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Technical Gaps in Hanford High-Level Waste Solids Settling Behavior and Settling Time Evaluation for Direct Feed High-Level Waste (DFHLW) Operations

July 2020

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Prepared for the U.S. Department of Energy
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Pacific Northwest National Laboratory
Richland, Washington 99354

Summary

Settling of high-level waste (HLW) solids in process vessels is a key conceptual process step in providing HLW feed directly to the Hanford Waste Treatment and Immobilization Plant (WTP) HLW Facility. Direct Feed High-Level Waste (DFHLW) is a potential flowsheet operations approach to initiating HLW vitrification prior to completion of the WTP Pretreatment Facility. Settling would be used with subsequent supernatant decant to concentrate HLW feed. In application, the solids in the settled layer would be remixed with the remaining supernatant liquid to provide the feed at required solids concentrations. Settling would be used in lieu of purpose-built filtration or other solids separation equipment. These latter unit operations increase facility capital costs and increase process complexity resulting is greater operations risk. Furthermore, total HLW mission duration estimates are directly related an assumed 2-week maximum settling period and conceptual facility sizing (i.e., number of tanks and tank capacities) is being estimated based on the cycle time needed to prepare HLW solids through settle-decent and feeding WTP HLW Facility at design capacity.

To support planning for DFHLW, Washington River Protection Solutions requested support from the Pacific Northwest National Laboratory to evaluate the current data set available to predict the time needed for HLW solids to settle, to identify gaps in the understanding and predictive capability of HLW solids waste settling times, and to provide scoping estimates of the potential settling time. In addition, since a resultant settled layer must be remobilized and mixed with the appropriate amount of supernatant liquid to meet feed solids loading requirements, the current data set available to predict the settled layer concentrations and mobilization resistance is evaluated and gaps in understanding and predictive capabilities therein are identified.

The following eight technical gaps were identified for predicting settling times and characteristics of the formed sediment layers:

- Gap 1: *In situ* Settling Rates Faster than Settling of Laboratory Samples
- Gap 2: Effect of Sludge Leaching/Washing on Predicted Settling Times
- Gap 3: Predicting Waste Settling from Waste Chemistry (Waste Type)
- Gap 4: Predicting Waste Settling from Particle Size and Density Distributions
- Gap 5: Insufficient Laboratory and *In situ* Settling Data to Represent Hanford Waste
- Gap 6: Methods for Real-Time, *In situ* Tracking of Settling
- Gap 7: Prediction of Sediment Erosion Resistance as a Function of Settling Time
- Gap 8: Prediction of Sediment Solids Content as a Function of Settling Time

In addition to the data gaps, an overarching observation of the settling rate and settled layer data is the significant variation in behavior. At similar solids concentrations, settling rates can vary by as much as 3 orders of magnitude depending on the source waste tank, and significantly different settling rates are noted between laboratory and *in situ* tests for the same waste tank. The average solids concentration in existing HLW sediment, which may have been quiescent for decades, can vary from less than 7 wt% to greater than 74 wt% solids. The shear strengths (or yield stresses) measured on laboratory samples range from less than 27 Pa to greater than 6400 Pa. These variations can challenge process planning for the application of a settle/decant process for DFHLW.

This report describes the significance of the technical knowledge gaps to the settle/decant process and presents uncertainties by way of examples. Potential technical approaches for resolving these gaps are described and the estimated difficulty in resolving these gaps is evaluated. Based on the significance of the gap and the difficulty of resolution, the following recommendations are made for the associated gaps (not all gaps result in a recommendation):

- **Gap 1 Recommendation**: Reconcile the disparity in settling rates between *in situ* and laboratory-scale solids settling tests to enable future defensible use of laboratory-scale settling results. One key uncertainty that has been identified is the potential for significant unexplained differences between laboratory- and full-scale settling behavior. This task would further the initial work to understand the impact of this uncertainty for full-scale process application.
- **Gaps 2 and 3 (can provide laboratory information for Gaps 5, 7, and 8) Recommendation**: Leverage the existing experimental results for settling rate of *in situ*, as-received, and washed/leached actual waste to improve estimates of settling times for DFHLW operations. The initial review of data for the settling velocity of the upper liquid-to-solid interface for as-received waste is consistently suggestive of chemical-composition-related patterns with respect to settling rate. Therefore, evaluate the settling results for both as-received and washed/leached actual waste with respect to waste chemistry to estimate the range of settling times for HLW feeds to develop qualitative settling process operating parameters for settling rates to support mission planning depending on feed stream chemistry.

  Conduct actual waste sample testing. Develop testing techniques focused on settling rates before and following a washing/leaching, or a washing only, step using radiologically cold simulants in preparation for subsequent testing with actual waste. The actual waste testing should be conducted such that multiple aspects of the DFHLW settle/decant process will be informed; e.g., effect of waste chemistry on settling rate, effect of washing on waste settling rates, settled layer characteristics.
- **Gap 6 Recommendation**: Develop a test platform for evaluating instruments for *in situ* tracking of settling behavior to support optimization of DFHLW operations.

Scoping estimates of the potential settling times for DFHLW solids have been made based on the existing data set with its associated gaps. Depending on the process vessel depth and final sediment concentration, substantial fractions of the scoping estimate results for settling times for characterized HLW exceed the 2-week period that has been previously assumed for process planning. There is also significant disparity, potentially greater than a factor of 5000 difference, in the estimated settling times depending on process vessel depth and final sediment solids concentration. This variation in results underscores the significance of the identified gaps and uncertainties with respect to process planning for utilizing settle/decant operations for DFHLW.

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Acronyms and Abbreviations

1C	a type of bismuth phosphate process waste (sludge)
2C	a type of bismuth phosphate process waste (sludge)
224 Post-1949	lanthanum fluoride finishing process waste (sludge)
BL	B Plant low-level waste (sludge)
BP	bismuth phosphate (sludge)
CWP, CWP1, CWP2	types of PUREX cladding waste (sludge)
CWR	REDOX cladding waste (sludge)
DFHLW	Direct Feed High-Level Waste
DST	double-shell tank
ECR	effective cleaning radius
FIO	For Information Only
GC	general category
HLW	high-level waste
IEP	isoelectric point
NQA	Nuclear Quality Assurance
P3	PUREX high-level waste
PFeCN	a type of ferrocyanide process waste
PNNL	Pacific Northwest National Laboratory
PSD	particle size distribution
PSDD	particle size and density distribution
PUREX	plutonium-uranium extraction process
QA	quality assurance
R, R1	types of REDOX waste
R&D	research and development
REDOX	reduction-oxidation process
SRR	slurried PUREX sludge
TBP	tributyl phosphate process sludge
TFeCN	a type of ferrocyanide process waste
UDS	undissolved solids
WRPS	Washington River Protection Solutions
WTP	Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

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1.0 Introduction

Pacific Northwest National Laboratory (PNNL) is providing baseline technical support to Washington River Protection Solutions (WRPS) Flowsheet Integration group. A settle/decant process has been proposed to concentrate solids prior to delivery to the Hanford Waste Treatment and Immobilization Plant (WTP) High-Level Waste (HLW) Facility during Direct Feed High-Level Waste (DFHLW) operations. DFHLW is a potential flowsheet operations approach to initiating HLW vitrification prior to completion of the WTP Pretreatment Facility (Tilanus et al. 2017), and the settle/decant process for HLW solids is a key conceptual aspect of providing HLW feed to the WTP HLW Facility at desired solids concentrations.

The solids concentration of the settled layer resulting from the settling operations must be known in order to decant the appropriate volume of supernatant liquid so that the mixture of the settled layer and supernatant liquid has the desired solids concentration. It is also important to be able to predict the critical stress for erosion of the settled layer to allow assessment of whether the selected sediment mobilization method to mix the settled solids with the supernatant liquid, be it jet pumps or some other method, will be able to effectively remobilize the sediment.

The time required for the settling process is salient to the proposed settle/decant approach. The total HLW mission duration estimate is directly related to the settling time and conceptual facility sizing (i.e., number of tanks and tank capacities) is being estimated based on the cycle time needed to prepare HLW solids through settle-decent and feeding WTP HLW Facility at design capacity. Settling would be used with subsequent supernatant decant to concentrate HLW feed in lieu of purpose-built filtration or other solids separation equipment. These latter unit operations increase facility capital costs and increase process complexity resulting is greater operations risk.

To support planning for DFHLW, WRPS requested support from the PNNL to evaluate the current data set available to predict the time needed for HLW solids to settle and the solids concentration and strength of that settled layer, to identify gaps in the understanding and predictive capability of HLW solids waste settling times, and to provide scoping estimates of the potential settling time. The purpose of this report therefore is to document the technical gaps and provide estimates of HLW waste settling times based on existing models and data.

Section 2.0 summarizes the quality requirements for this work. Section 3.0 discusses technical gaps identified for predicting the settling times for HLW waste solids together with gap significance for DFHLW operations and examples highlighting each gap. For selected gaps, potential mechanisms for explaining the unexpected or uncertain behavior are provided. Brief discussions of potential approaches for resolving each gap are also provided.

Section 4.0 evaluates data collected for HLW settling rates reported after the summary provided in Wells et al. (2011) was completed.[1] In Section 5.0, scoping estimates of the potential settling times for DFHLW solids as functions of the process vessel depth and initial and final solids concentrations are made based on the existing data set. Section 6.0 summarizes previously collected data for predicting the solids content and erosion resistance of settled layers, and the transient change over time for these parameters, and how the remobilization of the settled layer is impacted. Technical gaps associated with the settled layer properties are discussed. A summary of this study is provided in Section 7.0 together with recommendations.

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[1] Reference is made throughout this document to Wells et al. (2011). For the topic of solid particle settling behavior, the section of Wells et al. (2011) being referenced is Section 3.2.6, “UDS Particle Settling”.

2.0 Quality Assurance

This work was conducted with funding from WRPS under PNNL project 75807, contract 36437-301, Requisition 331833, dated November 18, 2019.

All research and development (R&D) work at PNNL is performed in accordance with PNNL's Laboratory-level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications* (ASME 2000), to R&D activities. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for this work. The WWFTP QA program implements the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications* (ASME 2008), and NQA-1a-2009, *Addenda to ASME NQA-1-2008* (ASME 2009), and consists of the WWFTP Quality Assurance Plan (QA-WWFTP-001) and associated procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work.

The work described in this report was assigned the technology level "Applied Research" and was planned, performed, documented, and reported in accordance with procedure QA-NSLW-1102, *Scientific Investigation for Applied Research*. All staff members contributing to the work received appropriate technical and QA training prior to performing quality-affecting work.

Section 3.0, Technical Gaps and Uncertainties in Predicting Waste Settling Times, of this document contains new information that is presented solely as preliminary examples to provide insight into the significance of and the potential for the resolution of the gaps. This information is presented as "For Information Only" (designated by "FIO" in text and titles) and is not intended to be used for the design of operational systems or as a substantial factor in decisions to commit significant resources.

3.0 Technical Gaps and Uncertainties in Predicting Waste Settling Times

As described in Section 1.0, the settle/decant process for HLW solids is a conceptual key aspect of providing DFHLW feed to the WTP HLW Facility at desired solids concentrations. It is possible that, prior to a final settle/decant process step, waste leaching and/or washing will be conducted to dissolve and remove a portion of the HLW solids to improve waste loading during HLW vitrification. In conceptual application, the waste would be allowed to settle in a process vessel, and supernatant liquid would be decanted off the top of the resultant sediment so that, when mixed, a desired concentration of solids would be available for DFHLW feed. The duration of time needed for this settling step is uncertain and the focus of this section is to document the gaps and uncertainties in estimating appropriate settling times for the range of wastes being considered for DFHLW, and thereby provide opportunities to reduce process uncertainty and thus, mission risk.

Six gaps for waste settling times are discussed in the following subsections:

- Gap 1: *In situ* Settling Rates Faster than Settling of Laboratory Samples
- Gap 2: Effect of Sludge Leaching/Washing on Predicted Settling Times
- Gap 3: Predicting Waste Settling from Waste Chemistry (Waste Type)
- Gap 4: Predicting Waste Settling from Particle Size and Density Distributions (PSDDs)
- Gap 5: Insufficient Laboratory and *In situ* Settling Data to Represent Hanford Waste
- Gap 6: Methods for Real-Time, *In situ* Tracking of Settling

The significance of each gap to the settle/decant process is described, and uncertainties are presented by way of examples. Suggested approaches to resolving the gaps are provided.

Two additional gaps related to understanding of the settled layer’s solids concentration and erosion resistance during and following the settling process are discussed in Section 6.0:

- Gap 7: Prediction of Sediment Erosion Resistance as a Function of Settling Time
- Gap 8: Prediction of Sediment Solids Content as a Function of Settling Time

3.1 Gap 1: *In situ* Settling Rates Faster than Settling of Laboratory Samples

In situ and laboratory settling rates have been compared for waste tanks AZ-101 and AY-102, which received waste from tank C-106 (Wells et al. 2011). For both tanks, *in situ* settling was found to be faster than settling in laboratory tests. To date, there has been no explanation provided for the observed differences. Accordingly, there is a gap associated with *in situ* settling being faster than settling of laboratory samples. Additional details on this gap and observations are provided below, together with potential mechanisms that might explain these observations.

3.1.1 Significance: *In situ* Settling Rates Faster than Settling of Laboratory Samples

Settling times that are faster than predicted are unlikely to cause difficulty with DFHLW operations unless extended settling times result in sediment layers that are more challenging to remobilize. However, if wastes are predicted to settle more slowly than in actuality, unnecessarily long settling durations may be included in the planned schedule for operations. Resolving the gap associated with *in situ* settling rates being faster than the settling of laboratory samples would reduce unnecessarily-long planned settling times.

3.1.2 Examples: *In situ* Settling Rates Faster than Settling of Laboratory Samples

Wells et al. (2011) (see Section 3.2.6.3 and Figure 3.68, provided herein as Figure 5.2) present data on the difference between *in situ* and laboratory settling rates for AZ-101 and AY-102. For AZ-101, the *in situ* settling rate is as much as 1000 times faster than laboratory settling rates; note that the laboratory settling rates were at higher volume fractions of solids than the *in situ* rates. However, Wells et al. (2011) concluded that hindered settling alone could not cause the observed differences in the *in situ* and laboratory settling rates. In addition, while the AZ-101 sediment solids settling *in situ* had similar chemical composition to the sediment composite (Meacham et al. 2012), only a limited fraction of the sediment material was mobilized throughout the entire supernatant liquid layer (Wells and Ressler 2009), and the particles were of a smaller size distribution than the composite sediment.[2] Thus, the faster *in situ* measured settling rate was for smaller particles than the laboratory-measured settling rates, while both likely had similar chemical compositions.

For AY-102, the *in situ* settling rate is shown as a range in Figure 5.2, which was noted by Wells et al. (2011) to most likely be an underestimate. The *in situ* settling rate in AY-102 was about 10 times faster than the laboratory settling rates, which again were at higher volume fractions of solids than the *in situ* conditions. Both these comparisons show the unexplained observation of the *in situ* settling rates being much faster than setting rates measured on laboratory samples.

3.1.3 Potential Mechanisms for Explaining Faster-than-Expected *In situ* Settling Rates

Several mechanisms might explain the faster-than-expected *in situ* settling rates, but none appear at this point to be likely explanations for the 1000-fold difference between *in situ* and laboratory settling rates observed for AZ-101. Wells et al. (2011) identified four potential mechanisms that can give faster settling rates: particle agglomeration, particle collision and capture, wake capture, and vertical streaming, which is sometimes also called channeling. Other mechanisms have been identified in addition to these four, and are also discussed below.

3.1.3.1 Particle Agglomeration

It is well known that when particles aggregate into flocs, the settling rate may increase if the flocs settle faster than the individual particles (Wells et al. 2011). Wells et al. (2011) briefly discussed whether it was plausible for more extensive agglomeration to occur for *in situ* waste compared to laboratory samples, and primarily considered whether there was more shearing and smaller agglomerates (hence, slower settling)

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[2] Wells BE and SK Cooley. 2019. *Comparison of Hanford Waste Solids Physical Characteristics to Specific Requirements of the Hanford Tank Waste Treatment and Immobilization Plant Pretreatment Facility Interface Control Document*. PNNL-SA-145785, Pacific Northwest National Laboratory, Richland, Washington.

for laboratory samples compared to *in situ* waste. They concluded that this seemed unlikely. Although not discussed in Wells et al. (2011), the radiation dose rate for *in situ* waste should be higher than in laboratory samples. It is unclear, however, if particles being in a higher radiation field would somehow increase agglomeration (hypothetically, by changing the surface charge on particles). The presence of radioactive species within the particles themselves, should this affect agglomeration, would likely be similar for both *in situ* waste and laboratory samples.

3.1.3.2 Particle Collision and Capture

When particles, or flocs, settle with different rates, the faster-settling particles/flocs can collide with and pull down slower-settling particles, giving an overall faster settling rate (Wells et al. 2011). Wells et al. (2011) briefly discussed whether it was plausible for particle collision and capture to occur more extensively for *in situ* waste compared to laboratory samples, which could then cause faster settling for *in situ* waste, and concluded that it was not clear whether this might occur.

3.1.3.3 Wake Capture

Wake capture occurs when a smaller, slower-settling particle is entrained in the wake of a larger, faster-settling particle and is dragged down with the larger particle, giving a faster overall settling rate (Wells et al. 2011). Wells et al. (2011) briefly discussed whether it was plausible for wake capture to occur more extensively for *in situ* waste compared with laboratory samples. For AZ-101, they noted that the most rapidly settling particles, which are the particles most likely to cause a wake capture effect on slower-settling particles, were not thought to be suspended in the settling layer that was used for measuring the settling rate, and concluded that it was not clear whether *in situ* conditions were more conducive to wake capture than in laboratory samples.

3.1.3.4 Vertical Streaming (Channeling)

Vertical streaming (also described as channeling by other authors) occurs when particles move laterally and form columns (i.e., channels) of rapidly settling particles that are separate from columns of slowly settling (or rising) particles (Wells et al. 2011). Wells et al. (2011) cited three articles related to this mechanism and noted that the three references do not exhaust the literature on this mechanism. As discussed below in this subsection and in Section 3.1.3.5, there is rather extensive literature on vertical streaming and a closely related phenomenon of cluster formation where identical particles will move closer together than the average particle separation and then settle more quickly as a dense cluster of particles. The lateral movement of particles into channels suggests that the effect of vertical streaming may be dependent on the dimensions of the test vessels, with larger container dimensions (larger diameters and increased height) allowing more channel formation (provided sufficient sample volume exists to fill the container). There are no data, however, that show accelerated settling with increasing test-container dimensions.

Kaye and Boardman (1962) give one of the first discussions and experimental observations of cluster formation and accelerated sedimentation. Weiland et al. (1984) show careful experiments demonstrating that settling of two particles of different size or density can be unstable, with vertical fingers of faster- and slower-settling particles forming from an initially uniform suspension. Batchelor and Janse van Rensburg (1986) further studied vertical streaming and conducted systematic experiments with pairs of different particles and developed criteria for the onset of vertical streaming based on combinations of the ratios of the sizes, densities, and volume fractions of the particles. These two studies used spherical particles.

Guazzelli and Hinch (2011) noted that the settling of fiber suspensions can also be unstable and spontaneously form fast-settling, fiber-rich channels. While instability leading to vertical streaming has certainly been demonstrated, both experimentally and theoretically, there is very little or no information on how vertical streaming may increase the observed settling rate of the top interface of a settling layer in a suspension. (Glasrud et al. 1993 is one article where settling curves were provided for suspensions that exhibit vertical streaming.)

A thorough literature review on vertical streaming/channel formation during settling was not attempted, but there are a number of additional studies on this topic that provide further insight into, and examples of, this behavior (see, for example, Fitch 1966; Dell and Kaynar 1968; Glasrud et al. 1993; Vesilind and Jones 1993; Holdich and Butt 1996; Nam et al. 2008). There are also a number of studies on the related topic of cluster formation from Tory and co-workers (Tory and Pickard 1977, 1985; Tory et al. 1992; Tory and Kamel 1997; Burger et al. 2002; Tory and Ford 2004; Berres et al. 2005; Bargiel et al. 2005) and others (Oliver 1961; Snabre et al. 2009).

3.1.3.5 Vertical Streaming from Bubble Release (Buoyant Particle Channeling)

Vertical streaming induced by the presence of buoyant or neutrally buoyant particles is a subset of the vertical streaming mechanism discussed above in Section 3.1.3.4, though the behavior appears to be stronger with buoyant or neutrally buoyant particles. Because bubbles are thought to create vertical streaming similar to buoyant particles (Fessas and Weiland 1981), and that radioactive waste is known to generate gas (hydrogen together with other species) bubbles, this version of vertical streaming is discussed separately, in this section, from the general behavior of vertical streaming with particles of different size or density discussed in Section 3.1.3.4.

Whitmore (1955) was likely the first to notice that the addition of neutrally buoyant particles would accelerate settling. This initial work was followed, much later, with a number of studies by Weiland and co-workers (Weiland and McPherson 1979; Fessas and Weiland 1981, 1982, 1984; Weiland et al. 1984) and also Lin (1984). These studies demonstrated that the presence of buoyant or neutrally buoyant particles [and it was suggested that small bubbles would induce the same behavior (Fessas and Weiland 1981)] would cause an initially uniform settling suspension to spontaneously form separate, fast-moving channels of dense and buoyant particles that accelerated overall settling. Fessas and Weiland (1982) noted that the enhancement in the settling rate increased as the density difference between dense settling particles and the suspending fluid became smaller, and reported a settling rate enhancement as high as a 10-fold. Glasrud et al. (1993) reported experiments where air bubbles would rise through a settling suspension and form channels that would allow the suspending fluid to escape from the settling suspension, resulting in faster settling.

Of all the potential mechanisms for causing enhanced settling rates, the mechanism of bubble-forming channels seems a more likely explanation than the others for why *in situ* settling rates are larger than settling rates in small laboratory tests. As also noted in Section 3.1.3.4, the lateral movement of particles into channels suggests that the effect of vertical streaming may be dependent on the dimensions of the test vessels, with larger container dimensions allowing more channel formation. However, there are no data that show accelerated settling with increasing test-container dimensions.

3.1.3.6 Thermal Convection

Generally, large-scale convection is more associated with causing mixing, which generally opposes settling. However, the much larger dimensions of *in situ* conditions, in comparison to small laboratory tests, is a notable difference that would lead to larger, thermally-driven convection for *in situ* conditions. It is unclear, however, how this might accelerate the *in situ* settling rate of a solids layer.

3.1.3.7 Method of Measurement

Small laboratory tests that measure the settling rate of the interface between clear supernatant and the settling solids layer are different from *in situ* measurements. Wells et al. (2011) noted that AZ-101 *in situ* measurements used a suspended solids profiler, gamma-monitoring probes, an ultrasonic interface level analyzer, and grab-sample analysis. They discussed key differences between the *in situ* and laboratory settling test measurements (see also Section 3.1.2). One thing to note is the difference in laboratory settling rates, measured by two different researchers. For AZ-101, laboratory settling rates were measured on different composites by different researchers. Wells et al. (2011) report "fast" interface settling velocities (see Section 5.1 for explanation of "fast" interface settling velocity) for studies conducted in 1993 and 2000, which differ by about a factor of 30. While the cause of this difference is not clear, it is possible that (a) the waste samples were handled differently (method of measurement) when the settling tests were conducted or (b) the individual composites could also have been different.

