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Impact of Chemistry on Standard High Solids Vessel Design Mixing

M. R. Poirier
March 2016
SRNL-STI-2016-00081, Revision 0

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EXECUTIVE SUMMARY

The plan for resolving technical issues regarding mixing performance within vessels of the Hanford Waste Treatment Plant Pretreatment Facility directs a chemical impact study to be performed. The vessels involved are those that will process higher (e.g., 5 wt % or more) concentrations of solids. The mixing equipment design for these vessels includes both pulse jet mixers (PJM) and air spargers. This study assesses the impact of feed chemistry on the effectiveness of PJM mixing in the Standard High Solids Vessel Design (SHSVD). The overall purpose of this study is to complement the Properties that Matter document in helping to establish an acceptable physical simulant for full-scale testing.

The specific objectives for this study are (1) to identify the relevant properties and behavior of the in process tank waste that control the performance of the system being tested, (2) to assess the solubility limits of key components that are likely to precipitate or crystallize due to PJM and sparger interaction with the waste feeds, (3) to evaluate the impact of waste chemistry on rheology and agglomeration, (4) to assess the impact of temperature on rheology and agglomeration, (5) to assess the impact of organic compounds on PJM mixing, and (6) to provide the technical basis for using a physical-rheological simulant rather than a physical-rheological-chemical simulant for full-scale vessel testing.

The conclusions from the study follow.

- The important waste properties that control the performance of a vessel mixed with pulsed jet mixers are described in the Properties that Matter document.
- The primary impact of precipitation or crystallization of salts due to interactions between PJMs or spargers and waste feeds is to increase the insoluble solids concentration in the slurries, which will increase the slurry yield stress. The increase in insoluble solids concentration and yield stress is expected to be small.
- Slurry yield stress is a function of pH, ionic strength, insoluble solids concentration, and particle size. The key to developing a non-Newtonian simulant for testing is matching or bounding slurry yield stress. The yield stress of the waste feed qualification samples should be measured at the appropriate pH and ionic strength, and over the range of pH and ionic strength expected in the WTP. No testing of the effects of chemistry on yield stress during FSVT is recommended.
- Ionic strength and chemical composition can affect particle size. The key to developing a simulant for testing is matching or bounding the particle size. The particle size of the waste feed qualification samples should be measured at the appropriate pH and ionic strength, with subsequent characterization over the range of pH and ionic strength expected in the WTP should unanticipated behavior be seen. No testing of the effects of chemistry on particle/agglomerate size during FSVT is recommended.
- Changes in temperature can affect SHSVD mixing through its effect on properties such as viscosity, yield stress, solubility, and vapor pressure, or chemical reactions that occur at high temperatures. The key to developing simulants for testing is matching or bounding waste properties such as yield stress, viscosity, particle size, particle density, and particle concentration. The effect of increased temperature and vapor pressure on controlling the PJMs is being investigated separately.
- For most test objectives, organic compounds will affect SHSVD mixing through their effect on properties such as rheology, particle agglomeration/size, particle density, and particle concentration. These properties will be measured and verified to meet design during waste feed qualification. Organic compounds could affect gas retention, foaming, and aerosolization, but those phenomena are assumed to not be part of the test scope. Organic compounds could lead to an increase in vapor pressure, which may be enough to impact PJM refill. Previous work showed

the increase to be less than 4%, so therefore, this parameter does not have to be included for full-scale testing.

- The Properties that Matter document found physical simulants to be adequate for most to all of the potential test objectives. This Chemistry study identified three specific areas where waste chemistry considerations may play an important role in the selection of appropriate simulants and should not be overlooked for certain test objectives. These areas include understanding the effect of waste chemistry on gas retention and release, the effect of aging and long term settling on the development of shear strength in settled layers, and the development of adhesive and cohesive properties between particles. An approach to address these effects is further discussed in the document and summarized below.
    - Gas retention and release is assumed to not be a requirement for FSVT based on the current technical issue resolution path. If it returns to the test scope, testing needs to be performed with a chemical simulant or bench-scale testing needs to be conducted with actual waste and physical simulants to demonstrate that the physical simulants bound the actual waste for gas retention. If physical simulants are used for gas retention and release tests, there is a risk that they do not retain gas to the same degree that a chemical simulant or actual waste retains it.
    - Previous work by SRNL, ORNL, and PNNL has shown that allowing simulated and actual waste to settle for extended times can lead to large increases in slurry shear strength (up to 3X after 2 weeks and up to 16X after 6 weeks). Limited actual Hanford waste data exists describing the impact of settling time on slurry shear strength. If the PJMs did not operate for several days or several weeks, the shear strength could increase dramatically, potentially causing operational complexity for the WTP. The project should investigate the impact of settling time under prototypic conditions on slurry shear strength. This testing would require actual waste or chemical simulants. This data would allow the project to set a maximum idle time that a vessel could sit without adversely affecting WTP operation.
    - Adhesion of slurries to vessel internals has been observed at the SRS DWPF, and is a mechanism by which solids could accumulate in the WTP. In addition, an adhesive slurry may be more difficult to mix than a non-adhesive slurry with the same rheological properties. At present, there is no data describing the adhesiveness of Hanford waste slurries. SRNL has investigated a method to measure adhesiveness of slurries by measuring the increase in mass when a carbon steel coupon was dipped in a simulated slurry. A similar approach should be developed to measure cohesiveness and adhesiveness of Hanford waste and Hanford simulated waste, and relate the measured adhesiveness to fluid mixing and slurry mobilization.

