]
- Assess the ability to collect representative samples from a PJM mixed vessel. [MR7]

3.1 Summary of Properties Important to FSVT Simulants

Review of the existing data on Hanford waste as well as the mixing performance criteria for the vessels indicate that the most important parameters for testing with Newtonian slurries are the particle size, particle density, and the particle concentration (on a slurry basis). Particle size distribution is important and should be considered in simulant development rather than just a median particle size or a maximum particle size. In addition, the particle size and density must be considered together since their influence on mixing is highly correlated and since they are correlated in the waste during processing. They can be combined in a dimensionless parameter such as the Archimedes number or in an engineering metric such as settling velocity or critical suspension velocity. For some test objectives, the settled solids shear strength is important. The density of the bulk liquid by itself does not have a significant effect. However, the density difference between the bulk liquid and added liquid can have a significant effect if the difference is large enough to cause stratification. Because of particle settling between pulses, liquid viscosity can have a significant effect under some conditions.

The most important properties for testing with non-Newtonian slurries are the slurry yield stress, the slurry consistency, and the slurry shear strength. The solid-liquid density difference and the particle size are also important. The slurry yield stress, solid-liquid density difference, and particle size can be combined in a dimensionless Yield parameter. It is also important to match multiple properties (e.g., yield stress and shear strength) within the same simulant to achieve behavior representative of the waste.

Table 3 summarizes the important properties for Newtonian fluids, while Table 4 does the same for non-Newtonian fluids. Properties are ranked by potential significance as high, medium, or low for each test objective. The basis for the ranking is discussed in section 3.2. The effects of some properties were seen as either negligible or unknown, and these were omitted from the tables. Two factors were considered in making the ranking determinations. These were the exponents (coefficients) on the property in typical mixing or scaling correlations as well as the range of property values likely to be encountered in actual waste slurries. For example, a property with a wide range of possible values and a large coefficient was considered highly important while a property with a narrow range of possible values might be rated low even

though it had a higher coefficient. Data regression correlations for PJM tanks were preferred to those for other configurations when available, but a broad range of equations was examined to make the ranking judgments.

Table 3: Properties important for FSVT with Newtonian Slurries

Test Objective	d_p	$\Delta\rho$	Conc.	Shear Strength	Liquid Density	Liquid Viscosity
Accumulation	High	High	Medium	Medium	Low	Low
Transfer/Pumpout	High	High	Medium/High	Low	Low	Low
Sampling	High	High	Medium	Low	Low	Low
PJM Restart	High	High	Medium	High	Low	Low
Gas retention and release	High	High	Medium	High	Low	Low
Blending	High	High	Low/High	Low	Low/High	Low/High

Table 4: Properties important for FSVT with non-Newtonian Slurries

Test Objective	Yield stress	Consistency	Shear Strength	Density difference	Particle size
Accumulation	High	High	Medium	Medium	Medium
Transfer/Pumpout	High	High	Low	Medium	Medium
Sampling	High	High	Low	Medium	Medium
PJM Restart	Medium	Medium	High	Low	Low
Gas retention and release	High	High	High	Medium	Medium
Blending	High	High	Low	Medium	Medium

3.2 <u>Testing</u>

This section lists potential test objectives and identifies the important properties for Newtonian and non-Newtonian fluids, as well as a qualitative measure of their impact on PJM mixing. The impact of each property is ranked qualitatively as high, medium, or low. The rankings are based on the exponents in the metrics discussed in section 2.2.7, the range of properties values expected in the WTP, and the discussion in section 2.2. In some instances, the impact of the property depends on its magnitude, and multiple rankings are given.

The FSVT testing may evaluate *the accumulation of solids* as a function of test parameters and feed simulant properties. For Newtonian slurries, the important properties should be selected as shown.

- particle size - high
- solid-liquid density difference – high
- particle concentration - medium
- shear strength - medium
- liquid kinematic viscosity – low
- liquid density - low
- PSD can have additional impacts through its effect on particle packing

Particle size is ranked as high because it has the largest influence on particle settling (see equation [10]), it has a significant exponent in many of the engineering metrics (equations [16] and [17]), and it has a large range of values expected in the WTP (1 – 700 micron). The solid liquid density

difference is listed as high, because it has the largest exponent in many of the engineering metrics (equations [14], [16], [17], and [18]), the second largest exponent for unhindered settling (equation [10]), and a large range of values expected in the WTP (1.2 – 10.4 g/mL). Particle concentration, liquid density, and liquid viscosity are listed as medium and low, because they have a smaller influence on the engineering metrics described above. In addition, liquid density only varies by 50%.

For non-Newtonian slurries, the most important properties are
- slurry yield stress - high
- slurry consistency - high
- shear strength - medium
- solid-liquid density difference - medium
- particle size - medium

Slurry yield stress and consistency are listed as high, because they are the parameters of the Bingham plastic model, the shear stress produced to the PJMs must overcome the slurry yield stress before mixing occurs, and they can vary from 0 – 30 Pa and from 1 – 30 cP. The solid-liquid density difference and particle size are only important when they are large and the yield stress is small (see section 2.2.3). Shear strength is ranked as medium, because once fluid motion starts, the slurry yield stress is more important.

The FSVT may include *transfer and pump out tests*. One of the test objectives could be to verify that the transfer system will not plug under normal vessel operating conditions. For Newtonian slurries, the following properties are important.
- particle size - high
- solid-liquid density difference - high
- particle concentration – medium/high
- shear strength – low
- liquid density – low
- liquid viscosity - low

Particle size and solid-liquid density differences are ranked high, because they are the most significant parameters in critical pipeline transport velocity correlations such as equation [16]. In addition, they will have a large range of values in the WTP. The impact of particle concentration is medium under most operating conditions, but could become high at high solids concentrations. The impact of shear strength is listed as low because the slurry will be in motion, but it could be high if solid particles are allowed to settle for extended times in the transfer lines. The impacts of liquid density and viscosity are ranked low because of their small exponents in equation [16], and because the flow will be turbulent.

For non-Newtonian slurries, the following properties are important.
- slurry yield stress - high
- slurry consistency - high
- solid-liquid density difference - medium
- particle size - medium
- Shear strength – low

Slurry yield stress and consistency are listed as high, because they are the parameters of the Bingham plastic model, the shear stress produced to the transfer pump must overcome the slurry yield stress before transport occurs, and they can vary from 0 – 30 Pa and from 1 – 30 cP. The

solid-liquid density difference and particle size are only important when they are large and the yield stress is small (see section 2.2.3). Since the vessel contents will be mixed prior to starting a transfer or pump out, the shear strength is not an important parameter for this test function. Shear strength could be ranked high if solid particles are allowed to settle for extended times in the transfer lines.

Sampling capability tests may be performed. That testing should characterize sample variability relative to actual vessel content for key constituents/particles. The testing could be expanded to assess limits by increasing the size or density of the particle of interest for sampling. The important properties for Newtonian fluids follow.
- particle size - high
- particle/liquid density difference - high
- liquid viscosity – low
- liquid density – low
- particle concentration – medium
- shear strength – low

Particle size is ranked as high because it has the largest influence on particle settling (see equation [10]), it is a significant exponent in many of the engineering metrics (equations [16] and [17]), and it has a large range of values expected in the WTP (1 – 700 micron). The solid liquid density difference is listed as high, because it has the largest exponent in many of the engineering metrics (equations [14], [16], [17], and [18]), the second largest exponent for unhindered settling (equation [10]), and a large range of values expected in the WTP (1.2 – 10.4 g/mL). Particle concentration, liquid density, and liquid viscosity are listed as medium and low they have a smaller influence on the engineering metrics described above. In addition, liquid density only varies by 50%.