3.1.4 Approaches to Resolving Gap: *In situ* Settling Rates Faster than Settling of Laboratory Samples

Unfortunately, it is not clear what mechanism, or combination of mechanisms, is the cause of *in situ* waste settling being faster than laboratory measurements of settling rates on small waste samples. Accordingly, the approach to resolving this gap will need to begin with exploratory studies to identify the likely mechanism(s). The mechanisms that result in vertical streaming (channeling) are caused either by particles with different settling rates (Section 3.1.3.4) or the presence of rising bubbles (Section 3.1.3.5). Both phenomena suggest that the effect of vertical streaming may be dependent on the dimensions of the test vessels, with larger container dimensions (larger diameters and increased height) allowing more channel formation (provided sufficient sample volume exists to fill the container). There are no data, however, that show accelerated settling with increasing test-container dimensions. Accordingly, part of the initial exploratory studies should focus on measuring settling rates in vessels of different size. These tests should include simulants that have particles with different settling rates and include the introduction of bubbles.

Evaluations of *in situ* agglomeration, particle collision and capture, and wake capture, being more extensive and causing faster settling than in laboratory studies, do not appear easy to conduct because (1) making *in situ* measurement would be difficult, and (2) a measurement that would identify these mechanisms has not yet been identified.

3.2 Gap 2: Effect of Sludge Leaching/Washing on Predicted Settling Times

It is possible that DFHLW operations may include processing steps for caustic leaching and/or sludge washing. A number of actual waste studies have been conducted that report settling test data after individual process steps of leaching and washing waste samples. Tardiff (2019) provides a summary of most of the available settling data and Harrington (2011) provides a summary of all the leaching and washing studies together with comments noting when the studies included settling tests. Temer and Villarreal (1995, 1996, 1997) reported a series of tests, which were not summarized in Tardiff (2019), with settling measured after caustic leaching and washing steps. The reports from 1996 and 1997 give data for the maximum settling velocity for individual tests. The settling velocity after the second caustic leach was always higher compared to that after subsequent washing (first, second, or third wash), but ranged by a factor of 2 to 20 depending on the waste sample. In contrast, Brooks et al. (1998) reported a settling velocity (hindered settling rate) after the second caustic leach that was lower than after the first, second, and third (first of two parts) water washes. As noted by Tardiff (2019), literature for the sludges analyzed in leaching/washing studies seldom provided settling rates of the initial waste, therefore preventing a comparison with settling rates after leaching and washing, so it is unknown if there are differences between initial untreated waste and leached and washed waste. While more comparisons of settling data could be made, these studies demonstrate that there is a significant difference in the effects of leaching and washing on settling rates for different waste samples and there is too little data for comparing settling rates of initial untreated waste and leached and washed waste.

Although many factors affect the settling rate (such as liquid viscosity, particle density and shape, and flocculation behavior), the change in the primary particle size distribution (PSD) by leaching and washing is one mechanism that is expected to contribute to settling rate changes. To our knowledge, there are only two studies of actual waste where settling rate and PSD data were collected before and after leaching and washing; these are S-107 (Brooks et al. 1998) and C-107 (Temer and Villarreal 1996). In these two tests, leaching and washing reduced the PSD for both waste samples and the settling rate decreased about 10-fold for C-107 but increased about 2-fold for S-107 (first water wash after leaching compared with Retrieval 1 before leaching). These studies had different solids concentrations in the before- and after-leaching samples, so it is not clear if they support using changes in PSD to understand settling rate changes. There are more examples of PSD data before and after leaching and washing. Wells et al. (2011) evaluated reported PSD changes due to leaching and washing for five waste composites representing combined bismuth phosphate salt and sludge, combined plutonium-uranium extraction process (PUREX) and reduction-oxidation process (REDOX) cladding wastes, combined REDOX sludge and S saltcake, combined tributyl phosphate (TBP) and AY-102 sludge, and ferrocyanide wastes. They concluded that leaching and washing had different effects on the PSDs of each waste composite, with two composites having about an order of magnitude decrease in average particle size, one composite being unchanged, and one composite having a factor of two increase. Similarly, in the studies by Temer and Villarreal (1995, 1996, 1997), both increases and decreases in the average particle size were observed. While more comparisons of PSD data could be made, these studies demonstrate that there is a significant difference in the effects of leaching and washing on PSDs.

Overall, the available data show that leaching and washing can increase or decrease the settling rate by significant amounts, but to our knowledge there are no studies that have explained why these changes occur or that can predict the changes that might occur for different waste samples. Accordingly, there is a gap in predicting the effect of sludge leaching and washing on settling times.

3.2.1 Significance: Effect of *In situ* Sludge Leaching/Washing on Predicted Settling Times

For some wastes where settling data are available both before and after sludge washing, the effect of waste washing was to cause longer settling times. Currently, a method is not available to predict the effect of washing on settling times for waste without settling data with and without washing.

DFHLW operations may, or may not, include processing steps for caustic leaching and/or sludge washing. Should *in situ* sludge leaching and/or washing be used, there is uncertainty regarding whether this processing will cause an increase or decrease in HLW settling times, and by how much.

3.2.2 Approaches to Resolving Gap: Effect of *In situ* Sludge Leaching/Washing on Predicted Settling Times

A large body of data exists for waste settling after leaching and washing, but these data have not been analyzed using the Renko settling velocity model (Renko 1996, 1998) for consistency with Wells et al. (2011) in order to determine when settling times might be long. There are a few studies where settling was measured on waste samples both prior to and after leaching and washing, but these studies also have not been analyzed using the Renko model. To support future DFHLW operations with *in situ* settling, a first step would be to collect and analyze the available settling data and, in particular, seek to identify the cause of long settling times for specific wastes. This study should also seek to determine additional waste samples that should be collected and studied to further explain the cause of long settling times and the specific wastes (or tanks) that may have long settling times.

3.3 Gap 3: Predicting Waste Settling from Waste Chemistry (Waste Type)

Different types of Hanford wastes have undergone settling rate studies. The compositions of solid and liquid phases in Hanford wastes vary widely, and a substantial amount of that composition variation has been captured in the subset of wastes that were tested for settling behavior. There were hints of composition-related effects on settling rates in the unmodified or diluted sludges in Wells et al. (2011), but there has been no concerted effort to investigate these relationships, and therefore a gap in predicting waste settling from waste chemistry exists. This study preliminarily investigates those data further.

3.3.1 Significance: Predicting Waste Settling from Waste Chemistry (Waste Type)

There are a number of gaps in the current understanding of PSDDs and other waste-driven aspects of waste particle settling. The gaps are present partly because the settling data are limited (see Section 3.5). It might be possible to use the small data set more effectively for prediction of settling if it can be combined with knowledge of the chemical compositions of Hanford wastes and with general knowledge of chemical phenomena that could affect particle-particle interactions. This is investigated below.

3.3.2 Examples: Waste Settling Related to Waste Chemistry (Waste Type)

Wells et al. (2011) compiled solid phase and liquid phase compositions for all tank wastes in undiluted or diluted forms; however, washed and leached wastes were not included. The compilation provided measurement-based “fast” interface settling velocities for the upper interface and initial volume fractions for a limited set of single-tank saltcakes, single-tank sludges, and multi-tank waste composites for particular waste groups (numbered 1 through 8) defined by the M12 program. The fast interface settling velocities are defined [using the Renko model (1998)] as the average velocity during the initial period when the velocity decreases by 30% from its initial value. This velocity is likely to be set by the slowest-settling particles in the particle velocity distribution, so the velocity may be governed not by a major constituent but by a minor one that settles more slowly than the others. During the latter stage of settling, when the interface height has fallen 90% of the way from its initial level to its final level, the upper interface motion is controlled by compaction of the settled layer. In this stage the “slow” interface velocity is the governing velocity.

Figure 3.68 of Wells et al. (2011) showed substantial and possibly characteristic differences between CWP/CWR sludge and TBP sludge[3], and suggested the possibility that waste type (i.e., composition)

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[3] CWP: a PUREX cladding sludge waste type. CWR: a REDOX cladding sludge waste type. TBP: tributyl phosphate process sludge waste type. Waste types were originally defined in Agnew et al (1997), where they are listed in Appendix F. With some later updates, the same waste types appear in the Best Basis Inventory https://twins.labworks.org/twinsdata/Forms/About.aspx?subject=BestBasisInventory.

might be helpful as a predictor of settling. A further interrogation of the composition and settling rate data in that figure was carried out for this effort as an FIO[4] study, whose details can be found in Appendix A.

In summary of the results of the FIO investigation, which is detailed in Appendix A, the sludge solids were divided into six waste general categories (GCs) (numbered 1 through 6), defined according to the major constituents in the sludge solids:

- **[GC 1] Very high content of aluminum with other metals much lower, and no history of self-boiling in the tank:** PUREX and REDOX cladding wastes fell into this category, with aluminum compounds making up more than 80 wt% of the solid. These solids, of which three examples were tested, all showed relatively high values of the fast interface settling velocity [as defined by Wells et al. (2011)], even at relatively high solids fractions. The three examples fell along a line that had an interface velocity of, at most, 1×10^{-4} m/s as the solids concentration approaches 0, and about 1×10^{-5} m/s at 20 vol% solids.
- **[GC 2] High content of aluminum with other metals much lower, and a history of self-boiling:** Two examples fell into this category, where aluminum compounds made up more than 40 wt% of the solid and no other non-salt compound exceeded 7 wt%. At the same solids concentration, these solids consistently had smaller interface velocities than the high-Al solids that did not have a history of self-boiling. The examples fell into a scattered group that included interface velocities in a range from 9×10^{-7} to 1×10^{-5} m/s in a solids fraction range of 2 to 4 vol%, plus a single velocity datum of 3×10^{-7} m/s at 9 vol%.
- **[GC 3] High content of both iron and aluminum, with no information about boiling:** Four examples of BL, P3, 1C, or 1C+SRR[5] waste types fell into this category, where (a) iron compounds made up more than 25 wt% of the sludge, or Fe analyte measured by analysis was higher than 15 wt%; (b) aluminum compounds made up more than 25 wt%; and (c) lanthanum, bismuth, uranium, and zirconium compounds were relatively minor constituents. These solids tended to have high interface velocities at near-zero concentration – *in situ* settling interface velocities were between 2×10^{-5} and 7×10^{-4} m/s at less than 1 vol% solids. They settled slowly at moderately high solids concentrations: 4×10^{-7} m/s at 9 vol%.
- **[GC 4] Significant content of bismuth, iron, and aluminum with no information about boiling:** Four examples of 1C or 2C[6] waste types fell into this category, where (a) iron and aluminum compounds were present but not dominant; (b) bismuth compounds made up about 10 wt% or more of the solids; and (c) lanthanum, uranium, and zirconium compounds were minor constituents. These solids tended to have moderately high interface velocities at near-zero concentration, about 1×10^{-5} m/s at less than 1 vol% solids. They settled very slowly at moderate solids concentrations: 7×10^{-8} to 5×10^{-7} m/s at 6 vol%.
- **[GC 5] Significant content of lanthanum, phosphate, bismuth, and iron with no information about boiling:** Four examples of 224 Post-1949[7] waste type fell into this category, where (a) aluminum compounds were absent; (b) iron compounds were present but not dominant; (c) bismuth compounds were dominant at more than 20 wt%; (d) lanthanum phosphate was present; and

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[4] The information is presented solely as preliminary examples to provide insight into the significance of and the potential for the resolution of the waste chemistry gap. This information is presented as “For Information Only” (designated by “FIO” in text and titles) and is not intended to be used for the design of operational systems or as a substantial factor in decisions to commit significant resources.

[5] BL: B Plant low-level sludge waste type. P3: a PUREX high-level sludge waste type. 1C: a bismuth phosphate process sludge waste type. SRR: PUREX sludge waste type.

[6] 2C: a bismuth phosphate sludge waste type.

[7] 224: a lanthanum fluoride sludge waste type.

(e) uranium and zirconium compounds were minor constituents. It is worth noting that all of these wastes contained significant amounts of manganese compounds (15 to 22 wt%). These solids tended to have moderately high interface velocities at near-zero concentration, about 1×10^{-5} m/s at less than 1 vol% solids, but settled very slowly at fairly low solids concentrations: 1×10^{-7} to 6×10^{-7} m/s at 6 vol%. One of the wastes, from tank T-111, settled at 1×10^{-6} m/s or less, even at less than 0.5 vol% solids.

- **[GC 6] Significant content of uranium, but not matching other categories; no information about boiling:** The remaining data sets for sludge settling did not fit in the previously described categories. All contained 8 wt% or more of uranium compounds, often with significant amounts of iron or aluminum, but otherwise are not chemically similar to each other. These otherwise uncategorized uranium wastes did not show any consistent trend.

These waste GCs appear to have captured some differences in settling behavior, without providing much insight into the reasons. For most of the waste GCs, trends that appeared to exist when considering the GC as a whole were not clearly evident when separately evaluating the data sets for each individual tank waste within the GC. For example, the non-boiling, high-aluminum GC 1 included three different wastes. The T-102 (CWP2[8]) waste tests spanned solids concentrations of 2 to 5 vol%, while the tests with the M12 Group 3 and Group 4 wastes[9] spanned 16 to 20 vol%. Although the tests for both the lower-solids and higher-solids vol% appeared to fall on a single trend line, the concentration range of the tests for an individual waste was not great enough to confirm that the apparent multi-waste trend would have been followed over a wider range of dilutions for any of the individual wastes. Thus, the apparent trends are not firmly established. More detail can be found in Appendix A.

Some qualitative evidence of composition effects on settling has also been seen during preparation for performance evaluations of waste (Huber 2013). Sample jars containing waste from AY-102, AZ-102, and AW-105 were handled and then observed. After 2 minutes, AY-102 waste had a distinguishable supernatant layer, AZ-102 waste showed a suspension upper interface very near the top, and there was no discernible change in the AW-105 waste. No decantable amount of liquid was present at the top of the AW-105 sample until 2 days had passed.

Huber (2013) found that the AY-102 solids contained 33 wt% Fe-Mn-oxide, 39 wt% dawsonite, 26 wt% Na aluminosilicate, and 3 wt% gibbsite. The material was fine-grained, with the largest crystals being laths of dawsonite about 10 μm long. This waste falls into the high Fe/Al category, GC 3, which produced some of the higher values of fast interface settling velocity seen in the data set.

The AZ-102 solids were observed to contain 47 wt% dawsonite, 30 wt% Fe_2O_3, 7 wt% gibbsite, 5 wt% boehmite (a solid also present in the self-boiling high-Al GC 2), and 4 wt% Zr-oxyhydroxide. The material was very fine-grained, with much of it less than 5 μm in size. This waste qualifies for the high Fe/Al category, and therefore might have high interface velocity, but also contains a zirconium compound. The effect of zirconium could not be systematically assessed in the data set from Wells et al. (2011). However, the data set included C-104 waste, which did not fall into any of the five chemically well-defined categories GC 1 through GC 5. The C-104 waste contained a mixture of waste types whose average composition included 15 wt% ZrO_2 (the solid assumed to be present for Zr) but did not show unusually fast or slow interface settling velocities.

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[8] CWP2: a PUREX cladding sludge waste type.

[9] M12 Group 3 and Group 4 samples were composites of, respectively, PUREX cladding sludges and REDOX cladding sludges.

The AW-105 solids were found to contain 49 wt% Na-Zr-oxide, 9 wt% clarkeite ($Na(UO_2)O(OH).H_2O$), and 4 wt% gibbsite. These solids also had a high content of salt, 39 wt% sodium fluoride with crystals 5 to 30 μm wide. AW-105 waste did not fall into any of the waste categories discussed so far, although by default it would have been placed in GC 6. The waste's very low interface velocity might have been the result of the high zirconium content, or of the particular compound in which the Zr was found. It is worth noting that the zirconium-containing particles were 50-μm-long laths. Since particles with high aspect ratio tend to take up volume when settled – the gel formed by sodium phosphate needles being an example – the very slow settling might have been related to compaction behavior at low solids fraction, rather than a true fast interface settling velocity.

3.3.3 Mechanisms: Waste Settling Related to Waste Chemistry (Waste Type)

Particle settling is governed by the effective particle size, the difference between the effective particle density and the liquid density, and the liquid viscosity (for laminar settling, the likeliest regime for the slow-settling particles that are of concern). As a result, the settling properties of a Hanford tank waste depend on the compounds present in the solids and on the liquid composition.

The identities of solid-phase compounds determine the density of the particles and are associated with reasonably well-defined ranges of primary particle sizes (Wells et al. 2011), as well as with observations of whether the primary particles tend to aggregate into strongly bound agglomerates that may or may not have significant porosity. These size and density properties affect velocity directly, through well-known settling velocity relationships that can be expressed in PSDDs.

The size distribution is also related to flocculation. Particles of 1-μm size or less can often exhibit colloidal behavior such as flocculation (Rector and Bunker 1995). In addition, the compounds present on the surfaces of particles are part of what determines the potential for flocculation.[10] Flocs, being porous, have larger effective particle sizes and lower effective densities than the primary particles, and may also be significantly permeable to liquid flow through their pores. They can be expected to have higher settling velocities than the primary colloid.

The liquid-phase drivers of flocculation are ion concentration (ionic strength), the liquid pH – which for Hanford waste is typically alkaline even after dilution with water – and the concentrations of ions other than hydroxide. Colloidal suspensions become unstable – capable of flocculating – when the electrical double layer around each particle becomes thin enough that particles can approach each other closely enough for van der Waals attractive forces to come into action (Rector and Bunker 1995). For every colloidal solid phase and every liquid composition, there is a pH – the isoelectric point (IEP) – at which the particle surfaces are neutrally charged, the double-layer is minimized, and there is little repelling barrier to prevent flocculation even at very low ionic concentration.

At pH above and below the IEP, a colloidal dispersion can be stable, but only if the ion concentration in the liquid is low. Above a certain maximum ionic concentration, which varies with pH and depends on the ionic composition, the double-layer collapses and flocculation will occur no matter what the pH. Rector and Bunker (1995) give an example of colloidal boehmite in $NaNO_3$ solution, for which they used IEP equal to a pH of 8.5 and for which flocculation was predicted to always occur above concentrations of 0.1 M $NaNO_3$.

Kosmulski (2016) provides a detailed review of IEP data for particles of pure metal oxide or hydroxide in aqueous solution. Table 3.1 shows the results for solid phases that are of interest in Hanford sludge.

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[10] Here, "aggregation" is used to refer to agglomerates that have little or no porosity, while "flocculation" is used to refer to porous agglomerates.

However, as can be seen, many of these phases can be present at primary particle sizes that are too large to exhibit colloidal behavior. The minimum primary particle sizes are not discussed in the reference.

Table 3.1. Isoelectric points and maximum particle sizes for Hanford sludge phases.

Nominal Solid Phase	Notes about Ions in Liquid	IEP (pH)	*In situ* Maximum Spherical Primary Particle Diameter (μm)
Al_2O_3	1:1 electrolyte, 20 – 25 °C		n/a
	max. tested 1.0 M	9.4 – 9.5[(a)]	
	max. tested 0.1 M	7.3 – 9.7	
AlOOH (boehmite)	1:1 electrolyte, 20 – 25 °C		0.052
	max. tested 0.01 M	9.2	
AlOOH (diaspore)	1:1 electrolyte, 20 – 25 °C		n/a
	max. tested 1.0 M	9.5[(a)]	
$Al(OH)_3$ (gibbsite)	1:1 electrolyte, 20 – 25 °C		200
	max. tested 0.01 M	9.1	
$Al(OH)_3$ (amorphous)	1:1 electrolyte, 20 – 25 °C		200
	max. tested 0.01 M	8.5	
Bi_2O_3	1:1 electrolyte		3
	max. tested 0.01 M	8.2 – 9.4	(but $BiFeO_3$ is 0.1)
FeOOH (goethite)	1:1 electrolyte, 20 – 25 °C		0.015
	max. tested 1 M	7.6[(a)]	
	max. tested 0.1 M	7.5 – 9.7	
La_2O_3	1:1 electrolyte, 35 °C		3
	max. tested 0.1 M	9.6	
MnO_2	1:1 electrolyte, 25 °C		10
	max. tested 0.01 M	4.5, 5.6	
UO_2	1:1 electrolyte, 25 °C		n/a
	max. tested 0.01 M	5.8	
ZrO_2	1:1 electrolyte, 20 – 25 °C		50
	max. tested 0.1 M	7.8, 8.2	

(a) According to Kosmulski (2016), it is common for IEP to be higher for higher ionic concentration. This is not always evident in the selected data set, however.

The primary particles of boehmite, bismuth compounds, goethite, and perhaps lanthanum compounds stand out as being most plausibly colloidal in size. Of these, boehmite, goethite, and La_2O_3 have IEPs that are greater than pH 9 in a range of 0.1 to 1 M ionic concentration, while Bi_2O_3, in the same range of IEP, was only tested at ionic concentration of 0.01 M or less. Overall, it appears that flocculation is most likely in the range of pH from 8 to 10, even at low ionic concentration. (The IEP range is closer to pH 4 to 6 for MnO_2 and UO_2, however, making agglomerate behavior less likely within the more alkaline range of most Hanford wastes.) Unfortunately, the reference contained no information about the ionic concentration above which particles will consist only of flocs, not primary colloids.

As a typical Hanford waste is diluted with water, its pH will decrease to an extent controlled by the extent of dilution, the initial hydroxide concentration, and the presence of basic buffer salts. Aluminate, phosphate, hydrogen phosphate, carbonate, and hydrogen carbonate ions can potentially act as buffers, holding pH constant over a range of water dilutions. Thus, as ionic concentration decreases, tending to make colloidal stability more probable, pH may (possibly) hold constant – potentially in a less-alkaline range where flocculation is favored in spite of low concentration. On the other hand, dilution with inhibited water (0.01 M NaOH) will tend to force pH to 12. In this pH range, well away from the IEP, primary colloids are more likely to be stable at high dilution.

The preceding discussion of IEP and primary particle size suggested that flocculation was likeliest to have an effect on boehmite, goethite, and possibly lanthanum in the range of pH from 8 to 10, even at low ionic concentration. The more acidic range of IEP for MnO_2 and UO_2, pH 4 to 6, suggested that colloidal particles of these compounds would tend not to flocculate, at least at low ionic concentrations.
Many of the wastes in the interface velocity data set in Wells et al. (2011) had liquid densities in the range of 1.1 g/mL, indicating ionic concentrations of 1 M or higher. Even 3:1 or 4:1 dilution with water would leave the ion concentration above 0.1 M, possibly making flocculation unlikely.

Size distributions were measured for waste composites from the M12 waste groups: Group 1 (GC 4, Bi/Fe/Al), Group 3 (GC 1, non-boiling high Al), Group 4 (GC 1, non-boiling high Al), and Group 7 (high-U TBP, GC 6) (Lumetta et al. 2009; Snow et al. 2009; Edwards et al. 2009).[11] They all contained 5 to 10 vol% of submicron particles. Clearly, colloidal behavior does not affect all particles, but there is enough colloidal particle volume in any of these wastes to allow an effect on the trailing edge (upper interface) of the settling material. This holds even for wastes where the primary constituent has primary particle size much greater than 1 μm – e.g., the non-boiling high-Al wastes where gibbsite was specifically identified as dominant.

The review of data for the fast settling velocity of the upper interface is consistently suggestive of composition-related patterns, but those patterns do not seem to follow from the mechanism of IEP alone. Iron may hypothetically be related to low velocities and gibbsite to high velocities, but why this should be the case is not clear. One major item of missing information is the composition of submicron particles that might form the upper interface, as distinct from the overall composition.