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

BNI	Bechtel National, Inc.
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
ECR	effective clearing radius
EDTA	ethylenediaminetetraacetic acid
HEDTA	hydroxyethylethylenediaminetetraacetic acid
HLW	High Level Waste
HM	H Modified
i.e.p.	isolelectric point
FSVT	full-scale vessel testing
LAW	Low Activity Waste
MR	mixing requirement
ORNL	Oak Ridge National Laboratory
PJM	pulse jet mixer
PNNL	Pacific Northwest National Laboratory
PSD	Particle Size Distribution
PTF	Pretreatment Facility
SHSVD	Standard High Solids Vessel Design
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TBP	Tri-n-butyl phosphate
WRPS	Washington River Protection Solutions
WTP	Waste Treatment and Immobilization Plant

1.0 Introduction

1.1 Hanford WTP Background

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 and will separate it into:

1) a high-volume, low-activity, liquid process stream stripped of most solids and radioisotopes, and
2) a much smaller-volume HLW slurry containing the solids and most of the radioactivity, along with minimal soluble salts.

The PTF will remove solids and radioisotopes 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 interim storage.

The Pretreatment Facility will use Pulsed Jet Mixer (PJM) and air sparger technology for slurry mixing applications requiring solids suspension and solids mixing, as well as for fluid blending and release of evolved gas. The PJMs operate in different modes. The suction phase draws process fluid into the pulse jet mixer from the vessel. The drive phase pressurizes the PJM 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. During some operating scenarios, long times (several days or weeks) could occur between pulses. In PJM-mixed vessels, solids will tend to settle between PJM drive phases.[1] During some evolutions (e.g., sampling and during vessel content transfer), the project is considering use of air spargers to enhance the mixing performance.

In 2014, the U. S. Department of Energy (DOE) and Bechtel National, Inc. (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 (FSVT) of the prototypical design. A key aspect of the testing is developing an appropriate and defensible simulant. The plan for resolving technical issues regarding pretreatment pulse jet mixer vessel mixing capability directs a chemical impact study to be performed.[2] The chemistry impact study, along with the "Properties Important to Mixing and Simulant Recommendations for WTP Full-Scale Vessel Testing" document (this document will be referred to as the "Properties that Matter" document in the remainder of this text)[3], will assist the project in developing simulants for FSVT. This chemical impact study assesses the impact of feed chemistry on the effectiveness of PJM and sparger mixing in the SHSVD. The Properties that Matter document determined the important slurry properties for developing simulants for FSVT and provided technical justification for the properties. The objective of this chemistry study is to identify the relative impact of chemistry on waste properties (e.g., rheology, particle size) important to mixing and assess whether these effects need further consideration in selection of simulants for testing.

The objectives for these two studies follow.

- Identify the relevant properties and behavior of the in process tank waste that control the mixing performance of the system being tested and to select a simulant that replicates those specific properties and behaviors. [Described in the Properties that Matter document.]
- Provide the technical basis for using a physical-rheological simulant rather than a physical-rheological-chemical simulant for full-scale vessel testing. [Described in the Properties that Matter document. In addition, this study augments the earlier study and further explores specific aspects of chemical behavior that the project identified as possibly adversely affecting mixing performance.]
- Assess the solubility limits of key components that are likely to precipitate or crystallize due to PJM interaction with the waste feeds.
- Evaluate the impact of waste chemistry on rheology and agglomeration.
- Assess the impact of temperature on rheology and agglomeration.
- Assess the impact of organic compounds on waste properties relevant to the mixing system performance.

The two studies are complementary and supportive of establishing an appropriate simulant for use in full-scale vessel testing.

1.3 Full-Scale Vessel Testing Assumptions

The key assumptions for the FSVT that impact this study follow.[4]

- No gas release testing is required.
- No foaming/antifoam testing is required.
- No aerosolization testing is required.
- Plutonium metal mobilization and removal is not part of the planned testing.

2.0 Properties that Influence Mixing Behavior

The previously completed Properties that Matter document defined the most important parameters for mixing performance testing with Newtonian slurries as the particle size, particle density, and the particle concentration. For some test objectives (e.g., following extended particle settling), the settled solids shear strength is important.

The most important properties for mixing performance testing with non-Newtonian slurries are the slurry yield stress, the slurry consistency, and the slurry shear strength. The slurry shear strength is important when mobilizing solid particles that have been allowed to settle. The solid-liquid density difference and the particle size are important when they are large and the yield stress is small. 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. Their influence is usually observed through other physical properties such as yield stress or particle size, and they do not need to be emulated to provide sufficient testing of mixing performance.

Details can be found in the prior document.[3]

3.0 Basis for Conducting Tests with Physical Simulants

The Properties that Matter document determined that physical simulants should be adequate for meeting test objectives except when the purpose of the testing is measuring gas retention and release, assessing foaming, assessing aerosol generation, and assessing the impact of aging on slurry rheology. These potential objectives are not currently part of the test plan. Details can be found in the document.[3]

This study augments the earlier study and further explores specific aspects of chemical behavior that the project identified as possibly adversely affecting mixing performance.

4.0 Solubility Limits of Key Components

One objective of this study is to examine the solubility limits of key components of the feed which are likely to precipitate or crystalize due to interaction between the feed and the PJMs. The effects being considered include dehydration due to dry air contacting the feed, cooling of the vessel from contact with air, and interactions with carbon dioxide which may change the pH of the fluid causing changes in the solubility of compounds. Carbon dioxide in water will form carbonate, which can precipitate compounds such as strontium.

The main compounds of concern for this study are sodium oxalate, aluminum precipitates (i.e., gibbsite and boehmite), sodium aluminosilicate, sodium phosphate, sodium carbonate, sodium sulfate, and sodium double salts.