The following properties are important for the non-Newtonian slurries.
- slurry yield stress - high
- slurry consistency - high
- solid-liquid density difference - medium
- particle size – medium
- Shear strength – low

Slurry yield stress and consistency are listed as high, because they are the parameters of the Bingham plastic model, the shear stress produced by the PJMs must overcome the slurry yield stress before mixing occurs, and they can vary from 0 – 30 Pa and from 1 – 30 cP. The solid-liquid density difference and particle size are only important when they are large and the yield stress is small (see section 2.2.3). Shear strength is ranked as medium, because once fluid motion starts, the slurry yield stress is more important.

Testing to support *PJM restart following an extended mixing outage* may be performed. During off-normal conditions when PJM operation is stopped for a period of time, waste properties are expected to change. In both Newtonian and non-Newtonian tanks, solid particles can settle into beds that will develop a shear strength that the PJMs will need to overcome to resume waste mobilization. The following are important properties for settled Newtonian slurries.
- particle size - high
- solid-liquid density difference - high
- particle concentration - medium
- shear strength – high

- liquid density – low
- liquid viscosity - low

Shear strength is ranked as high, because it must be overcome before any fluid motion will occur. Once the shear strength is overcome, particle size and density are most important because of their effects on particle settling and particle suspension described above. The impact of particle concentration is medium under most operating conditions, but could become high at high solids concentrations. The impact of liquid density and viscosity is ranked low because they have a smaller influence on the engineering metrics described above.

For non-Newtonian slurries, the following are important properties.
- slurry yield stress - medium
- slurry consistency - medium
- shear strength – high
- solid – liquid density difference – low
- particle size – low

Shear strength is ranked as high, because it must be overcome before any fluid motion will occur. Chemical properties of the simulant could impact the behavior of the settled bed due to factors such as cohesiveness and adhesiveness. Once the shear strength is overcome and portions of the bed are remobilized, the properties that matter for the PJM restart task will mirror those that are important for other mixing functions (e.g., bottom motion, accumulation).

Testing in support of *gas retention and release* may be performed. This testing is assumed to be out of FSVT scope, but it is discussed because it could be added to the scope in the future. If demonstrating fluid motion throughout the vessel is sufficient for this testing, the important parameters for Newtonian slurries are
- particle size - high
- solid-liquid density difference - high
- particle concentration - medium
- shear strength – high
- liquid density – low
- liquid viscosity - low

Shear strength is ranked as high, because it must be overcome before any fluid motion will occur. Once the shear strength is overcome, particle size and density are most important because of their effects on particle settling and particle suspension described above. The impact of particle concentration is medium under most operating conditions, but could become high at high solids concentrations. The impact of liquid density and viscosity is ranked low because they have a smaller influence on the engineering metrics described above.

The important parameters for the non-Newtonian slurries are
- slurry yield stress - high
- slurry consistency - high
- shear strength - high
- solid-liquid density difference - medium
- particle size – medium

Shear strength is ranked as high, because it must be overcome before any fluid motion will occur. Once the shear strength is overcome, the yield stress must be overcome to release gas throughout

the vessels. The solid-liquid density difference and particle size are only important when they are large and the yield stress is small (see section 2.2.3).

Measuring gas retention and release is assumed to be out of scope for FSVT. If it is added to the test scope, a chemical simulant is recommended. An alternative to employing a chemical simulant for full-scale testing would be to conduct bench-scale testing with a chemical simulant and a physical simulant to verify that the physical simulant bounds the chemical simulant for gas retention and release. In addition, if gas retention and release remains critical to WTP operation, the Project should consider measuring gas retention during waste qualification.

Miscible liquid blending tests may be performed. One objective of the tests could be to determine the time required to blend miscible liquids under prototypic PJM operating conditions. For Newtonian slurries, the following properties are important
- particle size - high
- solid-liquid density difference - high
- particle concentration – low/high
- shear strength – low
- liquid density – low-high
- liquid viscosity - low-high

Particle size and solid-liquid density difference are ranked as high, because if the solid particles are not suspended to the surface of the vessel, they could form an interface with a well-mixed region below the interface and a stagnant region above the interface.[20,61,62] Based on work by Bujalski et al. and Kraume, the effect of concentration is low at less than 5 – 10%, but the effect is high at concentrations above 5 – 10%.[20,62] The density of the bulk liquid by itself has a low effect on miscible liquid blending. However, the density difference between the bulk liquid and the added liquid can have a large effect, if the difference is large enough to cause stratification and if the less dense liquid is added to the surface of a significantly higher density liquid, the blend time could be very long. For blending with impellers or jets, the effect of liquid viscosity is low. However, because of particle settling between pulses and the lower settling rate with higher viscosity, liquid viscosity can have a high effect under some conditions.[61]

For non-Newtonian slurries, the important properties are the
- slurry yield stress - high
- slurry consistency - high
- solid-liquid density difference - medium
- particle size - medium
- Shear strength – low
- Particle concentration - low

Slurry yield stress and consistency are ranked as high, because they are the parameters of the Bingham plastic model, the shear stress produced to the PJMs must overcome the slurry yield stress before mixing occurs, and they can vary from 0 – 30 Pa and from 1 – 30 cP.

Properties such as particle shape, breadth of the particle size distribution, number of fine particles, ionic strength, pH, particle surface charges, and particle concentration will affect particle agglomeration, slurry yield stress, slurry consistency, and shear strength, and these properties can affect the accumulation of particulate solids. These properties should be considered when developing simulants.

3.3 Recommendations on Chemical versus Physical Simulants

Chemical simulants attempt to match the chemical makeup of the waste, with or without matching the physical aspects of the waste. Physical simulants attempt to match some of the physical aspects of the waste, but do not contain the same chemical species as the waste. There are also simulants that have characteristics of both.

Chemical simulants can be prepared by matching chemical species present in the waste, by matching chemical compounds present in the waste, or by co-precipitation of the chemical compounds by processes that match the processes to which the waste is subject. For such testing, chemical simulants would typically also be required to match physical properties of the waste.

Clay slurries possess chemical effects although they are categorized as physical simulants because they match properties such as yield stress and shear strength. Physical simulants could also be composed of non-chemically matched minerals having particle sizes and densities representative of the waste.

Physical simulants are adequate for most testing of *solids accumulation*. Simulants need to cover and bound the property ranges expected in the WTP. If performing testing with non-Newtonian fluids and using a physical simulant, the simulant needs to match both yield stress and shear strength of actual waste or be conservative. The simulant needs to have comparable solids concentration. Properties such as particle shape, breadth of the particle size distribution, ionic strength, pH, and particle surface charges can affect the bottom motion and accumulation of particulate solids, and should be considered in developing the simulant. However, physical simulants leave a risk of not fully covering solids accumulation, since they do not mimic the cohesive nature of actual waste and may not show the changes in rheology properties with aging that have been observed with actual waste and chemical simulants.