There are substantial unknowns in working from theory alone to understand the effects of waste chemistry on settling velocity:

- What solids are present on the surface of a given waste? A particle could be coated with a phase other than that which makes up the bulk of the particle.
- What is the IEP of surface solids other than hydroxides, oxides, and oxyhydroxides? Kosmulski (2016) included no data for metal phosphates or silicates.
- How do the concentrations and identities of ions in solution affect the IEP? The IEP values provided by Kosmulski (2016) applied only to 1:1 electrolytes such as NaCl and $NaNO_3$, but ions with charges of 2 and 3 are common in Hanford wastes.
- How do the identities of ions in solution affect the ionic concentration limit, for each solid, above which primary colloidal particles always form flocs?
- Finally, does the presence of ionizing radiation change the surface charge behavior and the IEP? No information on this topic was found after searching literature on Google.

3.3.4 Approach to Resolving Gaps: Waste Settling Related to Waste Chemistry (Waste Type)

A desired end result would be to devise a set of rules that at least qualitatively relate waste composition (both solid and liquid phases) to the upper interface settling velocity and to the final settled solids fraction (which has not been discussed here). The existing Hanford waste data for settling velocity and final solids fraction should be assembled into a set that includes not undiluted and diluted wastes, but rather water-

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[11] M12 Group 1 samples were composites of bismuth phosphate process sludges. M12 Group 3 and Group 4 samples were composites of, respectively, PUREX cladding wastes and REDOX cladding wastes. M12 Group 7 samples were composites of tributyl phosphate process sludges.

washed, caustic-leached, and oxidative leached wastes. Liquid and solid compositions should be included in the database, with the solid phase information including inductively coupled plasma species concentrations and X-ray diffraction, scanning electron microscopy, or polarized light microscopy determinations or estimates of solid phases present at the surfaces of particles. Ideally, the surface solid phases would be determined or estimated separately for submicron particles and for larger particles. This database would be investigated for patterns of behavior by visualization of the data rather than by statistical approaches to grouping.

If sufficient waste sample material is already available, a waste in each of the waste categories should undergo settling tests at a wide range of dilution. These tests would show whether an individual waste's fast interface settling velocity is related to initial solids fraction in the same way as shown by the apparent trend for multiple wastes in the category, each of which had been tested only with a narrow dilution range. If the results confirm the trends already discussed, these would provide a firmer indication of future behavior.

Supplementary experiments could be conducted with chemical simulants containing Fe, Al, Bi, La, and Zr phases, as appropriate, for the wastes that appear to be of greatest concern in terms of low settling velocity or final solids fraction. If possible, a few of these simulant tests should include settling in the presence of realistic dose rates of beta and/or gamma radiation. This would explore whether radiation-modified surface charge causes different flocculation behavior in small samples of waste, versus large amounts of waste in the high-dose *in situ* environment, versus radiologically cold simulants.

Given the uncertainties and the sparse data, it is unlikely that a quantitative predictive tool can be produced by the work proposed above. However, it may be possible to develop a qualitative approach that rules out certain types of settling behavior for a particular waste category.

3.4 Gap 4: Predicting Waste Settling from PSDDs

In general, it is well understood that particle size and density affect solids settling rates. A method to predict the settling rate of HLW solids based on their PSDD characterizations could provide a rate prediction methodology to address the limited data set for Hanford HLW solids settling rates (e.g., see Section 3.5). A number of models are available for monodisperse particle settling, either as individual particles or at some concentration. However, a model addressing the complex polydisperse HLW solids is not currently available. Accordingly, there is a gap in predicting settling rates based on PSDDs for actual waste.

3.4.1 Significance: Predicting Waste Settling from PSDDs

There is a limited data set for HLW settling rates. Having a methodology to empirically predict settling rate based on a waste's PSDD or representation thereof would enable improved waste feed delivery and processing by optimizing the time required for settle/decant operations. For example, WTP waste acceptance criteria typically include maximum and median acceptable particle sizes as well as chemistry (e.g., 24590-WTP-ICD-MG-01-019), and feed pre-qualification is required to demonstrate the feed acceptability. There is therefore some potential, should an adequate model be available, to predict settling rates based on PSDD characteristics. Being able to predict waste settling times from information on the waste PSDD would reduce the uncertainty in predicted settling times.

3.4.2 Examples: Predicting Waste Settling from PSDDs

There have only been limited evaluations comparing waste settling rates and PSDDs, and a systematic comparison of measured laboratory settling rates of actual waste samples with setting rates calculated from PSDDs from the waste samples has not been completed. Brief investigation is made of the currently available concurrent waste data for settling rate and PSDD to estimate the viability of developing an empirical method to predict feed settling rate from PSDD of actual waste.

For the PSDD characterizations selected as the bases for simulant development for waste feed delivery demonstration testing (Lee et al. 2012; Kelly et al. 2013), 13 tanks, representing ~17% by volume of the total Hanford sludge inventory (Wells et al. 2012), are characterized. Of those 13 tanks with waste characterized for PSDDs, 6 tanks have laboratory settling rates (Wells et al. 2011). From the data of Wells et al. (2011), there are three instances of tanks with laboratory-measured waste sample settling rates at essentially equal solids concentrations that also have PSDD characterizations. These data are presented as FIO[12] in Figure 3.1, Figure 3.2, and Figure 3.3.

In Figure 3.1, adopted from Wells et al. (2011),[13] the measured laboratory settling rates are shown in the legend for AZ-101 and C-104 at approximately 3 vol% solids. The abscissa is the calculated settling velocity of the individual particles for the PSDD size and density pairs for the respective waste tank, and the ordinate is the cumulative vol% probability based on the probability of occurrence of the size and density pairs (see Wells et al. 2011 for full explanation of the calculation methodology). The average laboratory-measured fast interface settling velocity (see Section 5.1) of the AZ-101 waste sample at 7.7×10^{-7} m/s is slower than the C-104 rate of 3.2×10^{-6} m/s. While this result could be expected at the 50th percentile of the calculated individual particle settling rates for the two tanks, the expectation based on the upper ~25% of the particles would differ.

For Figure 3.2, the calculated individual particle settling rates of BX-107 and AZ-102 do not “cross-over” as discussed for AZ-101 and C-104. Thus, with the calculated individual particle settling rates in BX-107 showing lower at each percentile than AZ-102, it could be expected that the particles in BX-107 would have a slower measured interface settling rate. This expected result is demonstrated by the laboratory measured settling rates at ~ 2.5 vol% solids: 4.7×10^{-6} m/s for BX-107, 3.1×10^{-5} m/s for AZ-102.

A more convoluted result is shown for AY-102, C-104, and C-107 in Figure 3.3 at ~ 5.1 vol% solids. The calculated individual particle settling rates for AY-102 and C-107 have the opposite behavior compared to their laboratory-measured settling rates, as discussed for AZ-101 and C-104 (Figure 3.1). In addition, approximately 90% and 80% of the solids volume in C-104 have calculated particle settling rates faster than C-107 and AY-102, respectively, but the laboratory measured settling rate for C-104, 2.0×10^{-6} m/s, is only minimally faster than that for AY-102 at 1.8×10^{-6} m/s, and a factor of two less than that of C-107 at 4.3×10^{-6} m/s.

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[12] The information is presented solely as preliminary examples to provide insight into the significance of and the potential for the resolution of the PSSD/settling rate gap. This information is presented as “For Information Only” as defined in Section 2.0.

[13] The calculated individual particle settling rates in Wells et al. (2011) used the same liquid density and viscosity for all tanks. Thus, the trends indicated in this FIO investigation are of the primary significance, not specific results.

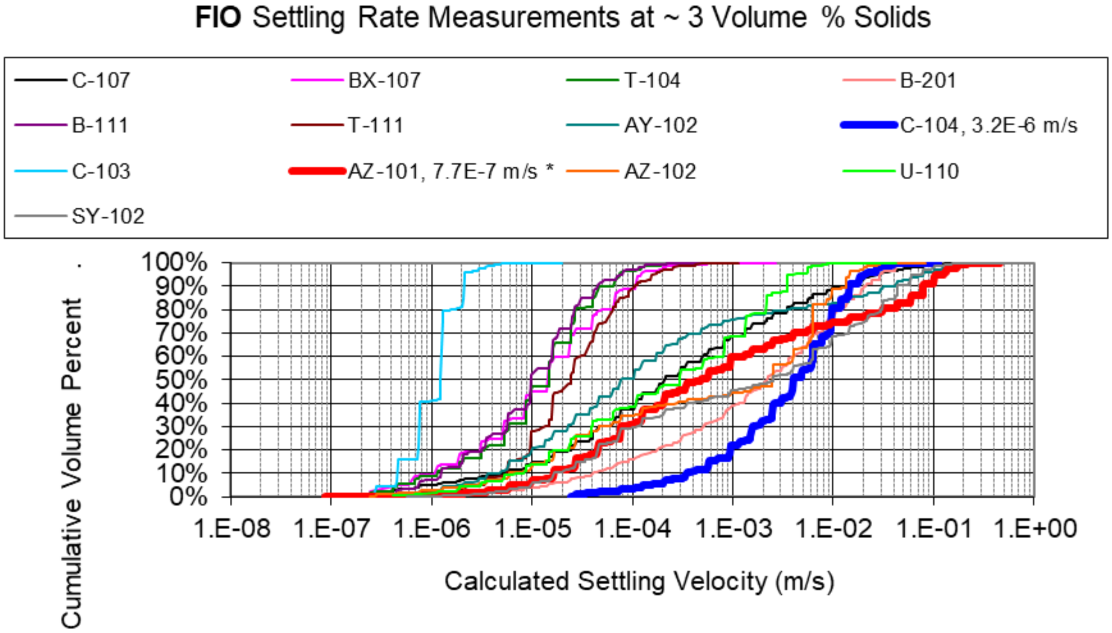

Figure 3.1. FIO. Calculated and measured particle settling rates, AZ-101 and C-104 example. Data and figure adopted from Wells et al. (2011). The * designation for AZ-101 in the legend indicates that the measured settling rate is the average of two values at the same solids concentration.

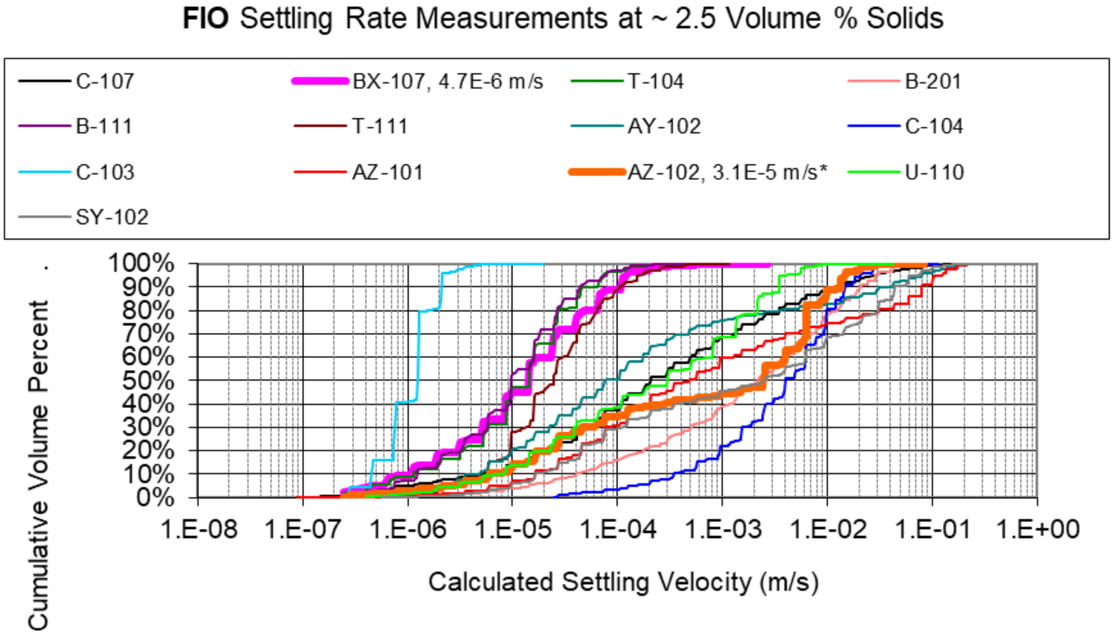

Figure 3.2. FIO. Calculated and measured particle settling rates, AZ-102 and BX-107 example. Data and figure adopted from Wells et al. (2011). The * designation for AZ-102 in the legend indicates that the measured settling rate is the average of two values at the same solids concentration.

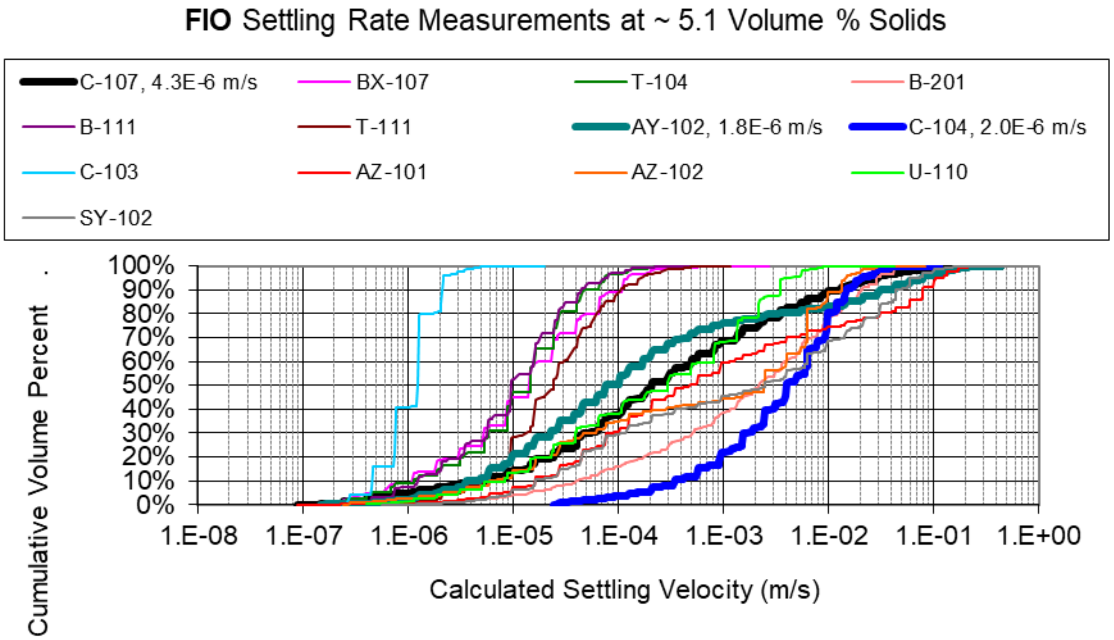

Figure 3.3. FIO. Calculated and measured particle settling rates, AY-102, C-104, and C-107 example. Data and figure adopted from Wells et al. (2011).

3.4.3 Approaches to Resolving Gap: Predicting Waste Settling from PSDDs

As discussed via the examples, the limited available actual waste data provides an extremely convoluted relationship for waste settling and PSDDs. This result would most likely be exacerbated by the lack of PSDD characterization requirements for waste feed pre-qualification. In addition, the time-intensive nature of creating PSDDs and the approximate nature of the PSDDS themselves further suggest that direct measurement of settling rate (other gaps discussed herein must be addressed) would be substantially more beneficial, and it is not recommended to pursue further resolution of the gap for predicting waste settling from PSDDs at this time.

3.5 Gap 5: Insufficient Laboratory and *In situ* Settling Data to Represent Hanford Waste

Wells et al. (2011) noted that laboratory settling rate data are only available for waste samples from 20 individual tanks and 7 waste-group composites (M12 waste groups), which represent 18 waste types. This is a small fraction of the 169 tanks with waste solids (8 of the 177 tanks in Table 3.1 of Wells et al. 2011 only have liquid) and less than half of the 54 primary waste types given in Table B.1 of Wells et al. 2007. It should be noted that assigning waste settling behavior and rate by waste type is a questionable approach and is subject to large uncertainty.[14] *In situ* settling rate measurements of the settling solids interface have only been reported for AZ-101, though Wells et al. (2011) note that settling has been observed in SY-101, SY-102, and AY-102, but only for the settled solids interface and not the interface between settling solids and the suspending liquid. Given the breadth of waste stored in Hanford tanks, the

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[14] In the letter report LTR-EMSP-0104 (2016), titled *Prototypic Settling Behavior Evaluation for Direct Feed Low-Activity Waste (DFLAW)*, BE Wells noted settling rates varied by over two orders of magnitude for different waste samples of the same waste type and that assigning a settling rate by waste type was likely a questionable approach and subject to large uncertainty.

laboratory and *in situ* measurements of settling are too limited, particularly considering the range of observed settling rates. Accordingly, there is a gap due to having insufficient laboratory and *in situ* settling rate data to represent Hanford waste.

3.5.1 Significance: Insufficient Laboratory and *In situ* Settling Data to Represent Hanford Waste

The variability (e.g., see Section 5.0) and limited number of measured waste settling rates in laboratory studies together with only one *in situ* measurement result in a significant range, with significant uncertainty, of the estimated settling times of HLW solids. This large and uncertain range will likely result in longer-than-needed settling durations in DFHLW operations, which will increase costs and may complicate the schedule for planned operations.

3.5.2 Approaches to Resolving Gap: Insufficient Laboratory and *In situ* Settling Data to Represent Hanford Waste

The greatest lack of data is for *in situ* settling behavior, particularly because the single *in situ* settling test for AZ-101 gave settling rates that are much different that settling rates measured on laboratory samples. Accordingly, the primary focus for resolving this gap is to conduct one or more *in situ* settling tests. The *in situ* tests will need to be designed, and the tanks selected, to provide information that will reduce the uncertainty in settling times for DFHLW operations.

3.6 Gap 6: Methods for Real-Time, *In situ* Tracking of Settling

In situ measurements of the height of settling solids with time have only specifically been conducted in AZ-101, where solids settling was tracked after being mixed with two 300-hp jet mixing pumps, which is representative of the baseline configuration for mobilizing and suspending solids in Hanford double-shell tanks (DSTs) (Carlson et al. 2001; Wells and Ressler 2009; Wells et al. 2011). The *in situ* measurement methods deployed were a suspended solids profiler (a laser-reflectance turbidity probe), gamma-monitoring probes, and an ultrasonic interface level analyzer. These methods were confirmed by grab-sample analysis and were self-consistent and gave good data for the settling rate of the suspended solids.

While the previously deployed instrumentation for monitoring settling was generally successful, there were limitations, including calibration ranges that did not extend to low enough solids concentrations and that the instruments could not be deployed when the mixer pumps were operational. In addition, it is expected that improved and/or new instruments may now be available that were not available at the time of the AZ-101 mixing and settling test. Accordingly, a gap exists for evaluating, testing, and selecting new instruments for monitoring *in situ* settling in real time to support DFHLW operations.

3.6.1 Significance: Methods for Real-Time, *In situ* Tracking of Settling

Real-time measurements of solids settling during DFHLW operations will provide definitive information for when settling is sufficiently complete that waste operations can continue without unwanted solids in decanted supernatant and with HLW feed sufficiently concentrated to be ready for the next step in the operation. In the absence of real-time measurements, conservative predictions of settling times might be used, which would negatively affect the schedule for waste operations.

3.6.2 Approaches for Resolving Gap: Methods for Real-Time, *In situ* Tracking of Settling

Many real-time measurement methods for tracking *in situ* settling could be selected and evaluated with simulants in a scaled tank (not gamma probes, for example). A test bed allowing multiple instruments to be deployed in a tank with a simulant that could be suspended then allowed to settle would allow the performance of the instruments to be evaluated and compared in advance of selecting instruments for *in situ* deployment.

4.0 HLW Solids Settling Times – New Data for Settling Rates

This section presents waste settling rates from tests with actual tank waste that were carried out after 2010, the time when data were collected by Wells et al. (2011). Two such sets of data were analyzed. The first was for C-104 solids settling, during and after retrieval, in tank AN-101, which is discussed in Section 4.1. The second was for the settling Savannah River sludges discussed in Section 4.2; the data are believed to have been from *in situ* settling, but the reference (Gillam et al. 2013) did not say so explicitly.

4.1 C-104 Solids Settling in Tank AN-101

There are two sources for information about the settling rate of retrieved C-104 solids in the destination tank AN-101. The first source is Tardiff (2019), which examines the period after retrieval ended on March 22, 2010. Temperature changes in AN-101 at four thermocouples were used to estimate the date of the midpoint of the temperature decrease that occurred after retrieval. It was assumed that the temperature drop occurred because decay-heated C-104 solids in the supernatant suspension were sinking, and that the upper interface height of the suspension was located at each thermocouple at the time when the midpoint temperature was reached. Based on this assumption, the interface velocities were calculated as 6 in./day (2×10^{-6} m/s) from 301 inches elevation to 277 inches, 5 in./day (1×10^{-6} m/s) from 277 to 253 inches, 5 in./day (1×10^{-6} m/s) from 253 to 229 inches, and 3 in./day (9×10^{-7} m/s) from 229 to 205 inches. It required a total of 23 days for the interface to move down to 205 inches.

These estimates of interface velocity are good to only one significant figure, considering that the time resolution is 1 day, the thermocouple measurements have their own uncertainty, and the relationship between midpoint temperature and interface location is useful but not precise. The fast interface settling velocity can be estimated at 5 to 6 in./day for the *in situ* settling. The initial solids concentration in the suspension is unknown.

The second source of information, Klinger (2011), is a mid-retrieval characterization report. On February 28, 2010, during a break in the C-104 retrieval, grab samples were taken at three different elevations in AN-101 within the supernatant suspension. The samples were mixed to obtain uniform solids concentrations before settling. The upper interface height in the sample jars was measured at three times: immediately after mixing (at an initial depth of 115 mm), 12 h after mixing, and 60 h after mixing. The height and time information allow calculation of the average interface velocity over each of the two time intervals. In the first 12 h, the average interface velocity ranged from 2.2 to 2.6 in./day for all of the samples; between 12 and 60 h, the average interface velocity was 0.5 in./day for all samples.

The in-jar average interface velocities and the *in situ* fast interface settling velocities may not be inconsistent with each other. The 12-h period for the first set of in-jar measurements may have been longer than the period during which fast interface settling velocity is applicable, i.e., the interval during which velocity decreases by 30% from the initial value (Wells et al. 2011). If compaction, which determines the slow interface velocity, began in the jars within 12 h, the average velocity would have been less than the true value of fast interface settling velocity. The settling measurement time intervals were not short enough to allow correcting for this, though.

The average interface velocity of 2.2 to 2.6 in./day in the first 12 h in the jars is similar to the 3 in./day estimated for post-retrieval in tank AN-101 after the C-104 solids had settled from 301 to 229 inches elevation. Considering the short distance available for solids to fall in the jars, the in-jar velocities might have been affected by incipient compaction at 12 h after the initiation of settling, in the same way as the *in situ* velocities were affected at 23 days after retrieval ended.

Klinger (2011) provided data for the centrifuged solids volume, centrifuged liquid volume, bulk densities of the liquid and solids, and weight fraction of water in the liquid and solids at all three elevations sampled. On the assumption that water was present only in liquid phase, including interstitial liquid in the centrifuged solids, it was possible to use water as a tracer to calculate the weight fraction and volume fraction of solids in the original samples. An initial suspension concentration, ϕ_0, of 4.8 vol% was estimated from data for a composite made from the samples at the different elevations. This concentration would not necessarily be the same as that observed after retrieval in March 2010, but is probably close.