The primary effect of changing the solubility of dissolved salts is to increase the insoluble solids concentration in the slurries, which will increase the slurry yield stress. The relationship between insoluble solids concentration and yield stress is typically a power law or exponential.[5] This means that at low yield stress (~6 Pa), a small increase in the insoluble solids concentration would have small impact on yield stress, while near the design limit yield stress (30 Pa) the impact could be large. Similarly, increasing the concentration of soluble components to the point they exceed their solubility will have nearly the same impact on slurry rheology as increasing the insoluble solids concentration with the exception that the corresponding reduction in the insoluble species will alter the viscosity and density of the liquid phase which will also have a modest effect on the overall rheology.

Cooling of the vessel from contact with air will decrease the solubility of most components (strontium carbonate is an exception, which has an increased solubility with decreasing temperature). Cooling could therefore, lead to increased precipitation followed by an increase in the slurry yield stress.

The absorption of carbon dioxide would have two effects on the solubility of compounds in WTP slurries. When carbon dioxide dissolves in water it forms carbonic acid. The carbonic acid reacts with sodium hydroxide to form sodium carbonate and water. The reaction consumes free hydroxide, which will decrease the pH, which could change the solubility of some components. Given the high free hydroxide concentration and high ionic strength of WTP slurries, the pH change should be small. The sodium carbonate formed has a low solubility in Hanford wastes and would likely lead to a small increase in the insoluble solids concentration, with a corresponding impact on slurry yield stress.

Herting developed a model based on experimental data to calculate the PO_4 solubility as a function of temperature, sodium concentration, free hydroxide concentration, and fluoride concentration.[6] The model is described by equation [1] where the concentration of the ions is in Molar.

$$[PO_4] = \exp[(-4911.5/T(^\circ K) + 13.890] * [Na]^{-0.91906} * [OH]^{-0.11309} * [F]^{-0.31445} \qquad [1]$$

The model and the database used to develop it do not identify the precipitated compound. Likely compounds are $Na_3PO_4 \cdot 12H_2O \cdot 1/4NaOH$, $Na_7F(PO4)_2 \cdot 19H2O$, and $Na_3PO_4 \cdot 8H_2O$. While the model does not include all compounds that could be present and all possible reactions, it does provide an estimate of the magnitude of the amount of precipitation that could occur from changes in temperature or removal of water. The author used System Plan 6 as a basis and identified 10 feed vectors to evaluate with the model (batches 2, 55, 62, 101, 122, 133, 176, 403, 421, and 439).[7] These vectors were selected to look at maximum concentrations of ions that could precipitate (e.g., Na, PO4, F).

The model was used to calculate the change in phosphate solubility and increase in precipitated solids concentration (assuming the precipitated compound is $Na_3PO_4 \cdot 12H_2O \cdot 1/4NaOH$) following a decrease in slurry temperature from 60 ˚C to 55 ˚C, a decrease in slurry temperature from 45 ˚C to 40 ˚C, and a 5% increase in salt concentration from dehydration of the slurry.[a] The calculations show a 5 ˚C decrease in temperature would increase the insoluble solids concentration by < 0.6 wt%. A 5% increase in salt concentration from dehydration would increase the insoluble solids concentration by < 0.40 wt% due to precipitation of phosphate compounds. The dehydration will also increase the insoluble concentration. The increase in precipitated phosphate solids could be doubled to account for other compounds such as gibbsite, boehmite, sodium oxalate, sodium aluminosilicate, sodium carbonate, or sodium sulfate which are potentially precipitated under these conditions. In that case, the increase in insoluble solids would be on the order of 1 wt%. Such increases in insoluble solids concentration from salt precipitation remain small and should not significantly increase slurry yield stress.

5.0 Impact of Chemistry on Slurry Rheology and Agglomeration

5.1 Impact on Rheology

Increases in rheology (i.e., slurry yield stress) could make mixing in the SHSVD vessel more challenging. When mixing Bingham plastic fluids, a mixing cavern forms, in which the fluid is well mixed inside the cavern, and stagnant, or unmixed, outside the cavern. For a well-mixed system, the cavern will extend throughout the working volume of the vessel (i.e., the cavern extends to the vessel walls and breaks through the top fluid surface). The cavern size decreases

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[a] A calculation of vessel temperature losses during a post DBE using the FATE model showed the temperature of HPL-VSL-00022A/B/C would decrease from 150 ˚F to 112 ˚F in 1000 hours [24590-PTF-ES-ENG-15-010, page G-5]. Therefore, a 5 ˚C decrease should be a conservative estimate of temperature loss.

with increasing yield stress. If the slurry yield stress increases significantly (and exceeds the design basis of 30 Pa) because of changes in chemistry (e.g., pH or ionic strength), the cavern size could decrease and not include all of the contents of the vessel, causing the vessel design to not meet the mixing requirement. Verification testing is pending and needed to confirm the SHSVD provides mixing performance for which the mixing cavern envelops the entire vessel contents.

Fluid pH, fluid ionic strength, slurry composition, and solid particle size have been found to affect rheology. This section will review previous work by Washington River Protection Solutions (WRPS) One System, PNNL, SRNL, and the technical literature describing the effects of physical and chemical properties of slurries on fluid rheology to assess the impact of chemistry on rheology in the WTP.

Rheological properties of wastes are affected by a balance between attractive and repulsive particle interactions, which are functions of the physicochemical properties of the waste, such as particle size, particle concentration, particle shape, pH, and ionic strength. The key interactions are the van der Waals forces and the electric double layer forces. The van der Waals forces are attractive, and are most easily changed through changes in particle size. The electric double layer forces are repulsive when the particles have like charges and attractive when the particles have opposite charges. The electric double layer forces are functions of pH and ionic strength. Given the high pH of WTP PTF slurries, the double layer forces are expected to be repulsive.