Physical simulants are adequate for the majority of testing of *pump outs and transfers*. The simulants need to cover property ranges expected in the WTP. If using a Newtonian fluid and testing for salt precipitation in the transfer line, WTP needs to use concentrated salt solution (i.e., a chemical simulant, near the point of saturation). If using non-Newtonian fluids, WTP needs to match yield stress and shear strength of actual waste or be conservative. The simulant needs to be comparable on solids concentration. The addition of cohesive and adhesive particles should be considered when developing the simulant, as these particles could affect the ability of a simulant to plug a transfer system.

Physical simulants are adequate for testing the *sampling* system with Newtonian and non-Newtonian fluids. The Newtonian simulants need to contain particles representing the most challenging particles to suspend, as well as particles representing other particles of interest for sampling. The non-Newtonian simulants need to match the yield stress and shear strength of actual waste, or be conservative. In addition, the simulants need to contain particles representing any settling particles expected, as well as particles representing other particles of interest for sampling.

Chemical or physical simulants could be used for testing *PJM restart.* WTP needs simulants to match both yield stress and shear strength of actual waste, or be conservative. When matching yield stress and shear strength, the solids concentration needs to be comparable to expected actual waste levels. Chemical simulants could match more of the waste properties that are not reflected in yield stress and shear strength. If simulants are needed to represent long-term settled solids in

WTP, chemical simulants are recommended. Alternatively, bench-scale testing could be conducted with chemical simulants or actual waste to determine the impact of long term settling on slurry yield stress, consistency, and shear strength.[32]

If demonstrating fluid motion throughout the vessel is sufficient for *gas retention and release* testing, a physical simulant is adequate. Measuring gas retention and release is assumed to be out of scope for FSVT. However, if measuring gas retention and release are part of the testing, a chemical simulant is recommended. An alternative to employing a chemical simulant for full-scale testing would be to conduct bench-scale testing with a chemical simulant and a physical simulant to verify that the physical simulant bounds the chemical simulant for gas retention and release.

Physical simulants are adequate for testing *miscible liquid blending* with Newtonian and non-Newtonian fluids. A compound needs to be included with the simulant to allow determination of the completeness of blending as a function of time.

If additional test objectives are added to simulate unit operations that perform chemical processes, a chemical simulant should be used.

In addition, there is a residual risk that the simulant does not fully bound the properties of Hanford waste as there are undoubtedly waste conditions that have not been studied or that may emerge during operations due to unforeseen factors.

3.4 Ranges for Important Simulant Properties

Table 5 contains the recommended ranges for testing. The values are based on the conservative WTP operating envelope, both before and after caustic leaching.

Table 5: Summary of Simulant Property Ranges Recommended for FSVT

	Design Basis Range	Limits Determination
Newtonian Test Objectives		
d_p [‡]	1 – 700 µm[^]	1,100 µm[^15]
μ_L	1.0 to 10 cP	N/A
ρ_L	1.0 to 1.5 g/mL	N/A
ρ_S [†]	2.2 - 11.4 g/mL	N/A
UDS concentration	up to 20 wt%	27 wt %
Shear strength	up to 1500 Pa	>1500 Pa
Non-Newtonian Test Objectives		
τ_{YS}	0 to 30 Pa	Up to 40 Pa
η	1 to 30 cP	Up to 40 cP
$\rho_S - \rho_L$ [†]	1.2 to 10.4 g/cm^3	N/A
d_p [‡]	1 – 700 µm[^]	1,100 µm[^]
Shear strength	up to 1500 Pa	>1500 Pa

[†]solid density for primary particles – excludes Pu metal

[‡] use a range of particle sizes

[^]minimum particle may actually be less than 1 µm

4.0 Recommended Simulants

The Newtonian simulant should have at least four different particles. One of the particles needs to be representative of the largest particles in the feed (i.e., the fastest-settling and most difficult to suspend), a second particle needs to represent the major aluminum compounds in the feed, a third particle needs to represent small dense particles, such as PuO_2 (density of 11.4 g/mL) or bismuth compounds (density of 6 – 9 g/mL), and the fourth particle needs to represent the fine particles in the feed. Additional particles can be added to provide a broad particle size distribution or to represent other compounds deemed important for the testing.

The largest particles will settle the fastest. Correlations for settling velocity in the intermediate regime show that settling velocity is proportional to $d_p^{1.18}$ (where d_p is particle size).[4] Particle density (i.e., solid-liquid density difference) influences settling rate also, but particle size has a larger influence. Large particles are more likely to settle between the drive phases of the PJM cycle or in the transfer line. In addition, correlations for solids suspension in mixed tanks and solids suspension in pipelines show that large, dense particles are the most challenging to suspend.[39,40,63]

Aluminum is a compound observed in many feed vectors at high concentrations. Representing the settling and suspensions characteristics of the aluminum compounds is important in developing simulants for full-scale vessel testing. Matching the aluminum compounds of interest is not necessary, unless the testing has a focus on washing and leaching of the slurries. Matching the settling and suspension characteristics of the aluminum compounds is sufficient for most test objectives.

The WTP PFT feed could contain plutonium dioxide, other fissile particles, or bismuth compounds. These types of particles have a large density (the density of PuO_2 is 11.4 g/mL, the density of Bi_2O_3 is 8.9 g/mL). Plutonium oxide particles cannot be used in the simulant. Finding particles with a density of 11.4 g/mL could be problematic. However, by adjusting the particles size, simulant particles could be identified that represent or bound the settling and suspension behavior of the plutonium dioxide and bismuth oxide particles.

Since the WTP feed could contain 50% or more fine particles, these particles need to be included in the feed. The fine particles settle slowly, or not at all, and are easy to suspend. Many models for suspending solids in mixed tanks consider the fine particles to be part of the liquid. Fine particles increase the slurry viscosity, which increases the decay of the jets produced by the PJMs. The fine particles may also reduce the settling rate of the large, fast-settling particles. Scaled testing with an 8 ft diameter vessel showed the fine particles to have a significant impact on PJM mixing.[64]

There may be value in adding another particle with density and particle size properties that exceed the bounding particle for the design basis feed as a means of assessing limits.

For testing of the mixing of non-Newtonian slurries, matching the rheological properties of yield stress, consistency, and shear strength is most important. This is best done with a slurry containing kaolin clay and/or bentonite and water. Large, fast settling particles need to be included in the non-Newtonian simulants. Kaolin/bentonite slurries have been used extensively at Hanford and the SRS to produce slurries that simulate sludge in the Hanford and SRS waste tanks. SRS used a kaolin slurry to measure the effective cleaning radius of slurry pumps with Bingham plastics fluids in an 85 ft diameter tank.[65] Based on the test results, pump sizes and

locations were selected for mixing waste tanks at SRS and preparing feed for the DWPF. The feed preparation has been successful. In addition, kaolin slurries were used to measure the pump requirements to transfer Bingham plastic fluids in inter-area transfer lines at SRS.[66] The inter-area transfers have been successful.

Other properties such as particle shape, concentration, surface charge, particle size distribution, slurry cohesiveness and adhesiveness, liquid pH, and ionic strength influence the simulant properties either directly or through other physical properties such as yield stress, shear strength, and particle size. If using physical simulants, these effects are best captured with the properties of particle size, yield stress, consistency, and shear strength. If using chemical simulants, these properties should be considered in developing the simulant.