For comparison, the in-laboratory fast interface settling velocity estimated for diluted C-104 solids in Wells et al. (2011) was 6.8 in./day at ϕ_0 of 5.1 vol%. In this case, C-104 waste was diluted with deionized water and tested in a graduated cylinder with a suspension height of about 200 mm. At a probably similar solids concentration, diluted C-104 solids had a fast interface settling velocity of 5 to 6 in./day when settling in AN-101. The cylinder provided about twice as much fall distance as was available in the grab sample jar (Klinger 2011), where the early average interface velocity was 2.2 to 2.6 in./day.

The *in situ* fast interface settling velocity of C-104 solids in AN-101 (Tardiff 2019) is slower than the in-laboratory fast interface settling velocity tabulated by Wells et al. (2011), though the two measurements might be considered equal within the uncertainty of the method used to estimate *in situ* velocity. The in-jar early average settling velocity of C-104 solids in AN-101 liquid, as measured by Klinger (2011) was a factor of two lower, but may not have been a true fast interface settling velocity and therefore may not be comparable. The differences in the two sets of laboratory settling data are relevant to Gap 1, in that they illustrate the kind of inconsistent behavior in lab-scale tests that causes great uncertainty in the ability to predict settling at full scale.

4.2 Savannah River Sludges

A conference paper (Gillam et al. 2013) discussed observations of, and models for, Savannah River PUREX sludge and high-heat H-modified sludge. There was no information about composition in the article, so it is not clear which Hanford waste, if any, these sludges most resemble, although a PUREX process was also employed at Hanford. It is also not clear whether the data were taken in waste tanks or in smaller lab-scale vessels. However, the authors state that the final settled-solids height used in their PUREX settling model was directly measured after a year of settling, which suggests *in situ* conditions, so the data are investigated herein.

The data provided by Gillam et al. (2013) included (1) a plot of suspension height versus time for Savannah River PUREX Sludge Batch 1A and (2) an equation that had been fitted to data for high-heat H-modified sludge. The data were used by estimating values off the reference's figure, for PUREX, and calculating “data” from the fitted equation, for the high-heat sludge. Because there was no information about initial solids concentration for these sludges, the Renko (1998) equation that was used by Wells et al. (2011) was modified into a form that did not explicitly depend on the solids concentration:

$$z = z_f + (z_0 - z_f)\, exp\left(-\frac{C}{z_f} t\right) \tag{4.1}$$

where z is the height of the upper suspension interface as a function of time t, z_0 is the initial suspension height at t=0, z_f is the suspension height at infinite time (a fitting parameter), and C (units of velocity) is another fitting parameter.

The modified Renko (1998) equation was a poor fit to the elevation-versus-time data for PUREX, with predicted interface elevations being up to 30% different from measured values. The PUREX settling showed a very steep downslope in the first day, apparently during the period of fast interface settling velocity, then with little transition changed to a shallow linear slope consistent with compaction and with a slow interface velocity. The best-model fit for Savannah River PUREX Sludge Batch 1A gave a fast interface settling velocity of 170 in./day. For comparison, Hanford P3 PUREX waste produced fast interface settling velocities of 1 to 3 in./day at initial solids concentrations of 9.2 vol% and 3.0 vol% (laboratory tests), 80 to 90 in./day at a concentration of 1.3 vol% (laboratory tests), and 2500 in./day at a concentration of 0.43 vol% (settling in AZ-101). The behavior of the Savannah River PUREX Sludge Batch 1A and the Hanford P3 PUREX may be similar, but without solids concentration data for the Savannah River PUREX, nothing definite can be said except that both types of PUREX sludge have exhibited very rapid settling under these *in-situ* circumstances.

The modified Renko (1996, 1998) equation (Eqn 4.2) was a good fit to the elevation versus time “data” for the high-heat H-modified sludge, with relative error within 7%. This was partly because the change in velocity from initial to compaction was more gradual than for the Savannah River PUREX sludge, and perhaps partly because the high-heat data had already been, in effect, smoothed by fitting. The fast interface settling velocity was 35 in./day for the high-heat H-modified sludge.

5.0 Settling Time Evaluation for HLW Waste

Scoping estimates of the potential settling times for HLW solids as functions of the process vessel depth and initial and final solids concentrations are made based on the existing data set. The data set and calculation methodology are provided in Section 5.1. The limitations of this data set are discussed in detail in Section 3.0. Settling time results are presented in Section 5.2.

5.1 Evaluation Methodology

The scoping estimates of the potential settling times for HLW solids are made using actual waste settling velocities and solids concentrations for HLW tanks where data are available, settling to potential DFHLW slurry feed and settled layer target solids concentrations in the formed sediment.[15] The data set for settling velocity and sediment solids concentrations are presented and discussed, and the calculation methodology is described.

5.1.1 Settling Rate and Solids Concentration Data Set

A summary and analysis of settling rate data for actual waste solids is provided in Wells et al. (2011). Discussion of the limitations of these data are provided in Section 3.0. The settling data are composed of the results of tests wherein samples at different concentrations of undissolved solids in liquids were mixed and then allowed to settle. The sediment depth was measured as the height from the bottom of the container to the visible interface between the clear supernatant and the opaque solid/liquid suspension and was recorded as a function of time.

As described in Wells et al. (2011), at the outset of gravity settling, the interface between the clear supernatant and the opaque suspension is usually observed to descend in a fast, linear manner that is consistent with a nearly constant velocity. During the later period when the almost completely settled sediment is gradually compacted under its own weight, the slow interface motion is not a constant velocity but, for practical purposes, can be treated as such. These “fast” and “slow” interface settling velocities are illustrated in Figure 5.1 together with a depiction of the settling model fitting (via Renko 1996, 1998; see Section 4.0) done in Wells et al. (2011).

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[15] These estimates follow the approach given in the letter report LTR-EMSP-0104 (2016), titled *Prototypic Settling Behavior Evaluation for Direct Feed Low-Activity Waste (DFLAW),* where settling rate data are used specific to each waste as characterized.

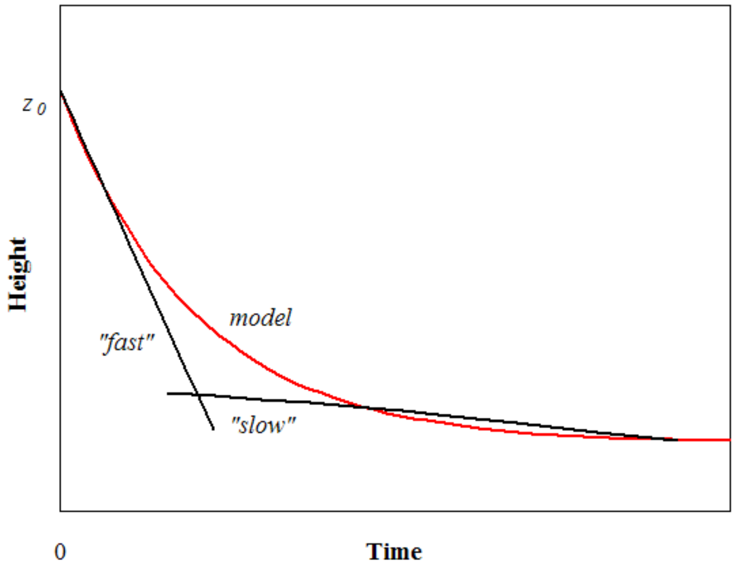

Figure 5.1. Sedimentation model and associated "fast" and "slow" interface settling velocities (Wells et al. 2011).

A summary of the calculated "fast" interface settling velocities from Wells et al. (2011), is provided in Figure 5.2. In Figure 5.2, the abscissa is the initial solids concentration by volume for the respective waste settling rate. Also included with the laboratory data in this figure are *in situ* interface settling rates for AZ-101 and AY-102 (depicted with a large red triangle symbol and red shaded area, respectively). As discussed in Section 3.1.2, and also listed as a technical uncertainty for waste characterization in Gauglitz et al. (2009), the *in situ* settling rates are substantially faster than expected in comparison to laboratory tests.

The data of Figure 5.2 were down-selected to the HLW or sludge classification by waste tank as listed in Weber (2009).[16] The HLW settling data, by tank (those tanks with *in situ* settling rate data are designated as such), are shown in Figure 5.3. For example, the *in situ* AZ-101, at approximately 7×10^{-4} m/s fast interface settling velocity and 0.4 vol%, is shown by the pink square-black "×" symbol at the upper left of the figure, and one of the laboratory AZ-101 samples, at approximately 4×10^{-7} m/s fast interface settling velocity and 9 vol%, is shown by the red square symbol at the lower right of the figure.

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[16] This earlier revision, Weber (2009), is used instead of Yarbrough (2019) as it is more representative of the waste conditions for the samples evaluated in Wells et al. (2011).

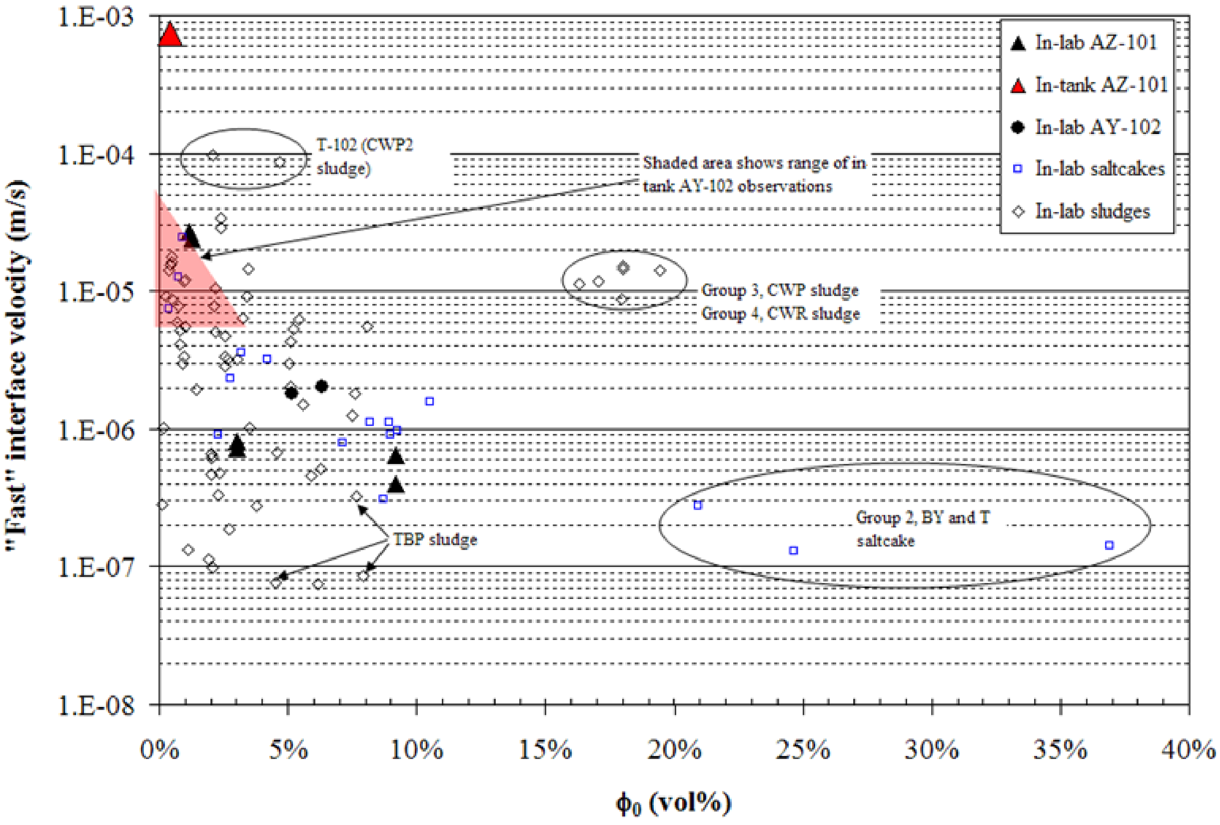

Figure 5.2. Actual waste calculated fast interface settling velocities (Wells et al. 2011).

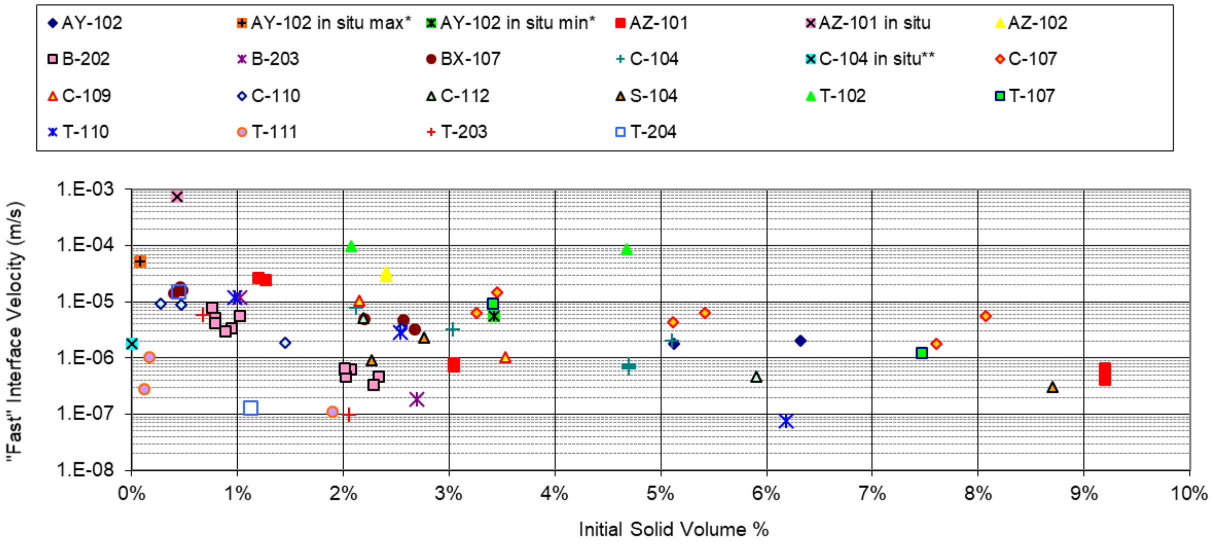

Figure 5.3. Actual waste calculated fast interface settling velocities for HLW as a function of volume % solids. The * for AY-102 *in situ* denotes that the rate may be underrepresented (see discussion in Wells et al. 2011), and the ** for C-104 *in situ* denotes that there is no initial solid volume fraction available.

The solids concentration of the resultant settled layer must be known in order to decant the appropriate volume of supernatant liquid so that the mixture of the settled layer and supernatant liquid has the desired solids concentration. The settled solids layer or sediment mass fractions were approximated for the *in situ* sediments in Hanford tanks in Gauglitz et al. (2010). Note that these values are averages for the sediment, and the wastes have typically been essentially quiescent for extended periods, up to decades. As described by Gauglitz et al. (2010), the sediment mass fraction is computed from simple conservation of mass using the tank-specific sediment and liquid densities from Weber (2009) together with the mass average undissolved solid (UDS) densities of Wells et al. (2007).[17] The resultant cumulative probabilities (waste storage tank count basis) of the mass UDS fractions from Gauglitz et al. (2010) are provided herein in Section 6.1. Figure 5.4 provides the same results in wt% as Gauglitz et al. (2010) for those HLW tanks that have settling data, i.e., the tanks represented in Figure 5.3. As listed in Figure 5.4, the maximum wt% solids for the represented tanks is 75%, median 39%, and minimum 6%.

Also provided in Figure 5.4 are potential DFHLW solids concentration targets. The red square data represent a potential DFHLW slurry feed target (20 wt%), while the blue triangle data represent a potential DFHLW settled layer target (40 wt%). The former therefore represents the minimum concentration that must be achieved in a settled layer in order to provide feed at that concentration with all supernatant liquid removed, while the latter represents a condition where supernatant liquid could be decanted to an extent that, when the remaining supernatant liquid and sediment are mixed, the potential feed slurry solids concentration can be achieved. Clearly, wastes that have a calculated *in situ* concentration in the sediment of less than 20 wt% can be expected to be problematic with respect to using a settle/decant process to achieve that concentration for slurry feed.

Figure 5.5 provides the Figure 5.3 data converted from vol% to wt% solids using the Weber (2009) and Wells et al. (2007) data sources. As an example, the AZ-101 laboratory data that were discussed with respect to Figure 5.3 at approximately 4 × 10^{-7} m/s fast interface settling velocity and 9 vol%, are shown in Figure 5.5 by the red square symbol at the lower right of the figure at an initial solids concentration of almost 20 wt% solids.

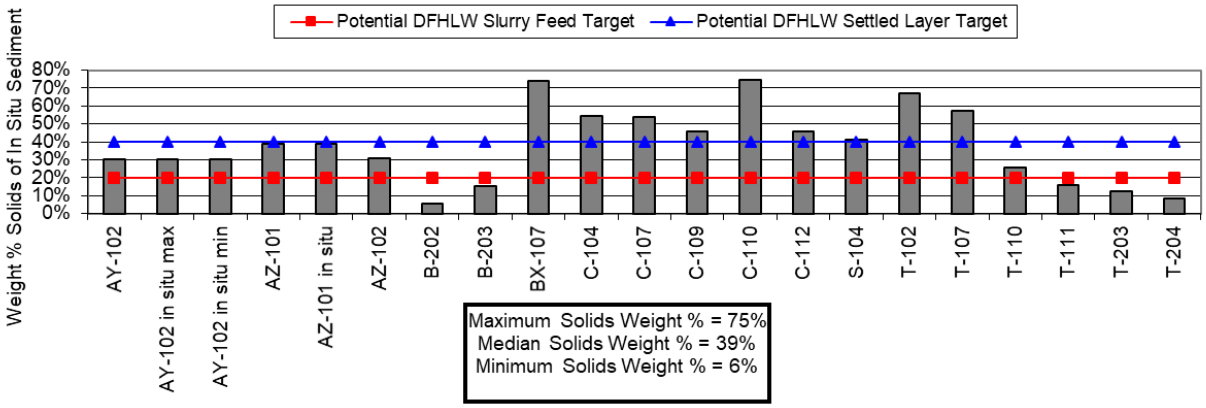

Figure 5.4. Calculated HLW *in situ* sediment wt% solids.

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[17] This earlier work, Wells et al. (2007), is used instead of the updated Wells et al. (2011) to enable the use herein of the Gauglitz et al. (2010) results. Any differences realized between the references for bulk solid phase densities would not substantially impact the settling time results relative to the spread of the settling rates.

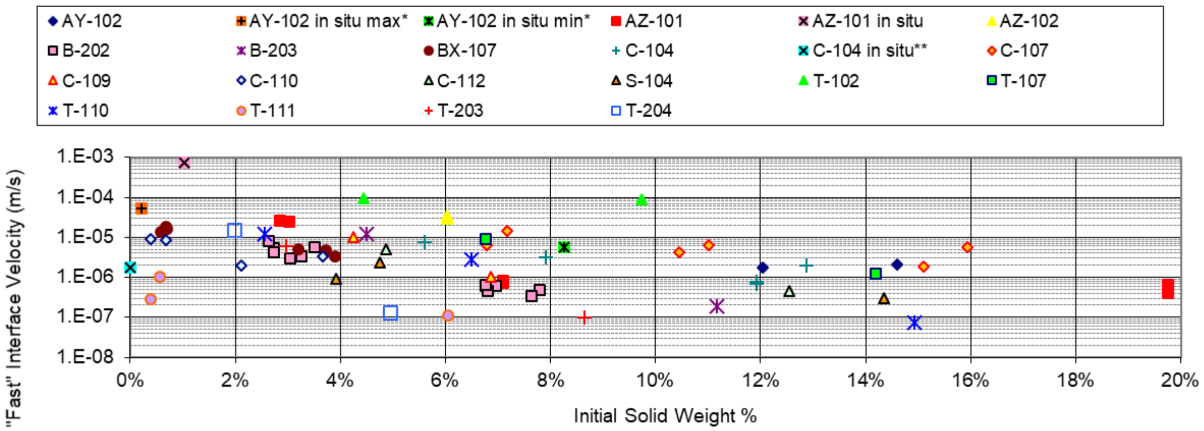

Figure 5.5. Actual waste calculated fast interface settling velocities for HLW, wt% solids. The * for AY-102 *in situ* denotes that the rate may be underrepresented (see discussion in Wells et al. 2011), and the ** for C-104 *in situ* denotes that there is no initial solid volume fraction available.

5.1.2 Settling Time Calculation Methodology

Settling time estimates are made for the wastes in the HLW for tanks with actual settling rate data (i.e., tanks listed in Figure 5.5). The scoping evaluation approach uses the following assumptions:

- The process vessel depths for settling are 10 m, representing a Hanford DST, and 3 m, or 30% of the representative DST depth.
- Two final sediment average solids concentrations are evaluated at each process vessel depth: 20 and 40 wt% solids.
- The initial condition prior to settling has the entire solids inventory (ϕ_0, initial waste solids fraction by volume) as specified by the individual sample results (i.e., Figure 5.3), homogeneously distributed through 10 or 3 m of waste depth.
- The solid-liquid interface falls at the measured fast interface settling velocity until the concentration equals the final sediment average solids concentration of 20 or 40 wt%. Thus, in addition to the discussion of the actual *in situ* sediment solids concentrations (see Figure 5.4, one or both of the potential DFHLW solids concentration targets may not be plausible based on the calculated average *in situ* concentration), the settling times are as fast as possible based on the data.

With the listed assumptions for the initial and final conditions, scoping estimates of the settling time required for the solid-liquid interface to reach a target height/elevation (corresponding to an assumed final solids concentration) can be determined via conservation of mass from

$$Interface\ Settling\ Time = \frac{h_s}{U_f} \tag{5.1}$$

where U_f is the fast interface settling velocity (e.g., Figure 5.3) and h_s is the settling depth to the final sediment (that is, how far the solids at the top of the mixed layer, i.e., at 10 or 3 m, have to fall to reach the sediment at the final concentration) given by

$$h_s = h_0\left(1 - \frac{\phi_0\left(w_f + \frac{\rho_S}{\rho_L}(1 - w_f)\right)}{w_f}\right) \tag{5.2}$$

where

h_0 = process vessel depth (assumptions, 10 and 3 m)
ϕ_0 = initial waste solids fraction by volume (Figure 5.3)
w_f = final sediment mass fraction of solids (assumptions, 0.2 and 0.4)
ρ_S = solid density by tank (Wells et al. 2007)
ρ_L = liquid density by tank (Weber 2009)

5.2 Settling Time Evaluation Results

Scoping estimates of the settling times for HLW solids based on the methodology described in Section 5.1 are presented and discussed. The calculated interface settling times for an initial mixed height of 10 m, settling to a sediment with an average solids concentration of 20 wt%, are provided in Figure 5.6. The abscissa is the settling depth to the final sediment, Eq. (5.2), and the ordinate is the interface settling time in days, Eq. (5.1). As expected, the laboratory and *in situ* AZ-101 settling data points referenced as examples for Figure 5.5 have relatively short settling times. The AZ-101 example laboratory sample has a short settling time because, even though the settling rate is relatively slow, the settling depth is very low because the initial sample conditions are nearly at the final. In contrast, the AZ-101 *in situ* example with a very dilute initial condition also has a very short settling time, but the settling depth is large and the short settling time is now due to the very fast settling rate. Depending on the waste/sample considered, the calculated settling time can differ significantly; T-102 waste with ~ 8-m settling depth requires about 1 day, whereas T-204 waste with a similar settling depth requires about 675 days. The maximum settling time is shown at 749 days, median at 20 days, and minimum at 0.1 days.