Changes in the chemical properties of the slurry cause changes in the surface potential of the particles. Flocs or networks form when attractive van der Waals interactions dominate over the repulsive interactions (e.g., electric double layer), creating a continuous particulate network with yield stress. When repulsive forces increase, yield stress decreases. When repulsive forces exceed van der Waals attraction at pH far away from the isoelectric point, disperse suspensions are generated and the yield stress decreases. Waste chemistry affects disperse suspensions differently from flocculated suspensions.

Meacham (WRPS One System) conducted a literature review for the potential effects from waste mixing and blending on slurry rheology.[8] He found no good predictive tool for estimating yield stress and viscosity in mixed/blended wastes. SRNL conducted a review of rheology models for Hanford waste blending. They found some success in predicting the rheology of blends of similar type wastes when existing data waste available for each of the streams. The investigation recommended determining the rheology by direct measurement rather than by modeling.[9]

Meacham found the rheological properties of the wastes to be affected by a balance between attractive and repulsive particle interactions, which are influenced by the physicochemical characteristics of the waste. Changes in the chemical properties of the slurry will cause changes in the surface potential of the particles. Flocs or networks form when attractive van der Waals interactions dominate over the repulsive interactions (i.e., decrease in the surface potential), leading to increases in yield stress. When repulsive forces dominate, yield stress decreases. Changes in particle size, particle size distribution, particle density, and particle shape can change the balance between attractive and repulsive forces, leading to changes in yield stress.

The study also found the addition of rod-like particles is expected to increase the yield stress over a comparable slurry with spherical particles.[8] SRNL has observed rod-like boehmite particles in SRS waste.[10]

Another investigation of Hanford waste rheology showed the yield stress can vary significantly between waste tanks and waste types. The authors developed models to predict yield stress as a function of insoluble solids concentration. The fitting parameters of the models varied dramatically between different waste tanks.[11]

Wells et al. collected rheology data from 23 Hanford waste tanks as a function of insoluble solids concentration.[12] The data show that at an equal insoluble solids concentration of 10 wt %, the yield stress and consistency varied by two orders of magnitude. They attributed the variation to the differences in the wastes and sample conditions.

They looked at the effect of waste treatment processes (e.g., caustic leaching and washing) on slurry yield stress for eight waste groups representing 75% of the waste expected to be processed through the WTP. With Group 1 (Bismuth Phosphate Sludge) and Group 2 (Bismuth Phosphate Saltcake) waste, the yield stress increased following caustic leaching and washing. The effect after leaching and washing individually could not be determined because of differences in the insoluble solids concentration. With Group 3 (PUREX Cladding Waste) and Group 4 (REDOX Cladding Waste) waste, no conclusion can be drawn on the effect of caustic leaching and washing on yield stress, because of the significant difference in insoluble solids concentration between samples. With Group 5 (REDOX Sludge) and Group 6 (S Saltcake) waste, the caustic leaching increased slurry yield stress. Because of difference in insoluble solids concentration, no conclusion can be drawn to the effect of post caustic leach washing on yield stress. With Group 7 (TBP Sludge) waste, no conclusion can be drawn on the effect of caustic leaching and washing on yield stress, because of the significant difference in insoluble solids concentration between samples. With Group 8 (Ferrocyanide wastes), the caustic leaching had little effect on yield stress, but washing increased yield stress significantly.

SRNL filtration testing of simulated AN-102 waste found the yield stress of an ~ 20 wt% insoluble solids slurry to increase ~ 3X following washing (i.e., yield stress increased with decreasing ionic strength).[13]

Measurements of actual SRS DWPF Sludge Batch 2 rheology found sludge rheology to be affected by pH when the pH was between 5 – 7.[14] In another study, SRNL added NaOH to Sludge Batch 4 waste, similar to Hanford PUREX waste, to perform aluminum dissolution. As the sludge was leached, washed, and concentrated, increases and decreases were observed in the measured yield stress. After completion of leaching, washing, and concentration, the yield stress was larger at equivalent insoluble solids concentration.[15]

Work at the Savannah River Site has found HM sludge (high aluminum, low iron) to have a higher yield stress and consistency at the same insoluble solids loading than PUREX sludge (high iron, low aluminum).[16,17]

Leong et al. investigated the effect of particle size on colloidal slurry rheology.[18] They found the rheology to be better correlated with the fraction of fine particles than with the median particle size. Chun et al. investigated the effect of particle size distribution on rheology of LAW simulant slurries.[19] They found the percentage of colloid-sized particles to have an influence on rheology of the slurry. These results suggest that the concentration or fraction of fine particles has more influence on rheology than the median particle size.

Johnson et al. investigated the influence of pH and ionic strength on the rheology of suspensions of alumina, zirconia, and kaolin.[20] They found the slurry yield stress to vary with pH and zeta potential, with the maximum yield stress occurring at the pH where the zeta potential was equal to zero (i.e., the isoelectric point). They found the attractive van der Waals forces to be most easily manipulated through changes in particle size, and to be largely independent of conditions such as pH. They found yield stress to decrease with increasing ionic strength near the isoelectric point. With dissimilarly charged surfaces, the double layer force could be attractive or repulsive.