Physical simulants should be adequate for most or all of the potential test objectives. For the following potential test objectives chemical simulants are recommended: measuring gas retention and release, assessing foaming, assessing aerosol generation, and assessing the impact of aging on slurry rheology. These potential objectives are not part of the current test plan.

Investigating chemical effects in the WTP vessels is best tested at a bench-scale with more rigorous chemical simulants. The following work is recommended: investigating the impact of aging on slurry shear strength, measuring gas retention and release, measuring the adhesiveness of Hanford actual waste, and measuring the critical shear stress for erosion.

Very limited data is available on the effect of settling time on Hanford actual waste shear strength, and the samples analyzed previously may not be representative of the slurries to be processed in the WTP. Previous work by SRNL observed large increases in slurry shear strength when the slurries sat for extended times.[32] Similar testing should be conducted with actual waste for the WTP.

Developing a physical simulant to test gas retention and release would be very difficult. An alternative would be to conduct bench-scale tests to measure gas retention and release in chemical simulants or actual waste, and comparing the results to testing with physical simulants. With this data, physical simulant could be developed that bounds the gas retention properties of the expected WTP slurries.

Cohesiveness and adhesiveness are properties of solids that make them "tacky" or "sticky". Cohesive and adhesive particles could be more difficult to suspend and mobilize. A method was investigated by SRNL to measure adhesiveness of simulated waste slurries by measuring the increase in mass when a carbon steel coupon was dipped in a simulated slurry.[67] A similar approach should be investigated to measure adhesiveness of Hanford waste and Hanford simulated waste.

The critical shear stress for erosion is a metric that describes the physics of solid particle suspension well. Unfortunately, no measured data exists on the critical shear stress for erosion of actual Hanford waste. The project should investigate developing a method to measure this property for actual Hanford waste.

5.0 Conclusions

The slurry properties that are most important to FSVT depend on the test objective and rheological classification of the slurry (i.e., Newtonian or non-Newtonian).

The most important parameters for testing with Newtonian slurries are the particle size, particle density, and the particle concentration. The particle size distribution is important and should be considered in simulant development rather than just a median particle size or a maximum particle size. In addition, the particle size and density must be considered together. They can be combined in a dimensionless parameter such as the Archimedes number or in an engineering metric such as a settling velocity or a critical suspension velocity. For some test objectives, the settled solids shear strength is important.

The most important properties for testing with non-Newtonian slurries are the slurry yield stress, the slurry consistency, and the slurry shear strength. The solid-liquid density difference and the particle size are also important. The slurry yield stress, solid-liquid density difference, and particle size can be combined in a dimensionless Yield parameter. It is also important to match multiple properties (e.g., yield stress and shear strength) within the same simulant to achieve behavior representative of the waste.

Other properties such as particle shape, concentration, surface charge, and size distribution breadth, as well as slurry cohesiveness and adhesiveness, liquid pH and ionic strength also influence the simulant properties either directly or through other physical properties such as yield stress or particle size.

The FSVT will assist in determining limits for the WTP. This will be done in part by extending properties of the simulants beyond the bounding values discussed in this document.

The recommendations for properties for full-scale vessel testing follow.

- Particle Size

   For Newtonian fluids and non-Newtonian fluids, the recommended range of particle size to be investigated is 1 – 700 micron. The 700 micron particle size is based on the design basis fluid properties (and a particle density of 2.9 g/mL). Limits could be assessed by including a larger particle in the simulant. Since the WTP feed will likely contain particles less than 1 micron, the use of submicron particles should be considered in developing simulants.

- Particle Density

   Particle density should be selected to represent the densities of select particles that exist in Hanford waste. The simulant needs to have particles representative of the largest particles in the feed, the major aluminum compounds in the feed, small dense particles such as PuO_2 or Bi_2O_3, and the fine particles in the feed. Limits are more easily assessed by increasing the particle size rather than the particle density.

- Shear Strength of Settled Layers

   The simulant shear strength to evaluate PJM restart relative to gas retention and release should be 1500 Pa. This limit is based on a single measurement of an actual Hanford waste sample that sat for 72 hours.

- Yield Stress and Consistency for non-Newtonian Simulants

   The slurry yield stress should range between 0 Pa and 30 Pa. The slurry consistency should range between 1 cP and 30 cP. To assess limits, the slurry yield stress should be increased to 40 Pa, and the slurry consistency should be increased to 40 cP. These

values are based upon the estimated measurement and sampling uncertainty in yield stress and consistency measurements. Low values of yield stress and consistency (e.g., 0 Pa and 1 cP) may allow fast-settling particles to settle in these fluids, creating a challenge to meeting vessel mixing requirements.

- Solids Concentration
  The recommended insoluble solids concentration for tests with Newtonian fluids is 0 – 20 wt %. To assess limits, the insoluble solids concentration should be increased to 27 wt %. For non-Newtonian fluids, the insoluble solids concentration should be that which is needed to achieve the desired rheology.

- Viscosity
  The recommended viscosity for Newtonian fluids is 1 – 10 cP.

- Physical simulants should be adequate for most or all of the potential test objectives. For the following potential test objectives chemical simulants are recommended: measuring gas retention and release, assessing foaming, assessing aerosol generation, and assessing the impact of aging on slurry rheology. These potential objectives are not part of the current test plan.

6.0 References

[1] P. A. Meyer, J. A. Bamberger, C. W. Enderlin, J. A. Fort, B. E. Wells, S. K. Sundaram, P. A. Scott, M. J. Minette, G. L. Smith, C. A/ Burns, M. S. Greenwood, G. P. Morgen, E. B. K. Baer, S. F. Snyder, M. White, G. F. Piepel, B. G. Amidan, and A. Heredia-Langner, "Pulse Jet Mixing Tests With Noncohesive Solids," PNNL-18098, WTP-RPT-182, Rev. 0, May 2009.

[2] D. C. Koopman, C. J. Martino, and M. R. Poirier, "Properties Important to Mixing for WTP Large Scale Integrated Testing", SRNL-STI-2012-00062, Rev. 0, April 2012.

[3] P. S. Sundar, "Guideline for Simulant Development, Approval, Validation, and Documentation," 24590-WTP-GPG-RTD-004, Rev. 2, 12/08/2011.

[4] I. C. Walton, "Eddy Diffusivity of Solid Particles in a Turbulent Liquid Flow in a Horizontal Pipe", AIChE J., vol. 41, no. 7, pp. 1815-1820, 1995.

[5] V. A. Atiemo Obeng, W. R. Penney, and P. Armenante, "Solid-Liquid Mixing", in E. L. Paul, V. A. Atiemo-Obeng, and S. M. Kresta, Eds., Handbook of Industrial Mixing: Science and Practice, Hoboken:Wiley, 2004.

[6] C. O. Bennett and J. E. Myers, Momentum, Heat, and Mass Transfer, 3rd Ed., New York: McGraw-Hill, 1982.

[7] E. L. Paul, V. A. Atiemo-Obeng, and S. M. Kresta, Eds., Handbook of Industrial Mixing: Science and Practice, Hoboken:Wiley, 2004.

[8] M. Poreh, Y. G. Tsuei, and J. E. Cermak, "Investigation of a Turbulent Radial Wall Jet", Trans ASME - J. Applied Mechanics, pp. 457-463, June 1967.