The range of settling times from Figure 5.6 is presented as a cumulative distribution in Figure 5.7. This distribution is strictly based on the incidence of occurrence, that is, all individual results in Figure 5.5 are weighted equally. Also provided in Figure 5.7, on the same basis, is the cumulative distribution for all the waste tanks being analyzed that have "A" as the first letter of their designation (tanks AY-102, AZ-101, and AZ-102; see Figure 5.5). Settling time results from samples of these tanks are identified separately as these are the first candidate tanks for DFHLW.[18] The "A" tank results, a set of 3 tanks out of the 33 candidates, range from a minimum of 0.1 days, median 4 days, to a maximum of 108 days for the three tanks.[19]

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[18] Email communication from MD Britton (WRPS) to BE Wells (PNNL), *DFHLW Waste Selection*, Thursday, April 23, 2020, 1:21 PM. The first candidate tanks are AZ-101, AZ-102, AX-104, A-104, A-105, and A-106. The second group of candidate tanks are A-101, A-102, A-103, AN-101, AN-102, AN-106, AN-107, AP-102, AW-102, AW-103, AW-104, AW-105, AX-101, AX-102, AX-103, and AY-101, and the final group is AW-101, AW-106, AN-103, AN-104, AN-105, AP-101, AP-103, AP-104, AP-105, AP-107, and AP-108.

[19] Candidate tanks AN-101 and AN-106 contain solids from the C farm waste tanks transferred after the C farm samples included in Figure 5.6. Given the dispersion and layering of the C farm wastes in AN-101 and AN-106, the "C" waste results of Figure 5.6 are not included in the "A" tanks of Figure 5.7. It can be noted from Figure 5.6, however, that the AZ-101 results "bound" the spread of the "C" wastes, and would thus change the simple cumulative distribution shape but would not alter the maximum and minimum.

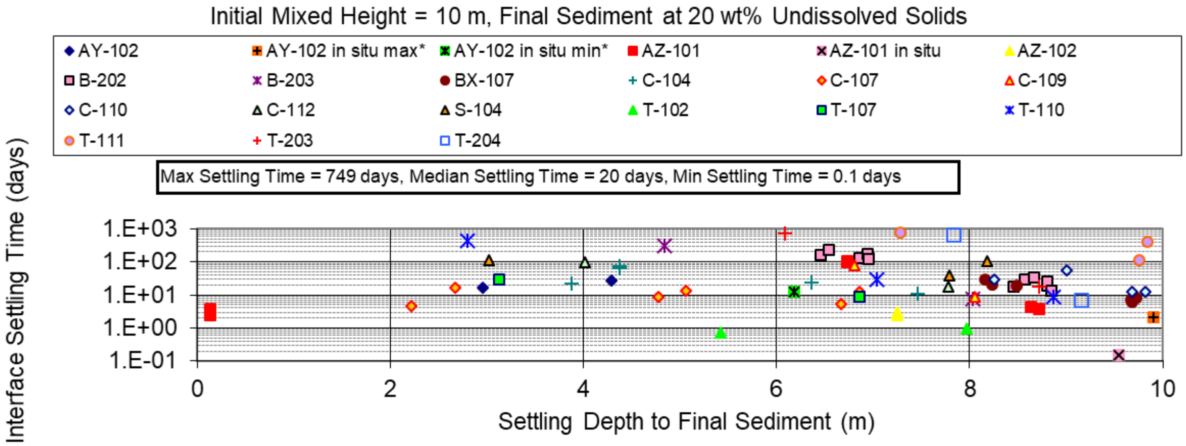

Figure 5.6. Calculated settling times; 10 m, 20 wt%.

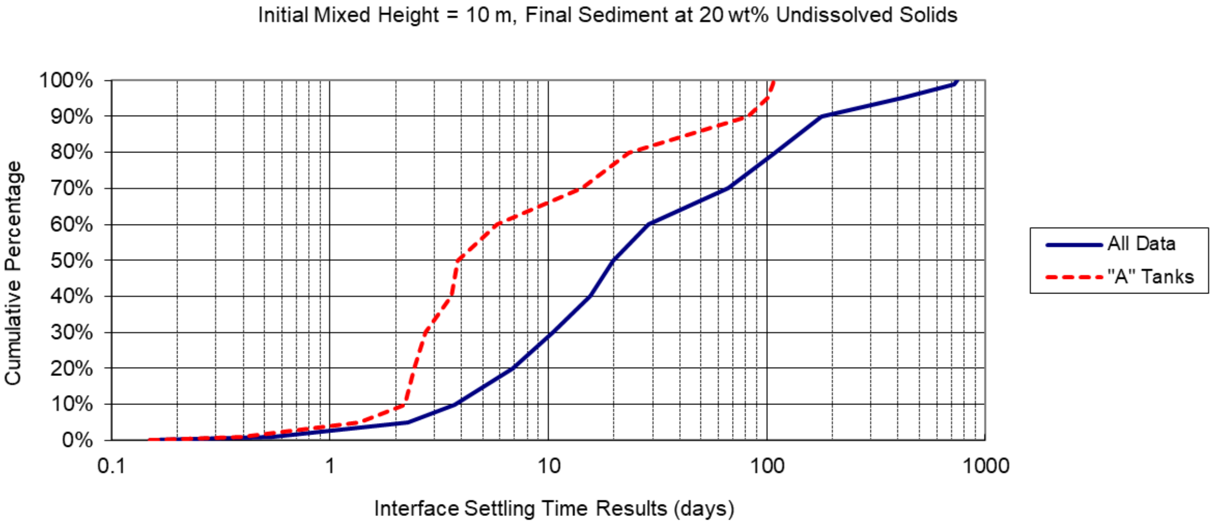

Figure 5.7. Cumulative distributions of calculated settling times; 10 m, 20 wt%

If the final sediment solids concentration is increased while the initial depth stays constant, the settling time is necessarily increased, Figure 5.8 and Figure 5.9. The maximum settling time is now increased to 1060 days, median to 32 days, and minimum to 0.2 days. The “A” tank minimum is increased to 0.2 days, median to 17 days, and the maximum to 165 days.

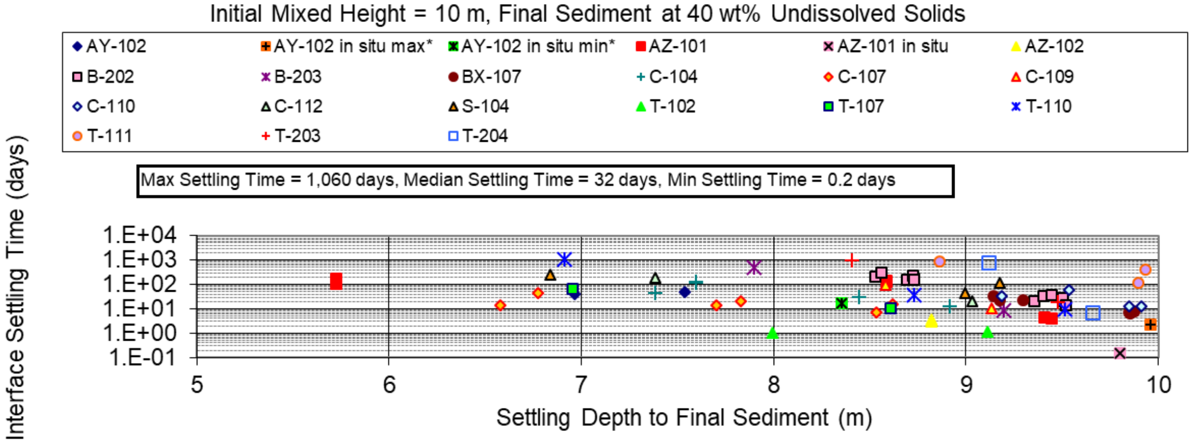

Figure 5.8. Calculated settling times; 10 m, 40 wt%.

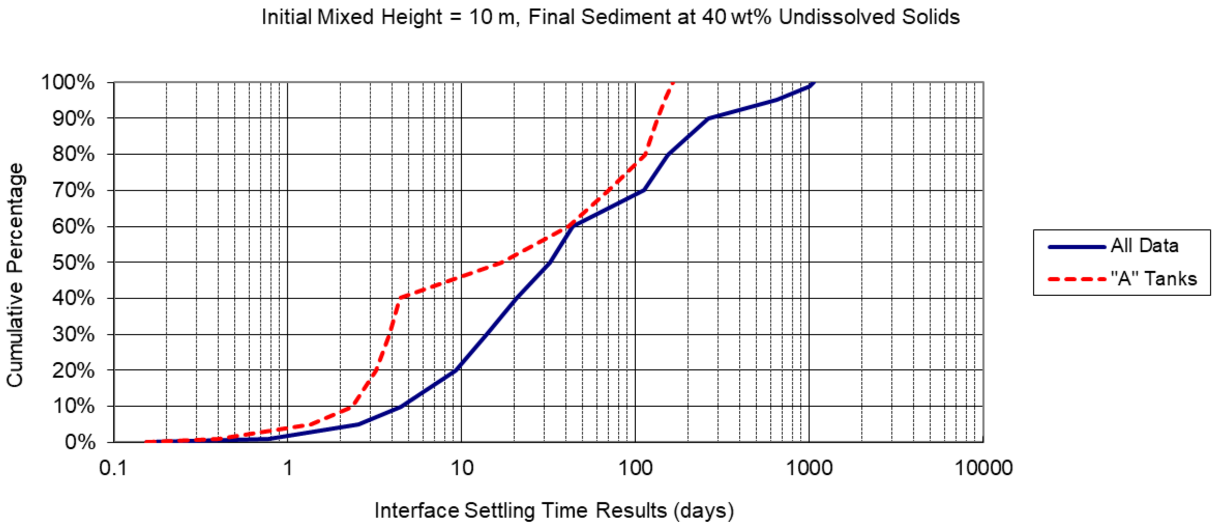

Figure 5.9. Cumulative distributions of calculated settling times; 10 m, 40 wt%.

Reducing the initial depth to 3 m with a final solids concentration in the sediment of 20 wt% yields a maximum settling time of 225 days, median of 6 days, and minimum of 0.04 days, Figure 5.10 and Figure 5.11. The “A” tank minimum is 0.04 days, the median is 1 day, and the maximum is 32 days.

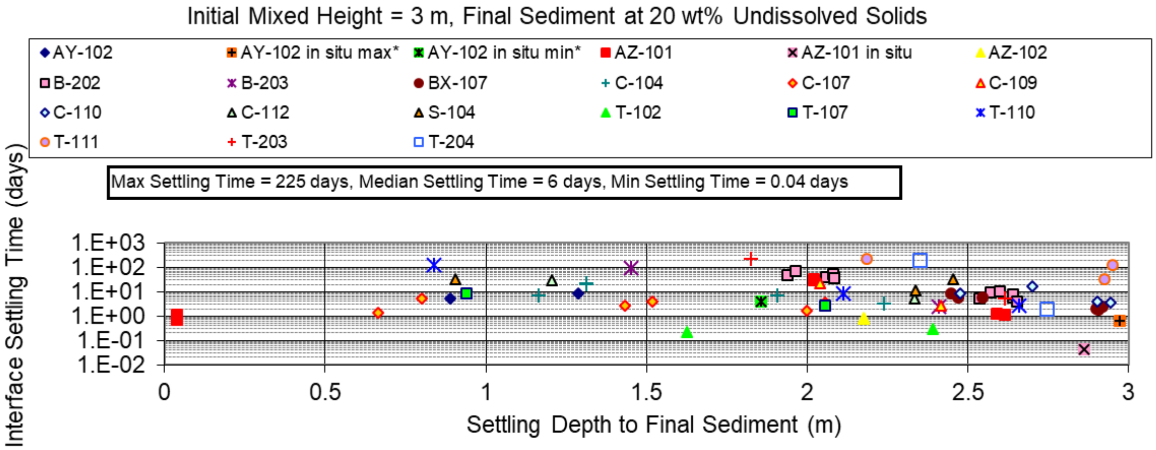

Figure 5.10. Calculated settling times; 3 m, 20 wt %

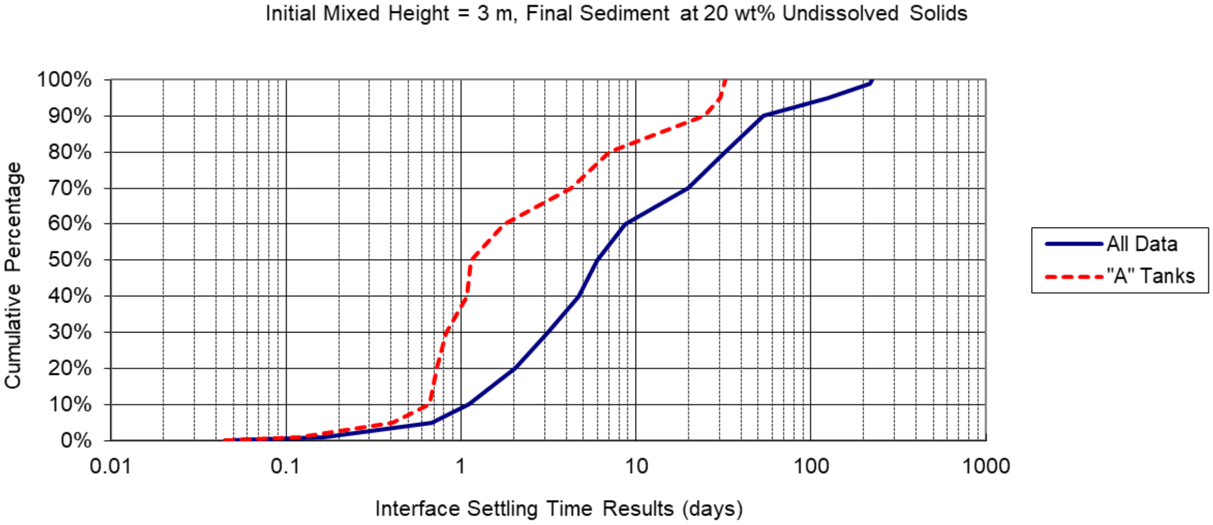

Figure 5.11. Cumulative distributions of calculated settling times; 3 m, 20 wt%.

Finally, as shown in Figure 5.12 and Figure 5.13, with the final sediment solids concentration increased to 40 wt% while the initial depth stays constant at 3 m, the maximum settling time is 318 days, median is 10 days, and minimum is 0.05 days. The “A” tank minimum is increased to 0.05 days, median to 3 days, and the maximum to 49 days.

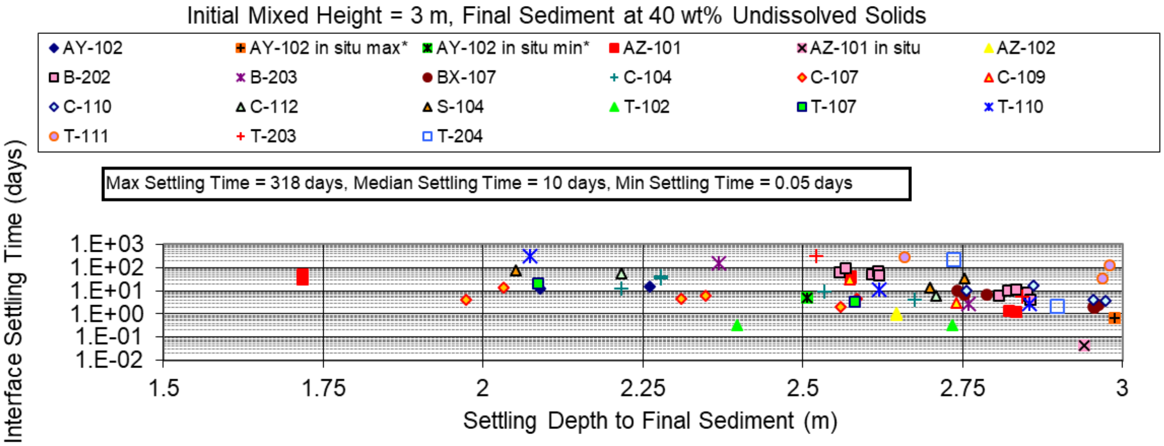

Figure 5.12. Calculated settling times; 3 m, 40 wt%.

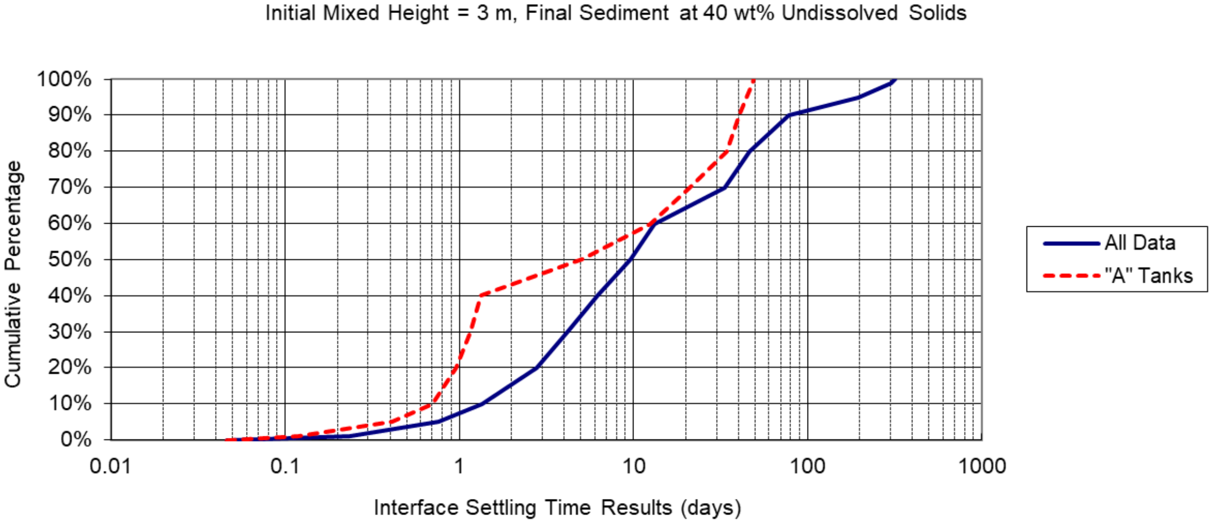

Figure 5.13. Cumulative distributions of calculated settling times; 3 m, 40 wt%.

For process planning, HLW solids have previously been assumed to settle to 15 wt% in 2 weeks.[20] As previously discussed, if a potential DFHLW slurry feed solids concentration is 20 wt%, the sediment must be at that concentration or higher to achieve that target via decanting supernatant liquid. Depending on the process vessel depth and final sediment concentration, substantial fractions of the scoping estimate results for settling times for characterized HLW are shown to exceed the 2-week period. While the median times (for range of initial heights from 3 to 10 m) can meet the previously assumed period of 2 weeks at 20 wt%, for the maximum settling time to be 2 weeks to settle to 20 wt%, the depth of the initial mixture cannot exceed 0.2 m.

Regardless of the magnitude of the results, the significant disparity – potentially greater than a factor of 5000 difference in the settling time for a fixed depth and final concentration (0.2 to 1060 days, for example) – indicates that process planning will most likely have to account for substantially varying waste settling rates.

It is reemphasized that these scoping estimate results employ the fast interface settling velocity and may therefore be underestimates for settling times. Further, there are substantial differences in Hanford waste settled layer average solids concentrations. Finally, as discussed in Section 3.0, the available waste settling rate data have substantial uncertainty, and only a limited fraction of the HLW inventory is characterized.

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[20] Email communication from MD Britton (WRPS) to BE Wells (PNNL), *Settling Assumptions in TOPSim*, Wednesday, April 22, 2020, 6:25 PM.

6.0 Prediction of Settled Layer Solids Content and Shear Strength

The settle/decant operations proposed to support DFHLW are a key process step in providing DFHLW feed at the desired UDS concentration to the WTP HLW Facility. The solids concentration of the resultant settled layer must be known in order to decant the appropriate volume of supernatant liquid so that the mixture of the settled layer and supernatant liquid has the desired solids concentration. To remobilize the sediment, it is also important to be able to predict the critical stress for erosion of the settled layer to allow assessment of whether the selected sediment mobilization method to mix the settled solids with the supernatant liquid, be it jet pumps or some other method, will be able to effectively (i.e., at an appreciable rate) mobilize all of that sediment layer.

The rate of sediment mobilization or erosion can be described by the applied stress (e.g., resulting from a fluid jet) required to overcome a sediment's resistance to erosion (Gauglitz et al. 2017).[21] Within the literature, the breakup or disassociation of particulate sediment materials is discussed in terms of material failure, mobilization, and erosion (Wells et al. 2009), in decreasing order of erosion rate. Effective and efficient mobilization of the sediment must use a mixing method capable of supplying an applied stress that is sufficient to cause material failure. For cohesive materials (e.g., Hanford waste sediments; Gauglitz et al. 2010), Wells et al. (2009) note that the sediment material yield stress in shear (shear strength) provides an upper bound for the applied shear stress necessary to initiate erosion and is associated with a maximum erosion rate.

Correlations exist for predicting the critical shear stress of cohesive materials at varied erosion rates, but there do not appear to be tools for predicting sediment erosion without obtaining data for similar or related types of material, and caution should be taken in applying a model outside of the specific study area used to develop the model. For example, Clark and Wynn (2007) compared different methods of determining the critical shear stress for erosion to experimental data, and the experimental results were as much as four orders of magnitude greater than the Shields diagram (e.g., Vanoni 1975; Julien 1998) and other empirical methods for cohesive materials. Thus, if models are being applied to materials outside of the specific study area that the model was developed for, they should be applied with substantial caution.

A related key point from the discussion in Wells et al. (2009) for the erosion of cohesive materials is that, although the shear strength of a sediment provides an upper bound for erosion and an applied stress equal to this value can be associated with a maximum erosion rate, different materials with the same shear strength may erode at substantially different rates under the same applied stress. Further, as exemplified in Gauglitz et al. (2017) via discussion of the work of Dunn (1959), the use of a simulant's shear strength relative to the shear strength of a simulant with a different composition can be significantly misleading with respect to the erosion rate at a given applied stress; a simulant with a higher shear strength can erode at a faster rate than a different simulant with a lower shear strength when the same stress is applied. Regardless, given that there are essentially no data to estimate the erosion rates of Hanford waste sediments, sediment shear strength will be used herein as a surrogate for the required applied stress for erosion/mobilization.

To summarize the potential magnitude and range as well as the inter-relationships of solids concentration and shear strength, this section discusses previous summaries of historical settled layer solids concentration and shear strength. Recent shear strength measurements of C-farm waste that was

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[21] The word "erosion" is used here to describe the mobilization of sediment material, not the erosion of system components.

transferred into AN-101 and AN-106 are included. Discussions of transient concentrations and shear strength are also provided. Finally, a brief summary of potential erosion requirements is presented.