Zhou et al. looked at the influence of surface chemistry on the rheology of metal oxide suspensions.[21] They found the rheological properties of flocculated suspensions to be determined by colloidal interactions between particles and their arrangement or microstructure. The key interactions are van der Waals forces and electric double layer forces. They found an increased surface charge density leads to an increased electric double layer repulsive force, which leads to a decreased net attractive force and a decreased yield stress. The maximum yield stress occurs where the zeta potential is near 0 (i.e., near the isoelectric point). Since most processing will not occur near the isoelectric point, the effect of pH will not be important for WTP operation. They found the electrolyte concentration to have more effect on yield stress than the pH for disperse suspensions. Increasing the ionic strength compresses the electric double layer, which reduces the range and magnitude of the repulsive force, decreasing the yield stress. As the ionic strength increases, a limit is reached and the yield stress increases with increasing ionic strength. They found the yield stress to increase with decreasing particle size. They found the relationship between yield stress and particle concentration to be power law.

Kelessidis et al. investigated the effect of ionic strength on the rheology of bentonite dispersions.[22] They found the yield stress to decrease with increasing ionic strength.

PNNL measured apparent viscosity of boehmite slurries as a function of pH and found the apparent viscosity to have a maximum near the isoelectric point.[23] Since most processing will not occur near the isoelectric point, the effect of pH will not be important for WTP operation. Another PNNL study measured the apparent viscosity of ferric hydroxide and boehmite slurries as a function of pH.[24] That work also found the apparent viscosity to be a maximum near the isoelectric point.

All liquids and solids are cohesive and adhesive to some extent. The cohesive and adhesive behavior of slurries is derived from the cumulative effect of the surface forces 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. Cohesive forces increase resistance to motion in a slurry. Slurry cohesiveness will depend on the particle size distribution, solid mass fraction, solid phase composition, and liquid phase composition. These forces will affect the rheological properties of the slurry and its behavior in a PJM mixed vessel, but under continuous mixing conditions, the impact of cohesiveness and adhesiveness is reflected in the slurry yield stress and consistency. The presence or absence of cohesive and adhesive particles in the simulant could affect slurry rheology. Including cohesive and adhesive particles in the simulant would allow it to better represent those effects.

At present there is no data quantifying the cohesiveness or adhesiveness of Hanford waste. SRNL has investigated a method to measure adhesiveness of waste, but has not performed any measurements with actual SRS waste.[25] This method measures the change in mass of a coupon that has been inserted into and removed from a slurry. The WTP should investigate measuring adhesiveness in a similar manner for future and existing Hanford waste samples, as well as simulants. The project could collect the data and attempt to correlate the measured adhesiveness with slurry rheology (i.e., yield stress, consistency, and shear strength), slurry mixing behavior, and slurry behavior in test vessels and in the WTP.

To summarize, yield stress is expected to be a function of pH with the maximum yield stress occurring at or near the isoelectric point, the yield stress increases with decreasing particle size, the yield stress decreases with increasing ionic strength, and the yield stress has been found to vary with waste composition.

While yield stress can change with changes in pH, ionic strength, particle size, and chemical composition, the key to developing non-Newtonian simulants for most test objectives is matching or bounding the fluid rheology (i.e., yield stress, consistency, and shear strength) in the WTP design basis. Since most processing will not occur near the isoelectric point, the effect of pH will not be important for WTP operation. The effect of ionic strength could be significant during caustic leaching and washing (i.e., UFP-02). When measuring rheology during waste qualification, WTP needs to ensure the samples have a pH, ionic strength, and undissolved solids concentration that represents the conditions expected in the WTP. If unusual behavior is observed during the qualification process (e.g., caustic leaching or washing), additional rheology measurements should be performed on samples from those steps. No testing for the effects of chemistry on slurry rheology is recommended.

5.2 Impact on Agglomeration

Increases in particle size by agglomeration could make mixing in the SHSVD vessel more challenging. Particle settling velocity increases with increasing particle size, and particle suspension becomes more challenging as the particle size increases. These effects are described in the Properties that Matter document.[3] Liquid pH and liquid ionic strength have been found to affect particle/agglomerate size.

This section will review previous work by PNNL, WTP, and the technical literature describing the effects of physical and chemical properties of slurries on particle agglomeration to assess the impact of chemistry on particle/agglomerate size in the WTP.

Wells et al. looked at the effect of waste treatment processes (e.g., caustic leaching and washing) on particle size for eight waste groups representing 75% of the waste expected to be processed through the WTP.[12] With Group 1 (Bismuth Phosphate Sludge) and Group 2 (Bismuth Phosphate Saltcake) wastes, they found the particle size distribution (PSD) decreased and narrowed after caustic leaching, and decreased again following washing. They suggested the change in particle size is likely from the dissolution of gibbsite and insoluble phosphates, along with precipitation of sodium phosphate and other sodium salts. With Group 3 (PUREX Cladding Waste) and Group 4 (REDOX Cladding Waste) wastes, the caustic leaching had relatively little effect of the particle size distribution of the composite. The post caustic leach washing led to a significant decrease in the PSD. With Group 5 (REDOX Sludge) and Group 6 (S Saltcake) waste, caustic leaching dissolved the majority of the largest particles, shifting the peak size from ~6 micron to ~ 2 micron, but the post caustic leach wash had little effect on particle size. With Group 7 (TBP Sludge), particle size distribution measurements could not be measured. With Group 8 (Ferrocyanide) wastes, the data show the caustic leaching and washing reduced the particle size distribution of the solids.

WTP investigated particle properties as waste is received and processed through the WTP. The investigation found the particle size to decrease following leaching and washing, and the mean particle density to increase following leaching and washing.[26,27] Another WTP study found that the agglomerated particles that could form have a much lower density than the primary particles due to the porous or diffuse structure of the agglomerates.[28]

Choi et al. investigated the influence of ionic salts on the particle size of silica slurry.[29] They observed no change in particle size when increasing the salt concentration from 0 to 0.01M. At higher salt concentrations, they observed an increase in particle size from adding the salt. The increase in particle size is due to a decrease in the electrostatic repulsion. They also observed the magnitude of the zeta potential to decrease with increasing ionic strength. The decrease was due to the suppression of the electric double layer around the particles.