[9] B. E. Wells, J. L. Huckaby, J. M. Tingey, D. E. Kurath, S. K. Cooley, R. C. Daniel, L. A. Mahoney, C. A. Burns, K. K. Anderson, Y. Onishi and E. C. Buck, "Hanford Waste Physical and Rheological Properties: Data and Gaps," PNNL-20646, EMSP-RPT-006, Rev. 0, August 2011.

[10] CRESP Review Team Letter Report 7 – PJM Vessels, July 1, 2010.

[11] W. L. Isom, T. J. Venetz, J. G. Reynolds, D. L. Herting, D. E. Place, T. L. Sams, C. H. Delegard, S. A. Jones, R. C. Hoyt, T. E. Jones, J. A. Teal, D. E. Bowers, D. C. Lind, and R. A.

Watrous, "Review of Plutonium Oxide Receipts into Hanford Tank Farms", RPP-RPT-50941, Rev. 0, October 2011.

[12] K. P. Lee, B.E. Wells, P.A. Gauglitz, and R.A. Sexton, "Waste Feed Delivery Mixing and Sampling Program Simulant Definition for Tank Farm Performance Testing," RPP-PLAN-51625, Rev. 0, March 20, 2012.

[13] R. Gimpel, Slurry Property Ranges in Non-Newtonian Pretreatment Vessels at WTP," 24590-WTP-RPT-PET-10-014, Rev. 2, 6/23/2010.

[14] R.S. Disselkamp, "Hanford Waste Mineralogy Reference Report," RPP-RPT-46618, Rev. 1, June 2010.

[15] RPP-9805, "Values of Particle Size, Particle Density, and Slurry Viscosity to Use in Waste Feed Delivery Transfer System Analysis", Rev. 0, March 14, 2002, CH2M Hill Hanford Group, Inc.

[16] D. Reid, "Basis of Design", 24590-WTP-DB-ENG-01-001, Rev2, October 16, 2014.

[17] K. P. Lee, B.E. Wells, P.A. Gauglitz, and R.A. Sexton, "Waste Feed Delivery Mixing and Sampling Program Simulant Definition for Tank Farm Performance Testing," RPP-PLAN-51625, Rev. 0, March 20, 2012.

[18] A. P. Poloski, J. M. Tingey, B. E. Wells, L. A. Mahoney, M. N. Hall, G. L. Smith, S. L. Thomson, M. E. Johnson, M. A. Knight, J. E. Meacham, M. J. Thien, J. J. Davis and Y. Onishi, "Estimate of Hanford Waste Rheology and Settling Behavior," PNNL-16857, WTP-RPT-154, Rev. 0, 2007.

[19] I. Milgate, "SHSVD Design Basis Properties and Mixing Requirements Based on Vessel Operating Mode", CCN 280302, September 30, 2015.

[20] W. Bujalski, K. Takenaka, S. Paolini, M. Jahoda, A. Paglianti, K. Takahashi, A. W. Nienow, and A. W. Etchells, "Suspension and Liquid Homogenization in High Solids Concentration Stirred Chemical Reactors", Trans. IChemE, vol. 77, Part A, May 1999, pp. 241-247.

[21] M. R. Poirier, E. K. Hansen, and S. D. Fink, "Comparing Options to Testing at Ambient and Elevated Temperatures", SRNL-STI-2014-00021, February 5, 2014.

[22] "ICD 19 – Interface Control Document for Waste Feed," 24590-WTP-ICD-MG-01-019, Rev. 7, September 19, 2014.

[23] R. B. Bird, R. C. Armstrong, O. Hassager, Dynamics of Polymeric Liquids, Vol. 1, Fluid Mechanics, John Wiley & Sons, New York, 1977.

[24] G. W. Govier and K. Aziz, "The Flow of Complex Mixtures in Pipes", Malabar: Krieger Publishing Co., 1982, p. 215.

[25] E. P. Shine and M. R. Poirier, "Defining and Characterizing Sample Representativeness for DWPF Melter Feed Samples", SRNL-STI-2013-00544, October 2013.

[26] Chhabra, R.P. Richardson, J.F.. (2008). *Non-Newtonian Flow and Applied Rheology - Engineering Applications (2nd Edition).* Elsevier. Online version available at: http://app.knovel.com/hotlink/toc/id:kpNNFAREAC/non-newtonian-flow-applied/non-newtonian-flow-applied.

[27] A. P. Poloski, P. A. Meyer, L. K. Jagoda, and P. R. Hrma, ""Non-Newtonian Slurry Simulant Development and Selection for Pulse Jet Mixer Testing", WTP-RPT-111, Rev. 0, August 2004.

[28] C. W. Macosko, Rheology; Principles, Measurements, and Applications, Wiley-VCH, 1994.

[29] W. King, R. Eibling, M. Hay, R. Peterson, G. Brown, B. Wells, C. Carlson, S. Fiskum, D. Rector, R. Russell, W. Kuhn, C. Burns, J. Fort, "FSVT Vessel Group 5 Simulant Supporting RLD-08T (90% Review Draft)", GD-FSVT-0017, February 2014.

[30] D. Paphitis, "Sediment Movement under Unidirectional Flows: An Asessment of Empirical Threshold Curves", Coastal Engineering, vol. 43, pp. 227-245, 2001.

[31] LA Snow, RC Daniel, LK Jagoda, RA Peterson, EC Buck, KE Draper, ED Jenson, RG Swoboda, AJ Casella, MK Edwards, AE Kozelisky, JV Crum, SK Fiskum, PJ MacFarlan, "Characterization and Leach Testing for PUREX Cladding Waste Sludge (Group 3) and REDOX Cladding Waste Sludge (Group 4) Actual Waste Sample Composites", WTP-RPT-167, Rev 0, February 2009.

[32] Michael R. Poirier, David Herman, Fernando F. Fondeur, Erich Hansen, and Samuel D. Fink, "MST/Sludge Agitation Studies for Actinide Removal Process and DWPF", WSRC TR-2003-00471, October 10, 2003

[33] W. King, R. Eibling, M. Hay, R. Peterson, B. Wells, S. Fiskum, R. Russel, G. Brown, and D. Rector, "FSVT Vessel Group 5 Simulant Basis Preliminary Results, Part 2 – Component Identity, Characteristics, and Development and Preliminary Recipes (60% Review Draft)."

[34] N. P. Brown and N. I. Heywood, Slurry Handling Design of Solid-Liquid Systems, New York: Elsevier, 1991.

[35] B. Camenen "Simple and General Formula for the Settling Velocity of Particles" Journal of Hydraulic Engineering **133**(2):229-233, 2007.

[36] J. A. Fort, P. A. Meyer, J. A. Bamberger, C. W. Enderlin, P. A. Scott, M. J. Minette, and P. A. Gauglitz, "Scaled Testing to Evaluate Pulse Jet Mixer Performance in Waste Treatment Plant Mixing Vessels", 10487, WM2010 Conference, March 7-10, 2010, Phoenix, AZ.

[37] R. N. Kale and A. W. Patwardhan, "Solid Suspension in Jet Mixers", Can. J. Chem. Eng., vol. 85, pp. 816-828, 2005.