6.1 Historical Sediment Solids Concentration

Figure 6.1 shows the calculated range of representative sediment UDS mass fractions for all DSTs and sludge DSTs (sludge DSTs are of particular interest for DFHLW, see Section 5.0), together with a comparison to AY-102 (predominantly C-106 sludge prior to transfer out of this waste) and AZ-101 (sludge tank with sediment mobilized via mixer pumps as discussed in Section 6.6). Figure 6.2 shows the calculated representative UDS mass fraction for all Hanford sediment (includes material in single-shell tanks) and for Hanford sludge sediment. The average UDS mass fractions (presented as wt%) for those sludge wastes with settling rate data are also presented and discussed in Section 5.0.

The plots summarizing the cumulative UDS data in Figure 6.1 and Figure 6.2 were originally provided in Gauglitz et al. (2010), and therefore precede the C-farm single-shell tank waste retrievals into DSTs AN-101 and AN-106 (see Section 6.2). The values are representative in that they are based on average individual tank layer and UDS densities, and the cumulative probabilities are strictly based on tank count. Further, they are representative of sediments that have been in that settled condition for extended periods, i.e., years. The vertical bars for AY-102 and AZ-101 are for clarity only. From Figure 6.1 and Figure 6.2 for each of the measurement types, the lowest 5th percentile is a UDS of 0.07 mass fraction and the highest 95th percentile is a UDS of 0.74 mass fraction. The average of the four 50th percentiles in Figure 6.1 and Figure 6.2 is 0.48 mass fraction.

The inclusion of single-shell tank wastes from Figure 6.1 and Figure 6.2 shows that the range of representative sludge sediment UDS concentrations, already quite broad in DSTs, is increased over the range of Hanford inventory germane to DFHLW. Thus, assuming the settling periods employed during settle/decant operations to support DFHLW can achieve similar sediments (the effect of time on UDS concentrations is subsequently discussed in more detail in Section 6.3), the DFHLW feed settle/decant operations may be expected to require substantial adjustment for decant volume depending on the particular waste in a given feed.

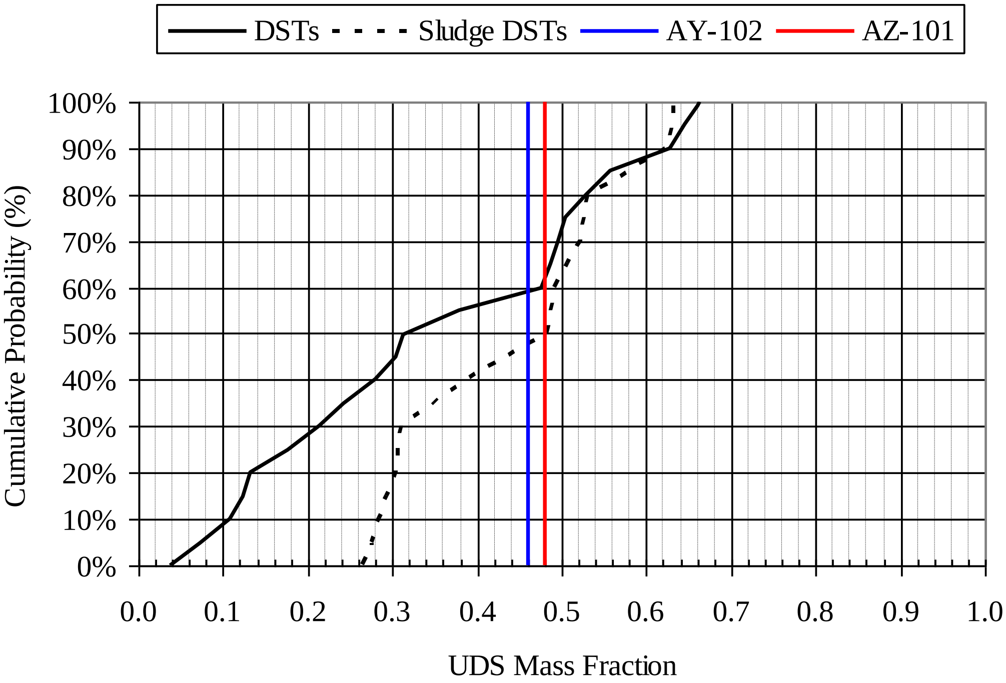

Figure 6.1. UDS mass fraction for sediment in all DSTs and sludge DSTs (from Gauglitz et al. 2010).

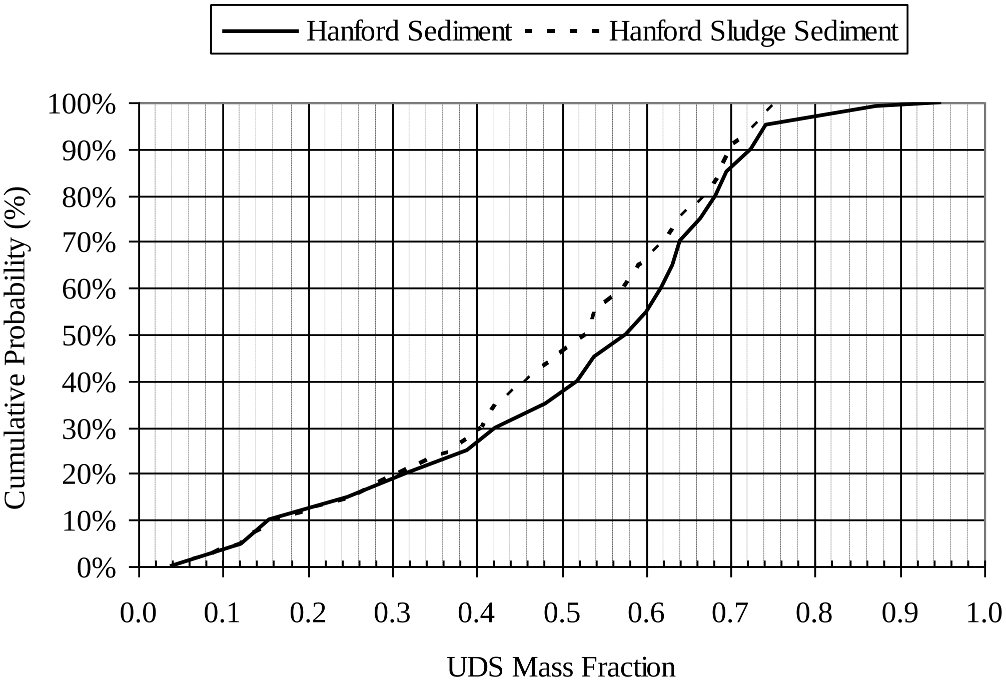

Figure 6.2. UDS mass fraction for all Hanford sediment and for Hanford sludge sediment (from Gauglitz et al. 2010).

6.2 Historical Sediment Shear Strength

Figure 6.3 and Figure 6.4 show summaries presented by Wells et al. (2011) for sludge shear strengths determined from shear vane and waste extrusion measurements. The cumulative probabilities for Figure 6.3 and Figure 6.4 are strictly based on the number of measurements. For example, a waste with five measurements is represented five times in the distribution, while a waste with one measurement is, perforce, represented one time. The lowest 5th percentile shear strength is 27 Pa and the highest 95th percentile is 6400 Pa, and the average of the 50th percentile is 740 Pa.

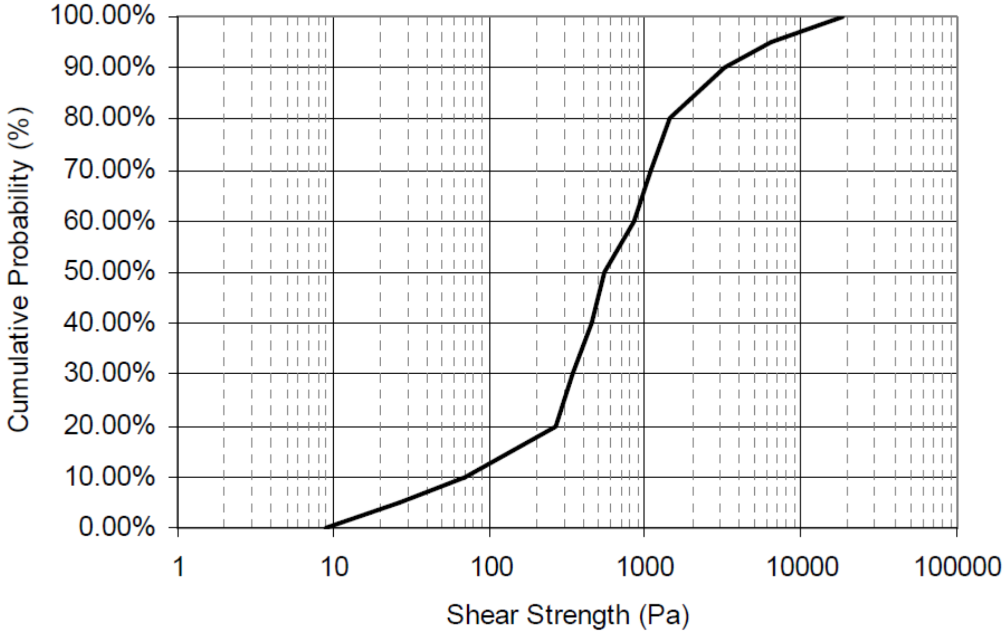

Figure 6.3. Sludge shear vane shear strength (Figure 3.75 from Wells et al. 2011).

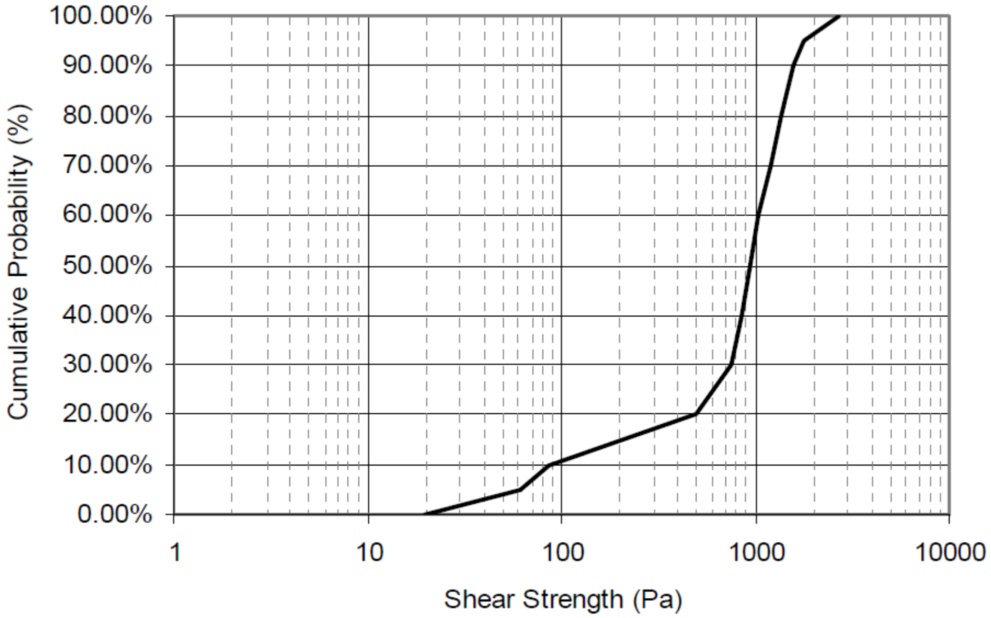

Figure 6.4. Sludge waste-extrusion shear strength (Figure 3.76 from Wells et al. 2011).

Figure 6.5 shows the effect of changing the UDS concentration by dilution on the shear strength of samples from four waste tanks. These results give information on how compaction of a sediment layer under gravitational settling, and the resulting increase in the UDS concentration, contribute to the increase in sediment shear strength. For a given sediment, the shear strength is shown as strongly dependent on the UDS concentration.

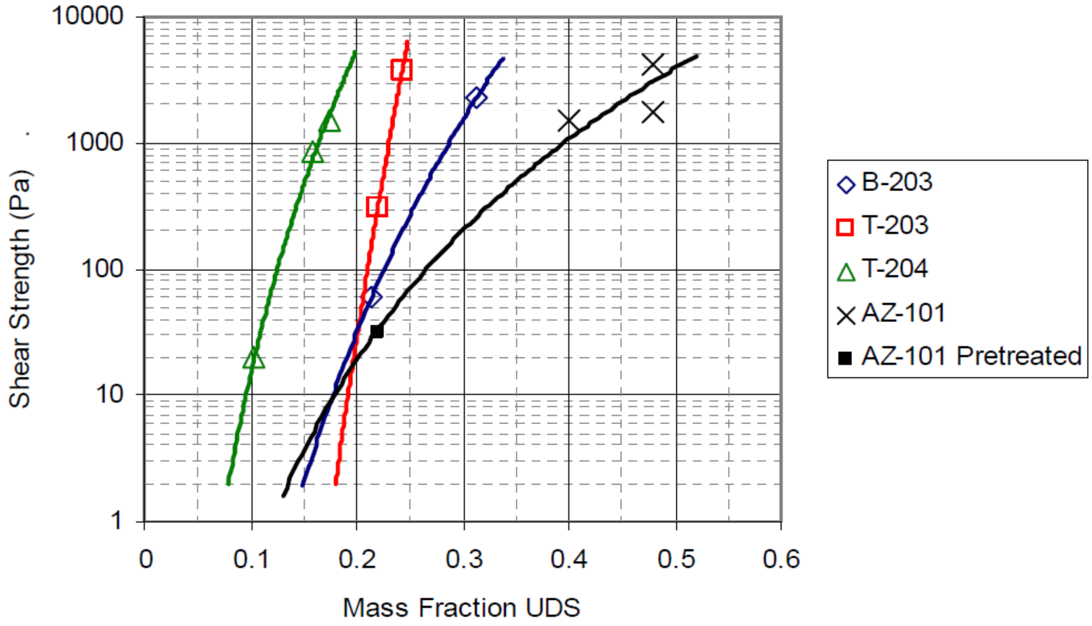

Figure 6.5. Shear vane shear strength as a function of UDS concentration for samples from four sludge waste tanks (from Wells et al. 2011).

Figure 6.6 shows shear strength as a function of UDS concentration for samples from tanks with a primary waste type of sludge. In this figure, samples are not identified by tank, so the effect of UDS concentration on shear strength for samples from an individual tank, such as shown in Figure 6.5, cannot be discerned. Figure 6.6, however, gives a broader view of how shear strength varies over the range of UDS concentrations for tanks with a primary waste type of sludge. The “expected value” is a simple curve fit to the entire data set that illustrates the general relationship that shear strength increases with increasing UDS concentration.

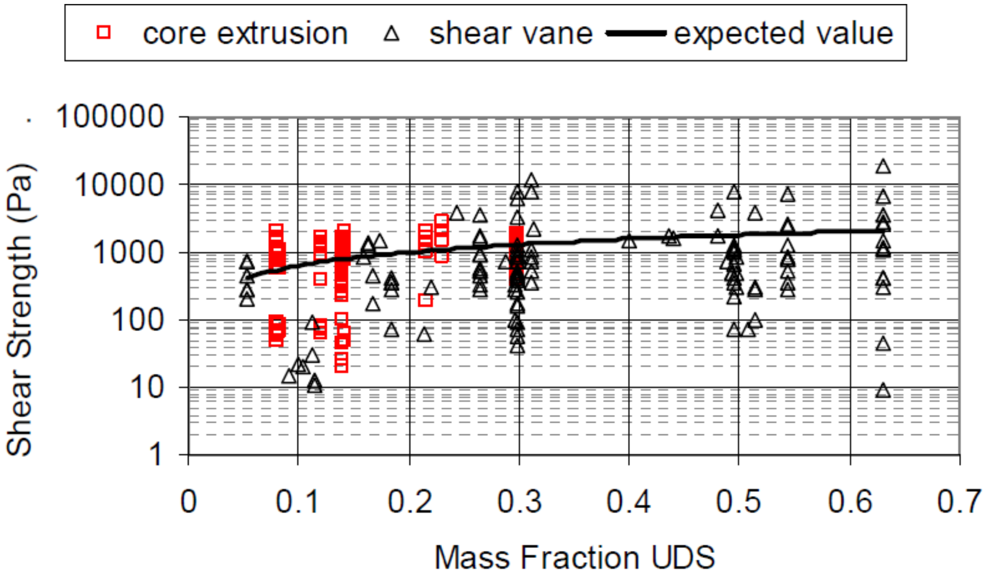

Figure 6.6. Shear strength as a function of average UDS concentration for tanks with a primary waste type of sludge (Figure 3.83 from Wells et al. 2011).

In situ shear strength measurements using a modified cone penetrometer were conducted on C-farm wastes after they were retrieved into AN-101 and AN-106 via sluicing (Follett 2014). The period of C-farm waste transfers into the tanks was approximately 3 years in AN-101 and 8 years in AN-106, and the ball penetrometer was deployed approximately 3 months after the final retrieval into AN-101, and 1 month in AN-106 (Meacham et al. 2014). In addition to potential aging effects (e.g., see waste “gel time” discussion in Wells et al. 2011, and Section 6.3 herein), the data in Figure 6.7 provide clear suggestion of lithostatic loading increasing the solids concentration, and thereby shear strength, with depth. This increase of sediment shear strength with depth in the sediment is evident for essentially all Hanford wastes where data are available (Wells et al. 2011).

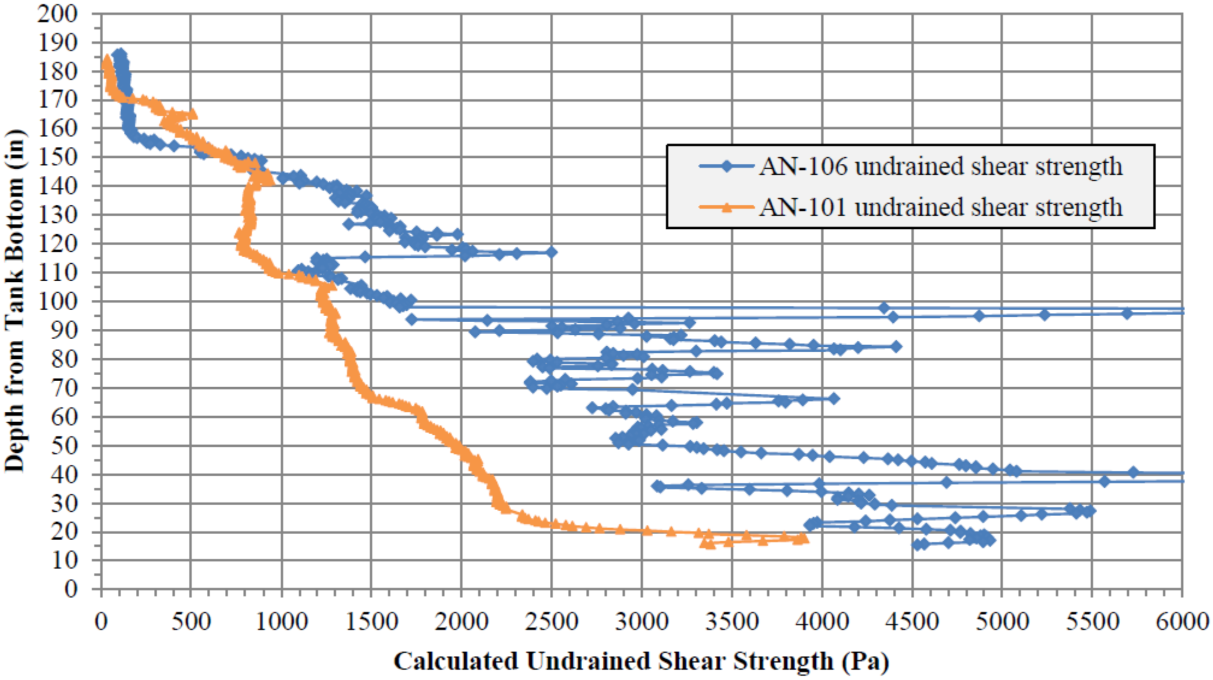

Figure 6.7. Shear strength from cone penetrometer measurements of C-farm sludge waste transferred to AN-101 and AN-106 (from Follett 2014).

6.3 Transient Sediment Solids Concentration and Shear Strength

The average strength of a sediment layer forming due to gravitational settling can increase over time due to continued settling and waste compaction. While mixer pumps similar to the baseline waste feed delivery design from DSTs of two rotating mixer pumps (Meacham et al. 2012) were capable of mobilizing waste across the entire tank bottom for AZ-101 (see Section 6.6), different wastes may be more difficult to mobilize, and the tanks and mixing systems of the DFHLW process vessels wherein settle/decant processes may be employed are not yet designed. Thus, the ability of a mixing system to mobilize the settled layers has not been determined, so understanding how quickly a sediment layer increases in strength will be important to planning DFHLW systems and operations.

As discussed in Gauglitz et al. (2009), the mobilized solids in AZ-101 had a period of nominally 25 days to the final completion of settling (indicated by the maximum value in sediment depth), which was followed by compaction of the layer. The shear strength of the sediment at 28 days, and before the compaction that occurred between 28 and 80 days, was estimated to be on the order of 1600 Pa. Pretreated sludge from AZ-101 required approximately 10 hours to reach 95% of its equilibrium shear strength (Wells et al. 2011).

Previously, Gauglitz et al. (2009) used the limited existing data to estimate the strength of settled layers as a function of time as a result of settling and compaction. Figure 6.8 shows the results of this analysis for the AZ-101 sediment layer and two simulants. In Gauglitz et al. (2009), the average solids content as a function of time was estimated from the settling behavior and then used to estimate the strength of the sediment layers. Gauglitz et al. (2009) also analyzed data for *in situ* settling of waste in AY-102, SY-101, and SY-102 and provided a limited discussion of the available information on the sediment strength for different durations of settling and compaction. Finally, there are a few studies reported in the literature that give measurements of the shear strength and the solids contents as a function of height and time in a compacting sediment layer for various simulants (see for example Hansen et al. 2012 and Bux et al. 2015).

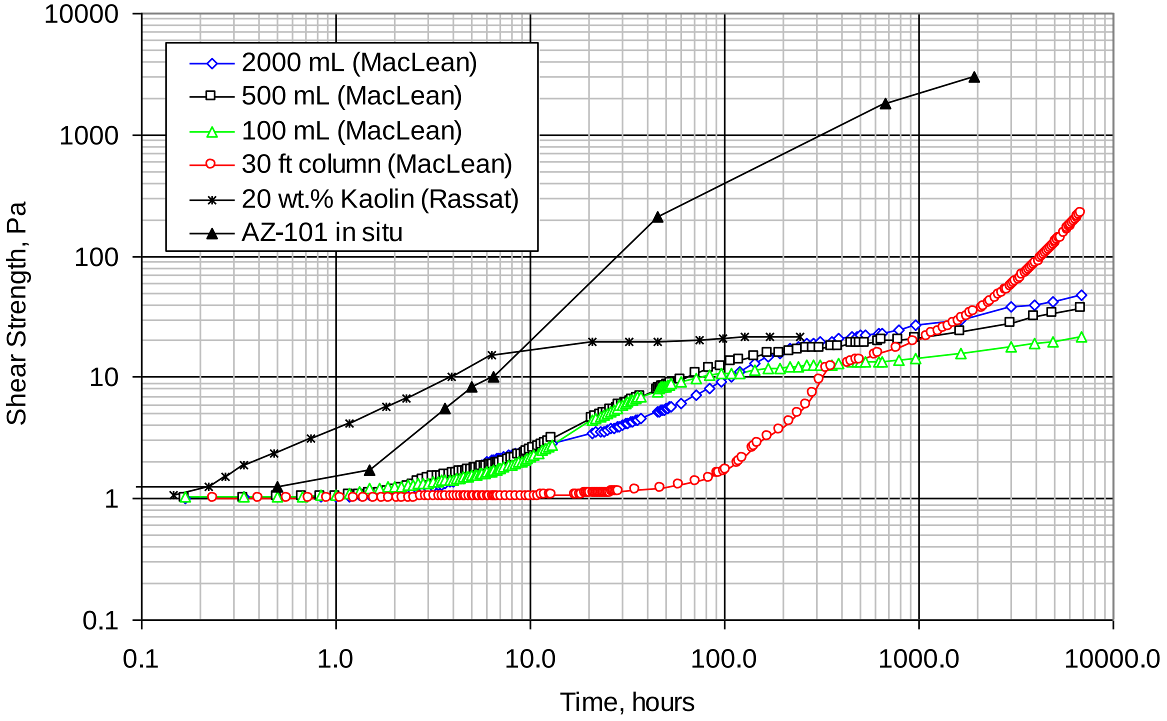

Figure 6.8. Estimated shear strength as a function of time for full-scale AZ-101 and simulants (Figure 2.4 from Gauglitz et al. 2009).