Sillanpaa et al. investigated the aggregation of titanium dioxide nanoparticles in fresh and brackish water.[30] They found larger agglomerates in brackish water compared to fresh water. They attributed the difference to the higher ionic strength of the brackish water.

The cohesive and adhesive forces described in the previous subsection could influence particle/agglomerate size. These forces will affect the solid particle size, which influences the settling and suspension behavior of the slurry.

The WTP has taken steps to mitigate the risks from agglomeration. The PJMs extend into the vapor space and have reduced amount of horizontal surface area on the top on which solid particles could settle and adhere.[31] Small-scale test in an 8 ft diameter vessel and a technical basis for scaling analysis suggest operating margin for bottom clearing.[32, 33] Temperature is controlled by external heat exchangers, which move the risk of fouling surfaces into the "gray" canyon, where maintenance and inspection features are more plentiful.[31]

To summarize, previous work has shown particle size (i.e., agglomerate size) to increase with increasing ionic strength due to the suppression of the electric double layer around the particles, and the degree of agglomeration could vary with different ions or dissolved salts.

While particle size can change with changes in ionic strength and chemical composition, the key to developing simulants for most test objectives is matching or bounding the particle size in the WTP design basis. The effect of ionic strength on particle/agglomerate size could be significant during caustic leaching and washing. When measuring particle size during waste qualification, WTP needs to ensure the samples have an ionic strength that represents the conditions expected in the WTP. If unusual behavior is observed during the qualification process (e.g., caustic leaching or washing), additional particle size measurements should be performed on samples from those steps.

Waste chemical properties such as pH and ionic strength can affect waste physical properties such as slurry rheology and particle/agglomerate size. Because the expected pH in the WTP is much greater than the isoelectric points of the solid compounds expected in the WTP, pH should not have a significant effect on these properties. Because of the changes in ionic strength from washing and caustic leaching, those processes could cause changes in slurry rheology.

6.0 Impact of Temperature

Changes in temperature can affect PJM mixing through its effect on properties such as viscosity or yield stress, through its effect on solubility, through its effect on vapor pressure, or through chemical reactions that occur at high temperatures.

Meacham et al. observed a decrease in yield stress and consistency with increasing temperature in most instances, but they did observe exceptions, such as Tank AN-104, where yield stress and consistency increased with increasing temperature.[8] Wells et al. collected data describing the effect of temperature on yield stress and consistency. The consistency decreased with increasing temperature, but the effect of temperature on the yield stress varied for different wastes.[12]

Liquid viscosity is affected by changes in temperature. The viscosity of water decreases by ~3% for every 1 ˚C increase in temperature.[34] Changes in liquid viscosity change parameters such as particle settling velocity, just suspended velocity, just suspended impeller speed, radial jet velocity, critical transport velocity, critical suspension velocity, critical shear stress for erosion, and cloud height.[35] Changes in liquid viscosity can also affect PJM mixing. These effects are discussed in the Properties that Matter document and can be covered with a physical simulant.[3]

Changes in fluid temperature are likely to change the solubility of compounds in the feed streams. The solubility of most compounds increases with increasing temperature. However, some compounds (e.g., $SrCO_3$) have a solubility that decreases with increasing temperature. The changes in solubility will affect the particle concentration for Newtonian fluids, and the yield stress and consistency for non-Newtonian fluids. The design basis for mixing is 700 micron for maximum particle size and the upper limit is 30 Pa, 30 cP for rheology.[36] The waste streams processed through the WTP are required to meet the design basis, and the testing can meet or bound the 30 Pa, 30 cP design basis with a physical simulant.

Increased temperature in the PJM mixed vessels leads to an increase in fluid vapor pressure. The increased vapor pressure combined with the vacuum used to refill the PJMs could cause flashing of the liquid and stall PJM refill. To prevent the flashing, the PJMs are refilled by gravity rather than vacuum when the temperature and associated vapor pressure would cause PJM refill to stall. Previous testing has shown the gravity refill to increase the refill time by approximately 2X.[37] This effect is being investigated in the PJM Controls testing and is not part of the SHSVD FSVT.

The increased temperature could cause chemical reactions to occur which could change the fluid properties. SRNL investigated the properties and behavior of sodium aluminosilicate solid phases that could form in the SRS Tank Farm. They found the sodium aluminosilicate to form alternative phases as a function of solution temperature.[23] Washington State University and PNNL investigated mineral transformations with silicon-rich solutions as a function of temperature with Hanford simulated waste. They found solution temperature to influence the minerals formed. [23] While Hanford waste contains more than just silicon and sodium aluminosilicate, these results show that changes in temperature could change the compounds present in the waste. The changing of compounds could change waste properties such as particle size, particle density, and slurry rheology. As long as physical simulants match or bound the design basis properties (e.g., 700 micron particle size, 30 Pa yield stress), they are adequate for testing with the current T4 requirements.

Previous work by ORNL and SRNL found that allowing simulated SRS waste slurries (sludge and monosodium titanate) to sit (up to six weeks) at elevated temperature (up to 50 ˚C) led to increases (up to 3X after 2 weeks and up to 16X after 6 weeks) in slurry yield stress, consistency, and shear strength.[38,39] This increased yield stress, consistency, and shear strength was due to settling time and settling temperature, but the slurry was remixed prior to measuring the yield stress and consistency. SRNL measurements of actual waste and simulant rheology found conflicting results on the impact of temperature (25 – 50 ˚C) on yield stress. Some work has found the slurry yield stress to increase (as much as 100%) with increasing temperature, while other work has found it to decrease with increasing temperature (as much as 70%).[14,40]

Changes in temperature can affect SHSVD mixing through its effect on properties such as viscosity, yield stress, solubility, and vapor pressure, or chemical reactions that occur at high temperatures. The key to developing simulants for testing is matching or bounding waste properties such as yield stress, viscosity, particle size, and particle density. The effect of increased temperature and vapor pressure on the PJMs is being investigated separately. No testing of temperature effects is recommended as part of FSVT.