[38] B. E. Wells, M. A. Knight, E. C. Buck, S. K. Cooley, R. C. Daniel, L. A. Mahoney, P. A. Meyer, A. P. Poloski, J. M. Tingey, W. S. Callaway III, G. A. Cooke, M. E. Johnson, M. G. Thien, D. J. Washenfelder, J. J. Davis, M. N. Hall, G. L. Smith, S. L. Thomson, and Y. Onishi, "Estimate of Hanford Waste Insoluble Solid Particle Size and Density Distribution", WTP-RPT-153, Rev. 0, 2007

[39] Th. N. Zwietering, "Suspending of Solid Particles in Liquids by Agitators", Chem. Eng. Sci., vol. 4, pp. 244-253, 1958.

[40] P. Ayazi Shamlou and A. Zolfagharian, "Suspension of Solids in Liquid-Jet Stirred Vessels", Fluid Mixing IV, pp. 365-378, 1990.

[41] R. Clift, J. R. Grace and M. E. Weber, "Bubbles, Drops, and Particles," Academic Press, Inc., 1978.

[42] K. Rietema, The Dynamics of Fine Powders, Elsiever Applied Sciences, 1991.

[43] J. N. Tilton, "Fluid and Particle Dynamics," in Perry's Chemical Engineers' Handbook, D. W. Green, R. H. Perry, eds., 8th Edition, McGraw-Hill, 2008.

[44] A. Haider and O. Levenspiel, "Drag Coefficient and Terminal Velocity of Spherical and Nonspherical Particles," *Powder Technology*, **58**, pp. 63 – 70, 1989.

[45] R. P. Chhabra, L. Agarwal and N. K. Sinha, "Drag on non-spherical particles: an evaluation of available methods," *Powder Technology*, **101**, pp. 288 – 295, 1999.

[46] G. H. Ganser, "A rational approach to drag prediction of spherical and nonspherical particles," *Powder Technology*, **77**, pp. 143 – 152, 1993.

[47] E. Loth, "Drag of non-spherical solid particles of regular and irregular shape," *Powder Technology*, **182**, pp. 342-353, 2008.

[48] E. Rabinovich and H. Kalman, "Incipient motion of individual particles in horizontal particle—fluid systems: A. Experimental Analysis," *Powder Technology*, **192**, pp. 318-325, 2009.

[49] H. Kalman, A. Satran, D. Meir, and E. Rabinovich, "Pickup (critical) velocity of particles," *Powder Technology*, **160**, pp. 103-113, 2005.

[50] R. B. Thorpe and P, Stevenson, "Suspension of Particles from the Bottom of Pipes and Stirred Tanks by Gassed and Ungassed Flows," *Canadian Journal of Chemical Engineering*, **81**, pp. 351-359, 2003.

[51] K. S. Hayden, K. Park, and J. S. Curtis, "Effect of particle characteristics on particle pickup velocity," *Powder Technology*, **131**, pp. 7-14, 2003.

[52] S. M. Barnes, "HLW Sludge Simulant Qualification Data Package," CCN 21493, March 23, 2010.

[53] D. L. Herting, "Simulant Qualification Data Package for LOAM Benchmark Testing (5 Component) – Supersedes 226286," CCN 228917, December 7, 2010.

[54] G. J. Lumetta, E. C. Buck, R. C. Daniel, K. Draper, M. K. Edwards, S. K. Fiskum, R. T. Hallen, L. K. Jagoda, E. D. Jenson, A. E. Kozelisky, P. J. MacFarlan, R. A. Peterson, R. W. Shimskey, S. I. Sinkov, and L. A. Snow, "Characterization, Leaching, and Filtration Testing for Bismuth Phosphate Sludge (Group 1) and Bismuth Phosphate Saltcake (Group 2) Actual Waste Composites," PNNL-17992, WTP-RPT-166, Rev. 0, February 2009.

[55] M. K. Edwards, J. M. Billing, D. L. Blanchard, E. C. Buck, A. J. Casella, A. M. Casella, J. V. Crum, R. C. Daniel, K. E. Draper, S. K. Fiskum, L. K. Jagoda, E. D. Jenson, A. E. Kozelisky, P. J. MacFarlan, R. A. Peterson, R. W. Shimskey, L. A. Snow, and R. G. Swoboda, "Characterization, Leaching, and Filtration Testing for Tributyl Phosphate (TBP, Group 7) Actual Waste Composites," PNNL-18119, WTP-RPT-169, Rev. 0, March 2009.

[56] S. K. Fiskum, J. M. Billing, E. C. Buck, J. V. Crum, R. C. Daniel, K. E. Draper, M. K. Edwards, A. E. Kozelisky, P. J. MacFarlan, R. A. Peterson, and R. W. Shimskey, "Characterization, Leaching, and Filtration Testing of Ferrocyanide Tank Sludge (Group 8) Actual Waste Composites," PNNL-18120, WTP-RPT-170, Rev. 0, February 2009.

[57] R. W. Shimskey, J. M. Billing, E. C. Buck, R. C. Daniel, K. Draper, M. K. Edwards, J. G. H. Geeting, R. T. Hallen, E. D. Jenson, A. E. Kozelisky, P. J. MacFarlan, R. A. Peterson, L. A. Snow, and R. G. Swoboda, "Filtration and Leach Testing for REDOX Sludge and S-Saltcake Actual Waste Composites," PNNL-17965, WTP-RPT-172, Rev. 0, February 2009.

[58] D. C. Koopman, "A Comparison of rheology data for Radioactive and Simulant Savannah RIver SIte Waste", WSRC-TR-2004-00044, March 2004.

[59] P. R. Burket, T. M. Jones, T. L. White, C. L. Crawford, and T. B. Calloway, "Evaluation of Foaming and Antifoam Effectiveness during the WTP Oxidative Leaching Process", WSRC-TR-2005-00263, REV. 0, September 2005.

[60] T. L. White, C. L. Crawford, P. R. Burket, and T. B. Calloway, "Stability of Dow Corning Q2-3183A Antifoam in Irradiated Hydroxide Solution", SRNL-STI-2009-00669.

[61] M. Malin and J. Huckaby, 2013. "8' Vessel Dye Test", CCN 255130.

[62] M. Kraume, "Mixing Time in Stirred Suspensions", Chem. Eng. Technol., vol. 15, 1992, pp. 313-318.

[63] R. M. Turian, F.-L. Hsu, and T.-W. Ma, "Estimation of the Critical Velocity in Pipeline Flow of Slurries", Powder Technology, vol. 51, pp. 35-47, 1987.

[64] P. J. Keuhlen, G. B. Josephson, and L. P. Moualeu, "Analysis of Bottom Motion for Standard High Solids Vessel Design", 24590-WTP-ES-ENG-15-014, September 8, 2015.

[65] B. V. Churnetski, "Effective Cleaning Radius Studies", DPST-81-282, February 19, 1981.

[66] T. Motyka, "Slurry Pipeline Tests in Support of the In-Tank Sludge Processing Program", DPST-83-266, January 25, 1983.

[67] M. E. Stone, "Evaluation of Method for Measurement of Sludge Simulant Adhesion", SRNL-ITS-2006-00003, January 5, 2006.

Appendix A: Other Dimensionless Groups

This appendix discusses other dimensionless groups that were considered, but determined not to be significant for developing simulants for full-scale vessel testing. Those dimensionless groups are the particle Reynolds number, the Froude number, the particle Froude number, the yield Reynolds number, and the Hedstrom number.