6.4 Gap 7: Prediction of Sediment Erosion Resistance as a Function of Settling Time

As summarized in Section 6.0, it is important to be able to predict the critical stress for erosion or erosion resistance of the settled layer for estimating if, and the rate at which, the selected mixing method will mobilize the settled solids sediment layer, be it jet pumps or some other method. Although insight has been gained into the critical stress for erosion of AZ-101 sediment (Wells et al. 2015) and there are additional erosion rate data to be determined from the AZ-101 mixer pump test performance reported in Carlson et al. (2001), there are essentially no data to estimate the erosion rates of Hanford waste sediments. Instead, sediment shear strength, with its associated caveats, is used as a surrogate for the required applied stress for erosion/mobilization. Therefore, the gap of sediment erosion resistance is addressed with respect to both indirect, i.e., shear strength, and direct erosion measurements.

While there are numerous data on shear strength measurements or estimates of sediment layers in Hanford tanks where the waste has settled and compacted for many years (see Section 6.2), there are few data on the strength of *in situ* settled layers as a function of time (see Section 6.3). Poloski et al. (2007) recommended that the AZ-101 pre-treated sludge behavior be applied to Hanford waste in the absence of additional information on transient shear strength.

The shear strength of a sediment layer is one of the parameters affecting erosion of the layer with turbulent jets and thus the mobilization of HLW solids prior to transfer. Settle/decant operations have been proposed to be a key process step in providing DFHLW feed at the required UDS concentrations, and the duration of the settling period will affect the strength of the settled layer that needs to be mobilized. In a previous study that estimated the strength of settled layers as a function of time, Gauglitz et al. (2009) concluded that scaling behavior, including the role of vessel size, the settling dynamics, and the buildup of strength in the settled layer, is not well understood. This uncertainty was noted to be particularly important for shorter settling times and for quantifying how strength increases with depth into a layer. If the waste settles to form a weak layer, there is the potential for an episodic bubble cascade gas release event. This is a global gas release event that can quickly release nearly all the retained gas (Gauglitz et al. 2015). In laboratory experiments, bubble cascades typically occur over a period of less than a minute. A bubble cascade is thought to have occurred in waste storage tanks at the Savannah River Site (Gauglitz et al. 2015). A bubble-cascade gas release event poses a flammable gas (hydrogen) safety issue and is not mitigated by the controls for avoiding buoyant displacement gas release events (e.g., Stewart et al. 2005). Accordingly, there is a gap in the prediction of sediment shear strength as a function of settling time.

6.4.1 Significance: Prediction of Sediment Erosion Resistance as a Function of Settling Time

Measuring a critical stress for erosion is a direct measurement to understand the required applied stress to erode the sediment at an effective rate. The shear strength of a sediment layer is a related but indirect parameter affecting erosion of the layer under an applied stress such as through turbulent jets, and thus these parameters affect the mobilization of HLW solids in support of DFHLW operations. If the sediment layer becomes too strong to be mobilized and transferred, an incomplete transfer will occur. It is further possible that incomplete mobilization and transfer could cause a buildup of HLW solids in process vessels that receive multiple transfers. Though not related to sediment erosion resistance, if weak settled layers form, there is the potential for an episodic bubble cascade gas release event, which is a flammable gas safety hazard.

6.4.2 Approaches to Resolving Gap: Prediction of Sediment Erosion Resistance as a Function of Settling Time

Direct measurement of the erosion rate of Hanford waste under an applied stress at *in situ* conditions can be a challenging task. However, as illustrated by Wells et al. (2015) for the AZ-101 mixer pump tests, erosion rate information can be inferred from process data, so more information may be available as waste retrievals progress. ASTM Standard D5852 (ASTM 2007) provides a commonly applied method to evaluate a sediment material’s resistance to erosion as a function of applied stress, and various commercial devices operating via the same principle are available. These devices have the potential to be deployed for laboratory evaluations of actual waste and can be used with waste simulant materials to develop possible relationships between erosion resistance and shear strength.

There are a number of approaches, with progressively more complexity and difficulty, that can be used to estimate the change in sediment strength as a function of time. Simulant studies, with periodic *in situ* shear strength measurements during settling and compaction, could be conducted at different size scales to quantify the rate of strength increase with time. Small samples of actual waste could be periodically suspended and then allowed to settle for different durations followed by shear strength measurements. This would examine the effect of settling duration on shear strength, but the small sample size would not allow investigation of the effect of compaction, which becomes more important in deeper sediment layers. Recent studies by Follett (2014) have demonstrated that a modified cone penetrometer can be used *in situ* to measure the shear strength throughout a sediment layer. If a penetrometer was deployed in different risers and at different time periods after the beginning of an *in situ* settling test, full-scale data with actual waste could be obtained.

6.5 Gap 8: Prediction of Sediment Solids Content as a Function of Settling Time

While there are numerous data on solids content of sediment layers in Hanford tanks where the waste has settled and compacted for many years (see Section 6.1), there are very limited direct measurements of the solids content of *in situ* settled layers as a function of time (see Section 6.3). Most laboratory-scale settling studies either report the average solids content in the settling solids layer as a function of time or provide information that would allow this to be determined. While these data are useful for understanding laboratory settling data, there are no *in situ* data for the solids content in a settling and compacting layer as a function of time. Accordingly, there is a gap in the prediction of the sediment solids content as a function of settling time.

6.5.1 Significance: Prediction of Sediment Solids Content as a Function of Settling Time

The available data for the solids content of settling and compacting waste layers suggest that a wide range of solids content can be expected. Direct feed to the WTP as part of DFHLW operations will likely need to be within a narrower range of solids contents, so improved predictions of solids contents in waste sediment with settling time will reduce the uncertainty in providing DFHLW feed in the desired range of solids content.

6.5.2 Approaches to Resolving Gap: Prediction of Sediment Solids Content as a Function of Settling Time

There are a number of approaches, with progressively more complexity and difficulty, that can be used to estimate the solids content in settling and compacting sediment as a function of time. Simulant studies with *in situ* solids content measurements collected during settling and compaction, such as using the acoustic backscatter method discussed in Bux et al. (2015), could be conducted at different size scales to quantify the rate of solids content increase with time. One approach for obtaining *in situ* measurement of solids content would be to develop a correlation between shear strength and solids content, and then deploy the *in situ* modified cone penetrometer developed by Follett (2014) to measure the shear strength throughout a sediment layer as a function of time.

6.6 Effect of Sediment Shear Strength on Effective Cleaning Radius

Waste mobilization studies have been conducted in AZ-101 using mixer pumps similar to the baseline waste feed configuration (e.g., Meacham et al. 2012) of two rotating 300-hp jet mixer pumps. Carlson et al. (2001) concluded from this study that between 95% and 100% of the sludge in AZ-101 was mobilized with full-power operation of the mixer pumps. Gauglitz et al. (2009) noted, in agreement with Carlson et al. (2001), that all thermocouples on the bottom of AZ-101, including those at the tank wall at numerous locations, showed temperature changes indicating that the waste was excavated (mobilized) at all these thermocouple locations. The median shear vane shear strength for AZ-101 sediment is 1770 Pa (Gauglitz et al. 2009), which is the shear strength value used by Gauglitz et al. (2010) in an evaluation of the effective cleaning radius (ECR) for different pump speeds in the AZ-101 test. While the ECR for different materials with the same shear strength is known to vary (see Section 6.0), in the absence of specific erosion rate information the shear strength is a useful sediment waste parameter for evaluating the expected ECR.

The AZ-101 mixer pump test suggests that waste sediment with a shear strength of 1770 Pa or less should be fully mobilized (ECR reaches the farthest tank wall) with a system similar to baseline configuration of two 300-hp mixer pumps, though there is uncertainty in this conclusion because different wastes with this shear strength may not have the same ECR. In addition, the sediment layer in AZ-101 was only approximately 17.5 inches deep (Gauglitz et al. 2009), and deeper sediments create additional performance challenges. The range of measured shear strengths for waste sediment was discussed in Section 6.2, and it was noted that the lowest 5th percentile shear strength for the different measurement techniques is 27 Pa and the highest 95th percentile is 6400 Pa. If 1770 Pa is the highest shear strength where there is confidence that the sediment will be fully mobilized, based on the AZ-101 test, there are a number of shear strength results that may limit full mobilization. From Figure 6.3, approximately 15% of the shear vane measured shear strengths exceed 1770 Pa. Wells et al. (2011) summarized the maximum measured sludge shear strength by waste tank and primary waste type, Figure 6.9. Approximately 14 of the 24 tanks with shear strength data have maximum shear strengths in excess of the referenced AZ-101 median.

It should be noted that AZ-101 had a substantial liquid volume when the mixer pump test was conducted (Carlson et al. 2001), but the waste level in a tank will decrease as slurry is transferred, and there is uncertainty in whether the mixer pumps will continue to be as effective in mobilizing a sediment layer as the waste level decreases. Finally, the primary focus of this discussion has been behavior in DSTs, but it is possible that a new tank design, potentially with a different mixing system than the baseline configuration of two mixer pumps, may be used for staging feed for DFHLW. Accordingly, for a different tank and mixing system, it may be even more important to know how the sediment shear strength increases over time.

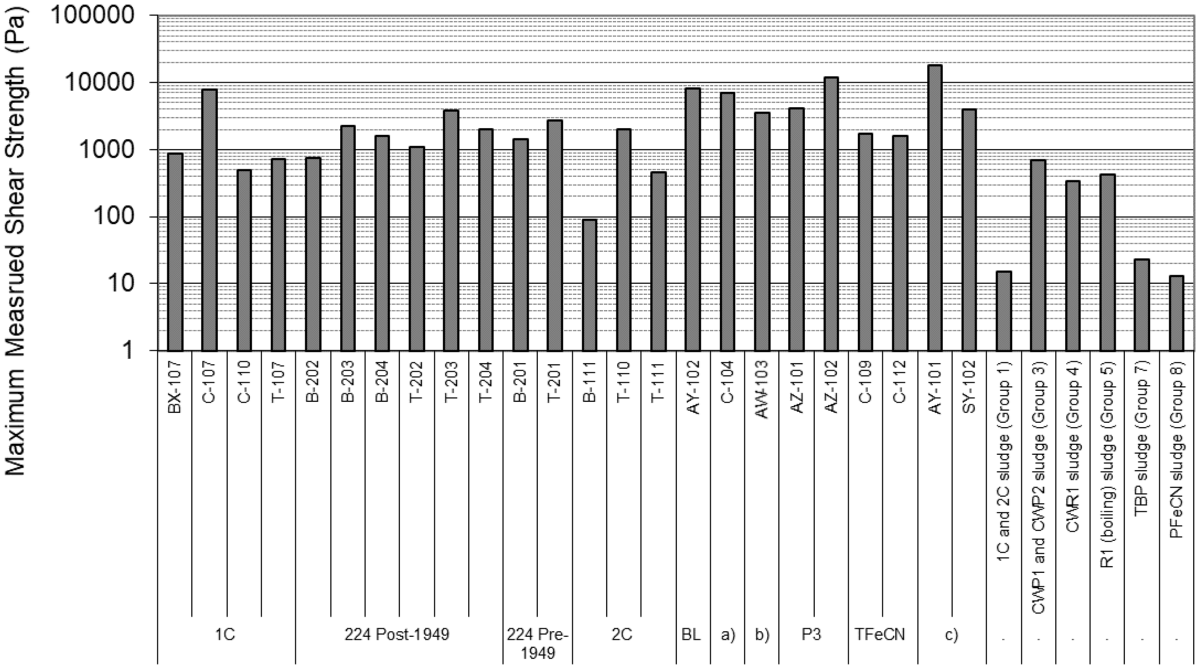

Figure 6.9. Maximum measured shear strength, sludge: a) CWP1, b) CWZr2, c) unidentified (from Wells et al. 2011).

7.0 Summary and Recommendations

A settle/decant process is a key conceptual method for DFHLW to concentrate solids, and separate sludge solids and wash water, and thereby provide feed to the WTP HLW Facility at desired solids concentrations. To support planning for DFHLW, WRPS requested support from PNNL to evaluate the current data set available to predict the time needed for HLW solids to settle and what the characteristics of that settled layer might be. Settling time estimates are required for preliminary design of the process including the selection of process vessel size and count as well as event sequencing and timing. Settling time will also affect the selection of the extent of sludge washing and the resulting wash solution composition and volume. In addition, predictive methods for settling times would enable process optimization to reach target feed solids concentrations and assure mobilization methods would be effective. This report documents the technical gaps and uncertainties of HLW settling behavior and provides estimates of HLW waste settling times based on existing models and data.

Six gaps for waste settling times have been identified:

- Gap 1: *In situ* Settling Rates Faster than Settling of Laboratory Samples
- Gap 2: Effect of Sludge Leaching/Washing on Predicted Settling Times
- Gap 3: Predicting Waste Settling from Waste Chemistry (Waste Type)
- Gap 4: Predicting Waste Settling from PSDDs
- Gap 5: Insufficient Laboratory and *In situ* Settling Data to Represent Hanford Waste
- Gap 6: Methods for Real-Time, *In situ* Tracking of Settling

In addition, two gaps related to understanding of the settled layer's solids concentration and erosion resistance during and following the settling process have been identified:

- Gap 7: Prediction of Sediment Erosion Resistance as a Function of Settling Time
- Gap 8: Prediction of Sediment Solids Content as a Function of Settling Time

For each gap, the significance to the settle/decant process has been described, and uncertainties have been presented by way of examples using data from previous tests with actual tank waste. Suggested approaches to resolving the gaps have also been recommended.

The available settling rate and settled layer data have significant variation. Settling rates can vary by as much as three orders of magnitude at similar solids concentrations, depending on the source waste tank. Significantly different settling rates are noted between laboratory and *in situ* tests for the same waste tank. The range of average solids concentration in existing HLW sediment, which may have been quiescent for decades, can vary from approximately 5 wt% to over 70 wt% solids. The shear strengths (or yield stresses) measured on laboratory samples, which directly affects the ease of the respective waste's mobilization, range from less than 27 Pa to greater than 6400 Pa. These variations can render process planning challenging for the application of a settle/decant process for DFHLW.

In Table 7.1, the technical gaps and uncertainties in waste settling behavior and their significance to the proposed DFHLW settle/decant process for concentrating waste feed are summarized. In addition to the significance, anticipated difficulties in resolving the gaps are listed. Consideration of the combination of the gap significance and the difficulty of resolution yields the following recommendations for the associated gaps (not all gaps result in a recommendation):

- **Gap 1 Recommendation**: Reconcile the disparity between *in situ* and laboratory-scale solids settling tests, by conducting laboratory tests that evaluate the most likely mechanisms that cause faster-than-expected settling rates (see Section 3.1.4), to enable future defensible use of laboratory-scale settling results. One key uncertainty that has been identified is the potential for significant unexplained differences between laboratory- and full-scale settling behavior. This task would further the initial work such that the impact of this uncertainty may be understood for full-scale process application.
- **Gaps 2 and 3 (can provide laboratory information for Gaps 5, 7, and 8) Recommendation**: Leverage the existing experimental *in situ*, as-received, and washed/leached actual waste settling rate results to improve estimates of settling times for DFHLW operations. The initial review of data for the settling velocity of the upper liquid-to-solid interface for as-received waste is consistently suggestive of chemical composition-related patterns with respect to settling rate. Evaluate the settling results for both as-received and washed/leached actual waste with respect to waste chemistry to estimate the range of settling times for HLW feeds to develop qualitative settling process operating parameters for settling rates to support mission planning depending on feed stream chemistry.

  Conduct actual waste sample testing. Develop testing techniques focused on settling rates before and following a washing/leaching, or a washing only, step using radiologically cold simulants for subsequent actual waste testing. The actual waste testing would be conducted such that multiple aspects of DFHLW settle/decant process will be informed; e.g., effect of waste chemistry on settling rate, effect of washing on waste settling rates, effect of settle/decant on the waste composition (such as through the potential removal of slow settling particles during decanting), settled layer characteristics.
- **Gap 6 Recommendation**: Develop a test platform for evaluating instruments for *in situ* tracking of settling behavior to support optimization of DFHLW operations.

Scoping estimates, based on the existing data set, have been made of the potential settling times for HLW solids as functions of the process vessel depth and initial and final solids concentrations. It is reemphasized that these scoping estimate results employ the fast interface settling velocity and may therefore be underestimates. The limitations of this data set are summarized in the gaps and uncertainties, and it has been shown that there are substantial differences in Hanford waste settled layer average solids concentrations.

A summary of the scoping estimate settling time results presented in Section 5 is provided in Table 7.2. Depending on the process vessel depth and final sediment concentration, substantial fractions of the scoping estimate results for settling times for characterized HLW exceed a 2-week period. The result values presented in Table 7.2 are strictly based on the incidence of occurrence, that is, all individual results, regardless of the number of data points for a given tank, are weighted equally. Regardless of the magnitude of the results, the significant disparity – potentially greater than a factor of 5000 difference in the settling time for a fixed depth and final concentration (0.2 to 1060 days, for example, at 10 m process vessel depth and 40 wt% solids in the settled layer) – indicates that process planning will most likely have to account for substantially varying waste settling rates. These results underscore the significance of the identified gaps and uncertainties with respect to process planning using settle/decant operations for DFHLW.

Table 7.1. Technical gaps and uncertainties in waste settling and their significance and anticipated difficulty in being resolved.

Gap (Section)	Description	Significance	Anticipated Difficulty in Resolving Gap
1 (Section 3.1)	*In situ* Settling Rates Faster than Settling of Laboratory Samples	For fast-settling solids, where the settling times does not negatively affect the schedule for operations, there is little impact in resolving this gap. For solids that are predicted to settle more slowly than they actually do, this gap becomes important because the planned schedule for operations may be unreasonably long should faster-than-predicted *in situ* settling actually occur.	Resolving this gap will be difficult because there is no specific mechanism that appears to explain the rapid *in situ* settling compared with settling in laboratory samples. Identifying a likely mechanism will require exploring several possible mechanisms and, potentially, no mechanism will be identified from laboratory tests and modeling. It is possible that this gap will remain even after significant study.
2 (Section 3.2)	Effect of *In situ* Sludge Leaching/Washing on Predicted Settling Times	For some wastes where settling data are available both before and after sludge washing, the effect of waste washing is to cause longer settling times. Currently, a method is not available to predict the effect of washing on settling times for waste without settling data with and without washing.	Sludge washing with water, caustic solutions, or dilute tank supernatant is a complex process that affects the waste chemistry and the PSDD of the washed waste. Established laboratory methods exist for conducting leaching, washing, and settling studies on actual waste and/or simulants.
3 (Section 3.3)	Predicting Waste Settling from Waste Chemistry (Waste Type)	Being able to predict, or correlate, waste settling times from information on waste chemistry would substantially reduce the uncertainty in predicted settling times by enabling the use of a larger set of data on waste chemistry than the existing data on settling.	The initial review of data for the fast settling velocity of the upper interface is consistently suggestive of composition-related patterns. Given the uncertainties and the sparse data, it is unlikely that a quantitative predictive tool can be produced by re-examining existing data and carrying out experiments on waste samples and radiologically cold simulants. However, such an effort may make it possible to understand settling behavior well enough to rule out certain types of settling behavior for a particular waste category.
4 (Section 3.4)	Predicting Waste Settling from PSDD	Being able to predict waste settling times from information on the waste PSDD would reduce the uncertainty in predicted settling times. This type of comparison might help identify where unexpected settling behavior occurs and where further study is needed.	The initial review of data comparing the fast settling velocity of the upper interface with settling rates calculated from PSDDs provides inconclusive and inconsistent results. Given that measuring the PSDD of a waste sample is a difficult challenge, and that there is currently little actual waste evidence supporting model development, directly measuring the settling times of actual waste samples would be a preferred approach.

Table 7.1. Technical gaps and uncertainties in waste settling and their significance and anticipated difficulty in being resolved.

Gap (Section)	Description	Significance	Anticipated Difficulty in Resolving Gap
5 (Section 3.5)	Insufficient Laboratory and *In situ* Settling Data to Represent Hanford Waste	The variability in the limited number of measured setting rates for wastes in laboratory studies, and the extremely limited *in situ* measurements, result in a significant range, with significant uncertainty, of the estimated settling times of HLW solids. This large and uncertain range will likely result, in some cases, in longer-than-needed settling durations in DFHLW operations, which will increase costs and may complicate the schedule for planned operations.	Though costly, collecting waste samples for conducting laboratory settling studies from tanks that have not previously been sampled is an established activity. *In situ* settling measurement has been conducted previously in AZ-101 and is also an established activity. The challenge in conducting either of these activities in an unsampled tank is primarily the cost to collect the samples or data.
6 (Section 3.6)	Methods for Real-Time, *In situ* Tracking of Settling	Real-time measurements of solids settling during DFHLW operations will provide definitive information on when settling is sufficiently complete that waste operations can continue without unwanted solids in decanted supernatant and with HLW feed sufficiently concentrated to be ready for the next step in the operation. In the absence of real-time measurements, conservative predictions of settling times might be used, which would negatively affect the schedule for waste operations.	Multiple *in situ* methods for tracking waste settling were previously deployed in AZ-101. It is expected that the selection of similar or more current versions of the previously deployed measurement methods will not be challenging. If methods with better sensitivity are needed for DFHLW, particularly if these methods are not established for settling of radioactive waste, selecting and confirming the performance of these new instruments will likely be more challenging and may involve large-scale simulant testing.
7 (Section 6.4)	Prediction of Sediment Erosion Resistance as a Function of Settling Time	The erosion resistance of the sediment layer formed during the HLW solids settling process is key to understanding the remobilization of that layer. If the sediment layer becomes too strong before it is mobilized and transferred, an incomplete transfer will occur. It is further possible that incomplete mobilization and transfer could cause a buildup of HLW solids in tanks that receive multiple transfers.	Direct measurement of the erosion rate of Hanford waste under an applied stress at *in situ* conditions can be a challenging task. However, opportunistic data exist and have been initially evaluated, and laboratory-scale methods are well developed. An additional challenge, as with all aspects of HLW waste characterizations, is understanding the range that may be expected from the varied waste.
8 (Section 6.5)	Prediction of Sediment Solids Content as a Function of Settling Time	The available data for the solids content of settling and compacting waste layers suggest that a wide range of solids content can be expected. Direct feed to the WTP as part of DFHLW operations will likely need to be within a narrower range of solids contents, so improved predictions of solids contents in waste sediment will reduce the uncertainty in providing DFHLW feed in the desired range of solids content.	There are a number of approaches, with progressively more complexity and difficulty, that can be used to estimate the solids content in settling and compacting sediment as a function of time, especially for simulant-based studies. An additional challenge, as with all aspects of HLW waste characterizations, is understanding the range that may be expected from the varied waste.