7.0 Impact of Organic Compounds on WTP Feed

For most test objectives, organic compounds will affect mixing through their effect on properties such as rheology, particle agglomeration/size, particle density, and viscosity. The impact of these properties on PJM mixing is described in the Properties that Matter document.[3]

Polymers and small organic molecules could attach to the surface of particles in WTP feed streams. Depending on the particles and the organic compounds, the effect could be attractive or repulsive. If the effect is attractive, slurry yield stress will increase. If it is repulsive, slurry yield stress will decrease.[21]

Organic compounds in the PJM mixed vessels could contribute to the vapor pressure in the vessels. Some organic compounds could increase the vapor pressure enough to decrease the temperature at which the gravity refill is needed. A calculation of vapor pressures of WTP feed streams found the organic species identified in potential feed streams to increase the vapor pressure by a maximum of 2 – 4%.[41]

For test objectives such as gas retention, foaming, and aerosolization, the organic compounds could influence waste behavior. The organic compounds could increase gas retention if they contain functional groups that can sorb or hold hydrogen gas generated by radiolysis. Gas retention is assumed out of scope for FSVT. If the organic compounds contain hydrophilic and hydrophobic functional groups, they could increase foaming or aerosolization. The WTP project has previously investigated and tested antifoams to prevent/mitigate foaming.[42,43,44,45,46,47,48] Foaming is out of scope for FSVT. The project has investigated aerosolization and selected conservative aerosol entrainment coefficients.[49,50,51] Aerosolization is out of scope for FSVT.

SRNL looked at the effect of antifoams on the rheology of simulated SRS DWPF melter feed and simulated Hanford AZ-102 washed sludge.[52] All of the antifoams tested with simulated DWPF melter feed increased the slurry yield stress. During tests with the simulated Hanford AZ-102 washed sludge, some of the antifoams increased the slurry yield stress and other antifoams decreased the slurry yield stress. The impact of antifoams on slurry rheology needs to be investigated during waste feed qualification.

Some organic compounds such as ethylenediaminetetraacetic acid (EDTA), hydroxyethyl-ethylenediaminetriacetic acid (HEDTA), oxalate, and glycolate can complex with components of Hanford sludge, causing them to dissolve. The dissolution of sludge components could change the insoluble solids concentration of WTP feed streams, leading to changes in slurry rheology. In addition, dissolution of sludge components could impact the removal of contaminants by the WTP ultrafilters (not in scope for FSVT). Radiolysis likely degrades the chelating agents. The degradation products may have equivalent or increased complexing capability.[53] If organic complexants or their degradation products dissolve components of Hanford sludge, they would affect slurry properties such as yield stress, particle concentration, and particle size, which would be measured during waste feed qualification. Previous work by PNNL postulated that chelating agents form hydrophobic surfaces on solid particles which enable the solid particles to have increased bubble attachment.[53] Gas bubble retention and release is assumed to be out of scope at this time.

Organic compounds could act as flocculants, increasing the size of solid particles/agglomerates. The larger agglomerates could increase the solid particle size in the WTP and make PJM mixing more challenging, but SRNL experience with flocculants has shown most of them to be ineffective at high pH and high ionic strength and the ones that are effective at high pH and high ionic strength to be easily sheared by pumps.[54] In addition, flocculants tend to be very high molecular weight polymers (much higher than the molecular weight of the organic compounds identified in Hanford waste). The effect of radiolysis would be to decrease the molecular weight of the organic compounds rather than to increase it. Given the expected pH, liquid ionic strength, molecular weight of the organic species, and the presence of shear (from PJMs and transfer pumps), flocculation by organic compounds is unlikely.

For most test objectives, organic compounds will affect mixing through their effect on properties such as rheology, particle agglomeration/size, particle density, particle concentration, and viscosity. For the planned FSVT, the simulant should match or bound the properties described in the Properties that Matter document.[3] These properties will be measured and verified to meet design during waste feed qualification. Organic compounds could affect gas retention, foaming, and aerosolization, but those phenomena are assumed to not be part of the FSVT scope. Organic compounds could lead to an increase in vapor pressure, which may be enough to impact PJM refill. Previous work showed the increase to be less than 4%. No additional testing is recommended to investigate the impact of organic compounds during FSVT.

8.0 Gaps in Understanding Waste Chemistry

In assessing the effects of chemistry on PJM mixing in the FSVT, the author identified three gaps that should be investigated. These gaps are the effect of waste chemistry on gas retention and release, the effect of aging or long term settling on slurry settled solids shear strength, and adhesion and cohesion of the slurry.

Gas retention and release is currently out of scope for FSVT. If WTP decides to conduct testing to add gas retention and release to the full-scale vessel testing program, they will either need a chemical simulant that retains gas similarly to actual waste or a physical simulant that bounds the gas retention properties of actual waste. Conducting testing with a simulant that does not match or bound the gas retention properties of the WTP feed creates a risk that the testing does not resolve the technical issues related to gas retention and release. This work would be best performed at a bench-scale with actual waste and simulant to determine the retention properties of bounding waste and develop a simulant that bounds the actual waste.