The Reynolds number for a settling particle, Re_P, is a function of the particle size, kinematic viscosity, and terminal settling velocity, V_S, and is defined as

$$Re_P = V_S\, d_P / \nu_L \qquad\qquad [3]$$

An analogous Reynolds number can be defined using the particle-to-liquid slip velocity, but this has no impact on the properties that matter to mixing. The settling Re_P is a two-constant function of the Archimedes number in each of three settling regimes (Stokes, Intermediate, and Newton) using the approximations for the drag coefficient given in Ref. 9 (page 2.2).

$$Re_P = C * Ar^n \qquad\qquad [4]$$

Stokes	$C = 1/18$	$n = 1$	Re_P variably defined as < 0.3 (or 0.1 or 1)
Intermediate	$C = 1/6.54$	$n = 5/7$	$0.3 < Re_P < 1,000$
Newton	$C = 1.74$	$n = 1/2$	$1,000 < Re_P < 200,000$

The Froude number – the ratio of flow inertia to the external force of gravity – is a third dimensionless group used in some studies that is related to the Reynolds and Archimedes numbers. The square root of the Archimedes number equals the Reynolds number divided by the Froude number. Knowing any two of these groups is equivalent to knowing all three through this relationship. The Archimedes number was selected for use in this document because it only contains physical properties. Both the Reynolds and Froude numbers contain a characteristic velocity.

Another dimensionless number is the particle Froude number. The particle Froude number is the ratio of inertia forces to buoyancy forces. The particle Froude number is described by equation [5]

$$Fr_p = \rho_l V^2 / (\rho_s - \rho_l) d_p g \qquad\qquad [5]$$

where V is the PJM nozzle velocity, ρ_l is the liquid density, ρ_s is the solid density, d_p is the particle size, and g is gravitational acceleration. Since the nozzle velocity will not change for different simulants and the liquid density does not vary much, the particle Froude number is inversely proportional to the product of the solid-liquid density difference and the particle size. Smaller values are expected to produce more challenging simulants.

Another dimensionless parameter is the yield Reynolds number. The yield Reynolds number is described by equation [6]

$$Re_\tau = \rho V^2 / \tau_s \qquad\qquad [6]$$

where V is the PJM nozzle velocity and τ_s is the slurry shear strength. [Alternatively, the slurry yield stress could be used.] This parameter allows the PJM nozzle velocity to be changed to account for variations in the slurry shear strength. Since the nozzle velocity will not change with different simulants, any differences in the yield Reynolds number between simulants will be due to differences in shear strength (or yield stress). Smaller values of the yield Reynolds number are expected to produce more challenging simulants.

Another dimensionless number is the Hedstrom number. The Hedstrom number is defined by equation [7]

$$He = D^2\rho_l\tau_y/\eta^2 \qquad\qquad [7]$$

where D is pipe diameter, ρ_l is the liquid density, τ_y is slurry yield stress, and η is slurry consistency. The Hedstrom number is essentially a ratio between slurry yield stress and slurry consistency. It is not recommended as an important property for FSVT simulants.

Appendix B: Impact of Chemistry on Waste Properties

The effects of the chemical composition of Hanford waste slurries need consideration in the test program, and in developing simulants. The pH, ionic strength, isoelectric point, and zeta potential can affect interparticle forces.

The *isoelectric point*, i.e.p., of a particle surrounded by a liquid corresponds to the pH where the number of positively charged surface sites equals the number of negatively charged surface sites, i.e., zero net surface potential. The electrostatic repulsive force, that normally tends to prevent small particles from agglomerating together, is minimized at the i.e.p. The range of i.e.p. for oxides and hydroxides of common elements is at least $2 < \text{pH} < 12$.[1] Electrostatic repulsive forces between like particles diminish as the liquid pH moves toward the i.e.p. allowing particle agglomeration to occur. The forces can affect fluid viscosity, slurry rheology, and particle agglomeration.

Electrokinetic experiments measure a potential in the double layer (the surrounding counterions) called the *zeta potential*. This measurement gives a lower bound for surface charge and helps in the determination of the i.e.p. Yield stress often reaches its maximum value when the system is near the net i.e.p. of the assembled particles. Measured rheology during acidification has also showed a maximum in yield stress passing through the neutral region.

The extent to which the particle surfaces interact electrostatically is modified by both the *ionic strength* and the pH of the surrounding liquid. Increasing ionic strength shields more of the surface charges from nearby particles, while pH changes the net charge of the surface itself. In the pretreatment facility, the range of ionic strength is observed through the sodium concentration and the dissolved solids concentration. The sodium concentration ranges from 0.1 – 10 Molar, and the dissolved solids concentration ranges from 0.8 – 56 wt %. The pH is ≥ 12.[2] The changes in ionic strength and pH resulting from leaching and washing could cause significant changes in the manner in which particle surfaces interact, causing changes in properties such as agglomerate size, fluid viscosity, and slurry rheology.

Ionic strength, pH, zeta potential, and isoelectric point are all quantities that help to describe the behavior of a slurry of colloidal solids at microscopic scale. These four quantities impact macroscopic slurry physical properties such as the yield stress, consistency, viscosity, particle size, cohesiveness, adhesiveness, and shear strength. Unfortunately, these influences are not well enough understood to directly predict or correlate the important physical properties for PJM mixing. Ionic strength and pH change during waste mobilization and transfer to WTP and during pre-treatment activities such as caustic leaching of aluminum and washing in the UFP vessels. In addition with both simulants and actual waste, lower ionic strength has been observed to result in peptization of the solids and the formation of a stable suspension which should be easier to pump and transfer. This phenomenon appears to be reversible. It has been observed during washing of sludge slurries to a sodium concentration <0.01 M. Since the causes of this behavior are not understood and have not been examined across a range of wastes, it is premature to attempt to mimic or bound this behavior in full-scale testing. This phenomenon has not been rigorously studied and should be looked at more closely at bench-scale.

All liquids and solids are cohesive to some extent. Cohesion and adhesion are similar thermodynamic concepts, defined as either a work term or a Gibbs energy associated with creating new free surface area.[3] Cohesion and adhesion as defined thermodynamically can be either microscopic or macroscopic scale quantities. Cohesive work creates a surface from within

a homogeneous material by subdividing it, while adhesive work creates a surface where there formerly was a phase boundary, e.g. the surface of contact between a fluid and the wall confining it. Cohesion and adhesion at the molecular scale are related to the macroscopic scale phenomena of surface tension and interfacial tension, that is, forces involved in changing surface area or the spreading of one material on another. The cohesive and adhesive behavior of macroscopic scale slurries is derived from the cumulative effect of the surface forces described above (summed over all sizes, compositions, etc.) coupled with the aqueous phase properties. Cohesion applies to particles of the same compound "sticking" together, and adhesion applies to particles "sticking" to particles of different compounds or surfaces such as vessel walls or internals.