Hanford data shows that allowing Hanford sludge to sit for extended periods of time can lead to significant increases in slurry shear strength. However, the amount of data is limited.[55] Previous SRNL and ORNL work has shown significant increases (up to 16X) in yield stress, consistency, and settled solids shear strength when simulated SRS wastes are allowed to sit for extended periods of time (0 – 2 months).[38,39] If the PJMs did not operate for several days or several weeks, the shear strength could increase dramatically, potentially causing operational issues for the WTP. Additional data is needed to better understand the effect of aging (i.e., sitting undisturbed) on the rheology and shear strength of Hanford sludge. Testing could be performed in a similar manner to the ORNL and SRNL testing. Samples of actual Hanford waste or simulated Hanford waste (i.e., a chemical simulant) would be collected, allowed to settle for an appropriate time (e.g., 24 hours, 72 hours, several weeks, or several months) at a representative WTP PTF temperature. After the settling was complete, measurements of yield stress, consistency, and settled solids shear strength would be performed.

There is currently no data available describing the cohesiveness or adhesiveness of Hanford or SRS sludge. 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.[3]

SRNL has investigated a technique for measuring adhesiveness of SRS sludge.[25] The technique involves placing a coupon in actual sludge or simulated sludge and measuring the change in mass of the coupon. WTP should consider performing similar measurements on actual and simulated

Hanford waste to develop a database of Hanford waste adhesiveness and to better understand the role that adhesiveness and cohesiveness play in meeting the WTP mixing requirements. The measured adhesiveness could be compared with test data or WTP operating experience to determine if there is a correlation between adhesiveness and vessel mixing effectiveness.

9.0 Conclusions

The conclusions from the study follow.

- The important waste properties that control the performance of a vessel mixed with pulsed jet mixers are described in the Properties that Matter document.
- The primary impact of precipitation or crystallization of salts due to interactions between PJMs or spargers and waste feeds is to increase the insoluble solids concentration in the slurries, which will increase the slurry yield stress. The increase in insoluble solids concentration and yield stress is expected to be small.
- Slurry yield stress is a function of pH, ionic strength, insoluble solids concentration, and particle size. The key to developing a non-Newtonian simulant for testing is matching or bounding slurry yield stress. The yield stress of the waste feed qualification samples should be measured at the appropriate pH and ionic strength, with subsequent characterization over the range of pH and ionic strength expected in the WTP should unanticipated behavior be seen. No testing of the effects of chemistry on yield stress during FSVT is recommended.
- Ionic strength and chemical composition can affect particle size. The key to developing a simulant for testing is matching or bounding the particle size. The particle size of the waste feed qualification samples should be measured at the appropriate pH and ionic strength, and over the range of pH and ionic strength expected in the WTP. No testing of the effects of chemistry on particle/agglomerate size during FSVT is recommended.
- Changes in temperature can affect SHSVD mixing through its effect on properties such as viscosity, yield stress, solubility, and vapor pressure, or chemical reactions that occur at high temperatures. The key to developing simulants for testing is matching or bounding waste properties such as yield stress, viscosity, particle size, particle density, and particle concentration. The effect of increased temperature and vapor pressure on controlling the PJMs is being investigated separately.
- For most test objectives, organic compounds will affect SHSVD mixing through their effect on properties such as rheology, particle agglomeration/size, particle density, and particle concentration. These properties will be measured and verified to meet design during waste feed qualification. Organic compounds could affect gas retention, foaming, and aerosolization, but those phenomena are assumed to not be part of the test scope. Organic compounds could lead to an increase in vapor pressure, which may be enough to impact PJM refill. Previous work showed the increase to be less than 4%, so therefore, this parameter does not have to be included for full-scale testing.
- The Properties that Matter document found physical simulants to be adequate for most to all of the potential test objectives. This Chemistry study identified three specific areas where waste chemistry considerations may play an important role in the selection of appropriate simulants and should not be overlooked for certain test objectives. These areas include understanding the effect of waste chemistry on gas retention and release, the effect of aging and long term settling on the development of shear strength in settled layers, and the development of adhesive and cohesive properties between particles. An approach to address these effects is further discussed in the document and summarized below.
    - Gas retention and release is assumed to not be a requirement for FSVT based on the current technical issue resolution path. If it returns to the test scope, testing

needs to be performed with a chemical simulant or bench-scale testing needs to be conducted with actual waste and physical simulants to demonstrate that the physical simulants bound the actual waste for gas retention. If physical simulants are used for gas retention and release tests, there is a risk that they do not retain gas to the same degree that a chemical simulant or actual waste retains it.

- Previous work by SRNL, ORNL, and PNNL has shown that allowing simulated and actual waste to settle for extended times can lead to large increases in slurry shear strength (up to 3X after 2 weeks and up to 16X after 6 weeks). Limited actual Hanford waste data exists describing the impact of settling time on slurry shear strength. If the PJMs did not operate for several days or several weeks, the shear strength could increase dramatically, potentially causing operational complexity for the WTP. The project should investigate the impact of settling time under prototypic conditions on slurry shear strength. This testing would require actual waste or chemical simulants. This data would allow the project to set a maximum idle time that a vessel could sit without adversely affecting WTP operation.
- Adhesion of slurries to vessel internals has been observed at the SRS DWPF, and is a mechanism by which solids could accumulate in the WTP. In addition, an adhesive slurry may be more difficult to mix than a non-adhesive slurry with the same rheological properties. At present, there is no data describing the adhesiveness of Hanford waste slurries. SRNL has investigated a method to measure adhesiveness of slurries by measuring the increase in mass when a carbon steel coupon was dipped in a simulated slurry. A similar approach should be developed to measure cohesiveness and adhesiveness of Hanford waste and Hanford simulated waste, and relate the measured adhesiveness to fluid mixing and slurry mobilization.

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