At SRS, three of the first eight batches processed thus far through DWPF exhibited some degree of adhesive behavior in waste both prior to and during waste processing.[4] In one case, an adhesive slurry caused an approximately quarter-inch thick coating of slurry on equipment internals that was resistant to removal. In other cases, adhesive slurries at neutral to basic pH caused coil fouling in equipment, where sludge adhered to coils and filled the narrow gaps between tubes. A practical engineering approach for predicting and modeling cohesive behavior is lacking for the wide chemical composition range applicable to PTF (and Hanford wastes). Because of the lack of a standard measurement for cohesiveness/adhesiveness and the lack of measured cohesiveness/adhesiveness data for Hanford and SRS waste, this property cannot be adequately represented in simulants at this time. The discussion later in this Appendix discusses approaches to reduce the risk from not matching cohesiveness and adhesiveness in slurries.

Cohesive forces increase resistance to motion in a slurry. However, cohesion is not equivalent to yield stress; some fluids have high cohesive strengths but exhibit no yield stress. Cohesiveness can also give rise to solid-like behavior. For example, partial recovery from deformation, or strain, has been observed in SRS simulants once the applied stress is removed.[5] The addition of solids to a liquid can increase the cohesiveness of the slurry relative to the solid-free liquid. For a given composition, finer solids have a larger impact on cohesion because of their greater surface area per unit mass. The slurry cohesiveness can impact properties such as yield stress, shear strength, and critical shear stress for erosion. A change in cohesiveness is not expected to impact all of the affected properties by the same amount in different systems. Slurry cohesiveness has not been measured for Hanford or SRS wastes.

Slurry cohesiveness will depend on the particle size distribution, solid mass fraction, solid phase composition, and liquid phase composition for the reasons described above. Potential methods for representing cohesiveness in a waste simulant involve matching some of the following aspects of the waste: chemical compounds, particle sizes, surface charges, and ionic strength and pH of the liquid phase. The goal would be to match yield stress, consistency, and shear strength with a simulant that has comparable UDS concentration with actual waste. In addition, preparing a non-Newtonian slurry with cohesive particles reduces the risk of missing an effect that is not directly manifested in rheology.

Tank farm samples of caustic slurries of these sludge batches tended to stick to the stainless steel sample containers as well as slurry pipettes when the sludge was removed for testing in the SRNL Shielded Cells. Other DWPF batches were relatively free flowing. Rheological properties of all of the DWPF sludge batches were similar. The observed behavior indicates that phenomena not captured in the yield stress and consistency produced effects that were visible during sludge handling and processing.

Similarities between PUREX wastes at Hanford and SRS would suggest that adhesive slurries could be encountered at some point during WTP processing. When that occurs, it can potentially

interfere with operations in PJM mixed vessels. Literature studies indicate that particle shape and surface roughness play a part in the adhesiveness of particles toward surfaces.[6,7,8] However, there is currently no technical basis to underpin forecasting when adhesion may occur, what the degree of adhesion might be, or what factors affect the onset or extent of adhesion.

Small bubbles in a yield stress/strength medium have insufficient buoyant force to rise through the medium and be released. Accumulation of bubbles becomes a bigger issue as the yield stress increases. When gas molecules are generated in a settled solid bed, they may diffuse out, or migrate to other locations to nucleate and grow bubbles, but the bubbles may be constrained by the surrounding bed of settled solids and unable to rise. The cohesiveness/adhesiveness of the settled solid bed is important to gas retention because a growing bubble will attempt to displace the particles around it, and the cohesiveness/adhesiveness of the bed works in opposition to the growing bubble. The yield strength of samples of different bed materials is one quantitative measure of the relative cohesiveness of different settled beds. The density of the bed material is also important, since mass per unit height contributes to the force that a rising bubble must overcome to push upwards through the settled solids.

A method was investigated by SRNL to measure adhesiveness of simulated waste slurries by measuring the increase in mass when a carbon steel coupon was dipped in a simulated slurry.[9] A similar approach could be developed to measure cohesiveness and adhesiveness of Hanford waste and Hanford simulated waste.

Agglomerates of precipitated inorganic chemical species made up of compounds of different elements have the ability to form biphylic particles.[10] These particles can behave similarly to surfactant chemicals (polar head/nonpolar tail). Non-Newtonian tanks in WTP will have air spargers, which would provide a method of introducing air bubbles into the vessel contents. In addition, PJM overblows may be employed to suspend settled beds of solid particles in some vessels. Foaming may occur, as was reported during the PEP tests, which used chemical simulants.[11]

Biphylic particles are important to gas retention as well. These particles preferentially reside at the gas-slurry interface instead of in the bulk slurry. The presence of one or more layers of biphylic particles around a bubble increases the drag force which can lead to the formation of a gas-in-slurry emulsion. This occurred during the early processing of the third DWPF sludge batch (or sludge batch 2 for clarity), but was mitigated by an increase in the acid added during processing. Mixing was unable to cause gas release in this waste slurry.

References

[1] G. A. Parks, "The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxocomplex systems," *Chem. Rev.*, **65**, pp. 177-198, (1965).

[2] R. B. Bird, R. C. Armstrong, O. Hassager, Dynamics of Polymeric Liquids, Vol. 1, Fluid Mechanics, John Wiley & Sons, New York, 1977.

[3] P. C. Hiemenz, Principles of Colloid and Surface Chemistry, 2nd ed., Marcel Dekker, Inc., New York, 1986.

[4] D. C. Koopman, "Factors Potentially Influencing the Tackiness of DWPF Streams," WSRC-TR-2000-00239, Rev. 0, Savannah River Site, 2000.

[5] D. C. Koopman, "Development of Alternative Rheological Measurements for DWPF Slurry Samples (U)"WSRC-TR-2004-00334, September 2005.

[6] Q. Li, V. Rudolph, and W. Peukert, "London-van der Waals adhesiveness of rough particles," *Powder Technology*, **161**, pp. 248-255, 2006.

[7] K. K. Lam and J. M. Newton, "Influence of particle size on the adhesion behaviour of powders, after application of an initial press-on force," *Powder Technology*, **73**, pp. 117-125, 1992.

[8] A. J. Matchett and B. Bland, "The adhesion of wet particles to walls in a model trough," *Powder Technology*, **65**, pp. 177-186, 1991.

[9] M. E. Stone, "Evaluation of Method for Measurement of Sludge Simulant Adhesion", SRNL-ITS-2006-00003, January 5, 2006.

[10] S. K. Bindal, A. D. Nikolev, D. T. Wasan, D. P. Lambert, and D. C. Koopman, "Foaming in Simulated Radioactive Waste," *Environ. Sci. Technol*., **35**, pp. 3941-3947, (2001).

[11] D. E. Kurath, P. W. Eslinger, S. M. Barnes, R. L. Aaberg, B. D. Hanson, J. L. Huckaby, E. C. Golovich, P. M. Aker, M. J. Minette, J. M. Billing, S. D. Rassat, C. E. Guzman-Leong, D. L. Baldwin, P. S. Sundar, C. F. Brown, M. L Kimura, B. M. Rapko, G. J. Josephson, J. G. H. Geeting, S. K. Sundaram, L. A. Mahoney, J. J. Toth, G. J. Sevigny, R. P. Pires, P. P. Schonewill, S. T. Yokuda, A. J. Casella, B. E. Wells, R. C. Daniel, E. B. K. Baer, J. R. Bontha and O. P. Bredt,"Pretreatment Engineering Platform Phase 1 Final Test Report," PNNL-18894,WTP-RPT-197, Rev 0, December 2009.