Table 7.2. Scoping estimate results summary for DFHLW settling times.

Process Vessel Depth (Initial Mixed Height) (m)	Final Sediment Weight % Solids	Interface Settling Time to Final Sediment Weight % (days)					
		Minimum		Median		Maximum	
		All Data	"A" Tanks[a]	All Data	"A" Tanks	All Data	"A" Tanks
10	20	0.1	0.1	20	4	749	108
	40	0.2	0.2	32	17	1,060	165
3	20	0.04	0.04	6	1	225	32
	40	0.05	0.05	10	3	318	49

(a) "A" tanks indicates only data for tanks with name designation with first letter "A" included.

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Appendix A – Settling Interface Velocity Versus Composition

Wells et al. (2011) compiled solid phase and liquid phase compositions for all tank wastes. The compilation also included measurement-based “fast” interface settling velocities for the upper interfaces and initial volume fractions for a limited set of single-tank saltcakes, single-tank sludges, and multi-tank waste composites for particular waste groups defined by the M12 program. The fast interface settling velocities represent the average velocity during the initial period when the velocity decreases by 30% from its initial value. This velocity is likely to be set by the slowest-settling particles in the particle velocity distribution.

The limitations of the composition and settling data for single tanks are discussed by Wells et al. (2011) and are not repeated in detail here. The main points to recall are that (a) the compositions were calculated as whole-tank averages and may not match those of individual core samples; (b) the prediction of liquid-phase pH was uncertain because of complications in putting the average compositions into charge-balanced form for model inputs; (c) to save computation time, the set of possible solids was limited to those that were considered most probable; and (d) the compositions were based on the inventories present in 2002, and predate many retrievals.

The M12 program testing of waste types studied composites of samples from multiple tanks to provide information for each M12 waste group (numbered 1 through 8). The waste group studies that included settling tests were a set of M12 reports consisting of Edwards et al. (2009), Fiskum et al. (2009), Lumetta et al. (2009), and Snow et al. (2009). Samples were washed to remove interstitial liquid contributions. The solid phases in the composites were studied by microscopic methods and consistency-checked against compositions determined by chemical analysis. It was not always possible to quantify or identify solids.

Table A.3 reprises the waste type and the fast interface settling velocities from Table 3.30 of Wells et al. (2011) and adds composition data either from that reference or from the M12 reports listed above. Major solid phases are included, with more focus on sludge solids than on salt solids. Concentrations are listed only for solids present at more than about 5 wt%; therefore, wt% of constituents listed in Column 1 of Table A.1 do not sum to 100%). Liquid density and pH (or free hydroxide) data are also included.

For this (FIO) effort, an examination of the tabulated data, the sludge solids were segregated by composition into six general categories (GC) (numbered 1 through 6), each discussed below and depicted in plots (Figure A.1 through Figure A.5). These plots repeat much of the same data plotted in Figure 3.68 of Wells et al (2011) (also found as Figure 5.2 of this report), but with markings added to show which points are in the waste GC being discussed. The waste GCs are defined below according to the major constituents in the sludge solids. This approach has the potential drawback that the rate of descent of the upper interface, the experimentally measured behavior, may be defined not by a major constituent but by a minor one that settles slowly. Therefore, the approach presented must be considered a first attempt rather than a final categorization.

A.1 [GC 1] Very high content of aluminum with other metals much lower, and no history of self-boiling in the tank

PUREX and REDOX cladding wastes (T-102, M12 Group 3, and M12 Group 4)[22] fell into this category with aluminum compounds making up more than 80 wt% of the solid. Figure A.1 shows where these

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[22] M12 Group 3 and Group 4 samples were composites of, respectively, PUREX cladding sludges and REDOX cladding sludges.

wastes fall on a plot of fast interface settling velocity [as defined by Wells et al. (2011)] versus initial solids volume fraction ϕ_0. The green-circled points show the non-boiling high-Al solids.

All solids in this category show relatively high interface velocity even at relatively high solids fractions. The three sets of data, taken together, span a wide range of ϕ_0, but each set taken alone comes from a narrow range. It is therefore not well-established that a waste in this category would, if diluted or concentrated, necessarily follow the superficially apparent trend over this range of ϕ_0.

It appears unlikely that laboratory-scale velocities for the non-boiling high-aluminum waste category would exceed 1×10^{-4} m/s as ϕ_0 approaches zero (where there is no effect of hindered settling).

A.2 [GC 2] High content of aluminum with other metals much lower, and a history of self-boiling

C-109 and S-104 fell into this category, with aluminum compounds making up more than 40 wt% of the solid and no other non-salt compound exceeding 7 wt%. Figure A.1 shows these wastes marked with a purple square. Boehmite (AlOOH) was the dominant solid phase. Its small primary particle size (Table A.3) indicates that colloidal effects are a possibility. Both these wastes have high salt content, so dilution is unlikely to reduce ionic concentration to the point where colloid primary particles are more stable than flocs.

This category of solids appears to show velocities that trend downward with increasing ϕ_0. However, the two sets of data should not be taken together as indicating a trend. Per Table A.3, the fast interface settling velocity for C-109 was 1×10^{-5} m/s at 2.2 vol% solids, but for S-104 the velocity was 9×10^{-7} m/s at 2.3 vol% solids. The trend of the boiling high-Al category is not well defined by the available data, as is perhaps also indicated by the different sludge types present in the two tanks: types TFeCN and SWP1 for C-109, but type R1 for S-104.[23]

The highest fast interface settling velocity seen in self-boiling high-aluminum data sets was 1×10^{-5} m/s at 2.2 vol% solids.

A.3 [GC 3] High content of iron and aluminum, with no information about boiling

The criteria for inclusion in this category were that (a) iron compounds made up more than 25 wt% of the sludge, or that Fe analyte measured by analysis was higher than 15 wt%; (b) aluminum compounds made up more than 25 wt%; and (c) lanthanum, bismuth, uranium, and zirconium compounds were minor constituents. The AZ-101, AZ-102, and C-109 wastes met these criteria closely, although AZ-101 waste contained 8% ZrO_2. The T-107 waste (primarily 1C waste type) was borderline because Na_2U_2O7 was present at 9 wt%. Figure A.2 shows data for these wastes marked with green circles.

Broadly speaking, the category shows a downward trend in fast interface settling velocity with increasing ϕ_0 that appears to be consistent among the in-laboratory tests. On a closer examination, individual tanks do not follow that trend with complete consistency. The two in-laboratory AZ-101 velocities that were

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[23] TFeCN: a ferrocyanide sludge waste type. CWP1: a PUREX cladding sludge waste type. R1: a REDOX waste type. Hanford waste types were originally defined by Agnew et al (1997), in which document they are listed in Appendix F. With some later updates, many of the same waste types appear in the Best Basis Inventory https://twins.labworks.org/twinsdata/Forms/About.aspx?subject=BestBasisInventory.

measured at 3.0 vol% solids fall well below the trend. The discrepancy is not easily explainable as scatter because of the points' agreement with each other. The velocity of C-107 waste at 8.1% solids was 5.5×10^{-6} m/s, above the apparent trend; this may be scatter, since the velocity at 7.6% solids was near the trend at 1.8×10^{-6} m/s. Taking the trend as meaningful, it appears unlikely that laboratory-scale velocities for the Fe/Al category would exceed 2×10^{-4} m/s as ϕ_0 approaches zero (where there is no effect of hindered settling). T-107 waste lies in the trend, which might mean that its uranium content did not control the upper interface velocity.

The *in situ* data for fast interface settling velocity suggest a higher limiting velocity as ϕ_0 approaches zero. The AZ-101 *in situ* fast interface settling velocity was 7.4×10^{-4} m/s at 0.43 vol% solids. The AY-102 fast interface settling velocities were considerably lower but are believed to have been underestimates of upper interface velocity because they were based on the motion of the lower interface – the top of the settled solids layer. The large factor of difference between *in situ* and in-laboratory fast interface velocities, and the difficulty in explaining the difference, has been discussed elsewhere (e.g., Wells et al. 2011).

A.4 [GC 4] Significant content of bismuth, iron, and aluminum with no information about boiling

The criteria for inclusion in this category were that (a) iron and aluminum compounds were present but not dominant; (b) bismuth compounds made up about 10 wt% or more of the solids; and (c) lanthanum, uranium, and zirconium compounds were minor constituents. The BX-107, C-110, and T-110 wastes met these criteria closely; BX-107 and C-110 wastes were type 1C, whereas T-110 waste was type 2C. The M12 Group 1 waste composite was a combination of 1C and 2C waste types.[24] Its inclusion in this GC was borderline because U analyte was relatively high, 11 wt%. Figure A.3 shows data for these wastes marked with green circles; the M12 Group 1 data are labeled "Group 1".

It is generally the case that these Bi/Fe/Al wastes exhibited fast interface settling velocities that fell off more rapidly with increasing ϕ_0 than was the case for the Fe/Al wastes in Figure A.2. However, the M12 Group 1 composite did not show any definite trend of velocity decrease over what was admittedly a narrow range of ϕ_0, about 4 to 6 vol%. It is not clear whether this might have been related to its uranium content or its size distribution. The samples of individual tank wastes did show the strong trend of decline in interface velocity, with the caveat that only one data point (for T-110) was outside the narrow range of 0 to 3% vol% solids, and this single point may skew the perception of trend.

It appears unlikely that laboratory-scale velocities for the Bi/Fe/Al category would exceed 5×10^{-5} m/s as ϕ_0 approaches zero (where there is no effect of hindered settling).

A.5 [GC 5] Significant content of lanthanum, phosphate, bismuth, and iron with no information about boiling

The criteria for inclusion in this category were that (a) aluminum compounds were absent; (b) iron compounds were present but not dominant; (c) bismuth compounds were dominant at more than 20 wt%; (d) lanthanum phosphate was predicted as part of the modeled composition; and (e) uranium and zirconium compounds were minor constituents. The tank wastes in this category all had modeled compositions; the actual iron and bismuth compounds present may have included phosphates as well as the oxides or oxyhydroxides shown in Table A.2. The wastes from the B-200 and T-200 farms met the

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[24] 1C, 2C: bismuth phosphate sludge waste types.

criteria closely, while the waste from T-111 (which included some CWP waste type)[25] was borderline because it contained 23 wt% of nominal FeOOH. It is worth noting that all of these wastes contained significant amounts of manganese compounds (15 to 22 wt%). Figure A.4 shows data for these wastes marked with green circles.

These Bi/La/PO_4/Fe wastes exhibited fast interface settling velocities that fall off more rapidly with increasing ϕ_0 than was the case for either the Fe/Al wastes in Figure A.2 or the Bi/Fe/Al wastes in Figure A.3. This behavior is consistent for all the B-200 and T-200 wastes, but the T-111 waste stands out as having lower interface velocities that, possibly, fell off less rapidly with increasing ϕ_0. It is not clear whether this might be related to its iron content, which is unique in the category. The T-111 waste produced some of the lowest interface velocities in the whole data set.

It appears unlikely that laboratory-scale velocities for the Bi/La/PO_4/Fe category would exceed 5×10^{-5} m/s as ϕ_0 approaches zero.

A.6 [GC 6] Significant content of uranium, but not matching other categories; no information about boiling

The remaining data sets for sludge settling did not fit in the previously described categories. All contain 8 wt% or more of uranium compounds, often with significant amounts of iron or aluminum, but otherwise are not similar to each other. C-104 waste (partly CWP waste type) was unique in containing high zirconium, 15% ZrO_2. C-112 waste (mostly TFeCN type) and the M12 Group 8 waste composite (PFeCN type)[26] contained significant amounts of calcium compounds. M12 Group 7 waste (TBP type)[27] contained higher iron than the others. Figure A.5 shows data for these wastes marked with green circles.

These otherwise uncategorized uranium wastes do not show any consistent trend, which is not surprising given their differences in composition. The M12 Group 7 waste, where iron was one of the most dominant analytes, produced some of the lowest interface velocities in the whole data set. Most of the other data from the otherwise uncategorized uranium wastes were not unusual in terms of their settling velocities or their apparent relationship to ϕ_0.

None of the data for this subset were taken at near-zero initial solids content, and trends are inconsistent between the different wastes. Therefore, nothing can be said about the maximum interface velocity that might exist as ϕ_0 approaches zero.

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[25] CWP: a PUREX cladding sludge waste type.

[26] PFeCN: a ferrocyanide sludge waste type.

[27] TBP: tributyl phosphate process sludge waste type.

Table A.3. Sludge waste composition and settling information (For Information Only).

Solids composition for major constituents only, wt%[*]; liquid properties are pH (or OH concentration) and density	Tank or M12 Group	Waste Type	Dominant Species [General Category]	Dilution	Initial Solids (vol%)	"Fast" Interface Settling Velocity (m/s)
Modeled: 49% FeOOH, 31% $Al(OH)_3$, 6% MnO_2; 1.15 g/mL liquid, pH 14.4	AY-102 composite	BL (B Plant low-level waste)	High Fe/Al [GC 3]	None	6.3%	2.0×10^{-6}
					5.1%	1.8×10^{-6}
Modeled: 27% FeOOH, 56% $Al(OH)_3$, 8% ZrO_2; 1.24 g/mL liquid, pH 13.9	AZ-101 composite (1993)	P3 (PUREX high-level waste)	High Fe/Al [GC 3]	70 wt% supernatant	9.2%	6.5×10^{-7}
					9.2%	4.0×10^{-7}
				90 wt% supernatant	3.0%	8.1×10^{-7}
					3.0%	7.2×10^{-7}
	AZ-101 composite (2000)			None	1.3%	2.4×10^{-5}
					1.2%	2.7×10^{-5}
	AZ-101, *in situ* settling			None	0.43%	7.4×10^{-4}
Modeled: 29% FeOOH, 30% $Al(OH)_3$, 22% dawsonite, 8% Na aluminosilicate; 1.14 g/mL liquid, pH 13.1	AZ-102 composite	P3	High Fe/Al [GC 3]	None	2.4%	2.9×10^{-5}
					2.4%	3.4×10^{-5}
Modeled: 30% Bi_2O_3, 18% La phosphate, 15% MnO_2, 15% FeOOH, 8% CaF_2; 1.17 g/mL liquid, pH 9.5	B-202 Seg. 2	224 Post-1949 (LaF finishing waste)	Bi/La/PO_4/Fe [GC 5]	DI water; 1:1 by vol.	2.0%	6.2×10^{-7}
					2.0%	6.6×10^{-7}
				DI water; 3:1 by vol.	1.0%	5.5×10^{-6}
					0.76%	7.8×10^{-6}
	B-202 Seg. 4			DI water; 1:1 by vol.	2.3%	4.8×10^{-7}
					2.1%	6.2×10^{-7}
				DI water; 3:1 by vol.	0.79%	5.2×10^{-6}
					0.79%	4.1×10^{-6}
	B-202 Seg. 6			DI water; 1:1 by vol.	2.3%	3.4×10^{-7}
					2.0%	4.7×10^{-7}
				DI water; 3:1 by vol.	0.95%	3.3×10^{-6}
					0.88%	3.0×10^{-6}
Modeled: 45% Bi_2O_3, 22% MnO_2, 19% La phosphate, 5% FeOOH, 5% CrOOH; 1.05 g/mL liquid, pH 9.5	B-203 composite	224 Post-1949	Bi/La/PO_4/Fe [GC 5]	DI water; 1:1 by mass	2.7%	1.9×10^{-7}
				DI water; 4:1 by mass	1.0%	1.2×10^{-5}
Modeled: 45% Bi_2O_3, 18% MnO_2, 20% La phosphate, 7% FeOOH, 7% salt; 1.17 g/mL liquid, pH 10.2	T-203 composite	224 Post-1949	Bi/La/PO_4/Fe [GC 5]	DI water; 1:1 by mass	2.0%	9.9×10^{-8}
				DI water; 4:1 by mass	0.67%	5.9×10^{-6}

Table A.3. Sludge waste composition and settling information (For Information Only).

Solids composition for major constituents only, wt%[*]; liquid properties are pH (or OH concentration) and density	Tank or M12 Group	Waste Type	Dominant Species [General Category]	Dilution	Initial Solids (vol%)	"Fast" Interface Settling Velocity (m/s)
Modeled: 51% Bi_2O_3, 20% MnO_2, 20% La phosphate, 6% FeOOH; 1.17 g/mL liquid, pH 10.2	T-204 composite	224 Post-1949	Bi/La/PO_4/Fe [GC 5]	DI water; 1:1 by mass	1.1%	1.3×10^{-7}
				DI water; 4:1 by mass	0.44%	1.6×10^{-5}
Modeled: 11% $BiFeO_3$, 10% Na aluminosilicate, 7% $Al(OH)_3$, 5% $FePO_4 \cdot 2H_2O$, 64% salt ($Na_7F(PO_4)_2 \cdot 19H_2O$); 1.17 g/mL liquid, pH 10.2	BX-107 Seg. 2	1C (1st cycle $BiPO_4$ process waste)	Bi/Fe/Al [GC 4]	DI water; 1:1	2.6%	4.7×10^{-6}
				DI water; 3:1	0.46%	1.8×10^{-5}
	BX-107 Seg. 4			DI water; 1:1	2.7%	3.2×10^{-6}
				DI water; 3:1	0.48%	1.6×10^{-5}
	BX-107 Seg. 6			DI water; 1:1	2.2%	5.0×10^{-6}
				DI water; 3:1	0.40%	1.4×10^{-5}
Modeled: 31% FeOOH, 30% $Al(OH)_3$, 26% salt ($Na_7F(PO_4)_2 \cdot 19H_2O$); 1.17 g/mL liquid, pH 9.6	C-107 composite	54 vol% 1C, 36 vol% SRR (SRR is slurried PUREX sludge)	High Fe/Al [GC 3]	DI water; 140 g UDS/L	8.1%	5.5×10^{-6}
				DI water; 140 g UDS/L	7.6%	1.8×10^{-6}
				DI water; 100 g UDS/L	5.4%	6.2×10^{-6}
				DI water; 100 g UDS/L	5.1%	4.3×10^{-6}
				DI water; 60 g UDS/L	3.5%	1.5×10^{-5}
				DI water; 60 g UDS/L	3.3%	6.4×10^{-6}
Modeled: 8% $BiFeO_3$, 12% Na aluminosilicate, 7% $Al(OH)_3$, 7% $FePO_4 \cdot 2H_2O$, 60% salt ($Na_7F(PO_4)_2 \cdot 19H_2O$); 1.10 g/mL liquid, pH 10.4	C-110 Seg. 2	1C	Bi/Fe/Al [GC 4]	DI water; 1:1	2.5%	3.3×10^{-6}
				DI water; 3:1	0.47%	8.7×10^{-6}
	C-110 Seg. 4			DI water; 1:1	1.5%	1.9×10^{-6}
				DI water; 3:1	0.27%	9.1×10^{-6}
Measured: $BiPO_4$ process sludge (Lumetta et al 2009): solids after washing with 0.01 M NaOH were 11% Bi (in $BiPO_4$), 11% Fe (in $FeAl_2(PO_4)_2(OH)_2 \cdot 6H_2O$ or other Fe phosphate), 15% Na (in $Na_4P_2O_7$), 11% U (in $Na_6U_7O_{24}$), 9% P, Al 3%, Cr 6%; reconstituted liquid @ 1.21-1.25 g/mL, free OH < 160 g/mL	M12 Group 1	high-Bi 1C and 2C (2C is 2nd cycle $BiPO_4$ process waste)	Bi/Fe/Al [GC 4]	None	6.3%	5.2×10^{-7}
					4.6%	6.7×10^{-7}
					3.8%	2.7×10^{-7}

Table A.3. Sludge waste composition and settling information (For Information Only).

Solids composition for major constituents only, wt%[*]; liquid properties are pH (or OH concentration) and density	Tank or M12 Group	Waste Type	Dominant Species [General Category]	Dilution	Initial Solids (vol%)	"Fast" Interface Settling Velocity (m/s)
Modeled: 5% $BiFeO_3$, 8% Na aluminosilicate, 26% $Al(OH)_3$, 28% $FePO_4{\cdot}2H_2O$, 9% $Na_2U_2O_7$, 8% dawsonite, 14% salt ($Na_4P_2O_7{\cdot}10H_2O$, NaF, $Na_7F(PO_4)_2{\cdot}19H_2O$); 1.17 g/mL liquid, pH 10.3	T-107	85 vol% 1C	High Fe/Al [GC 3]	DI water; 1:1	7.5%	1.2×10^{-6}
				DI water; 3:1	3.4%	9.1×10^{-6}
Modeled: 39% $BiFeO_3$, 33% $FePO_4{\cdot}2H_2O$, 12% dawsonite; 1.05 g/mL liquid, pH 8.4	T-110 composite	97 vol% 2C	Bi/Fe/Al [GC 4]	DI water; 30 wt% dilution	6.2%	7.5×10^{-8}
				DI water; 1:1	2.5%	2.8×10^{-6}
				DI water; 4:1	0.98%	1.2×10^{-5}
Modeled: 24% Bi_2O_3, 23% FeOOH, 15% $Mn_3(PO_4)_2$, 6% $LaPO_4{\cdot}2H_2O$, 24% salt ($Na_2P_2O_7{\cdot}10H_2O$); 1.17 g/mL liquid, pH 12.9	T-111 Seg. 8	55 vol% 2C, 45% 224 Post-1949	Bi/La/PO_4/Fe [GC 5]	DI water; 1:1	1.9%	1.1×10^{-7}
	T-111 Seg. 2			DI water; 1:1	0.12%	2.8×10^{-7}
				DI water; 3:1	0.17%	1.0×10^{-6}
Modeled: 37% $Al(OH)_3$, 15% ZrO_2, 9% Na aluminosilicate, 8% $Na_2U_2O_7$, 8% FeOOH, 19% salt (NaF); 1.17 g/mL liquid, pH 13.9	C-104	57 vol% CWP (PUREX cladding waste), 15% unident	Uranium [GC 6]	DI water; 140 g UDS/L	5.1%	2.0×10^{-6}
				DI water; 100 g UDS/L	3.0%	3.2×10^{-6}
				DI water; 60 g UDS/L	2.1%	7.8×10^{-6}
Measured: PUREX cladding waste (Snow et al 2009): solids after washing with 0.01 M NaOH were 88% $Al(OH)_3$, 6% Na aluminosilicate, 4% Fe oxide; reconstituted liquid @ 1.16 g/mL, free OH 5270 ug/mL	M12 Group 3	high-Al CWP	High Al (non-boiling) [GC 1]	None	18%	8.7×10^{-6}
					17%	1.2×10^{-5}
					16%	1.1×10^{-5}
86% $Al(OH)_3$, 7% dawsonite; 1.14 g/mL liquid, pH 11.6	T-102 Seg. 2	89 vol% CWP2 (PUREX cladding waste)	High Al (non-boiling) [GC 1]	DI water; 1:1	4.7%	8.7×10^{-5}
				DI water; 3:1	2.1%	9.6×10^{-5}
Modeled: 31% AlOOH, 11% dawsonite, 6% Na aluminosilicate, 6% FeOOH, 28% salt ($Na_7F(PO_4)_2{\cdot}19H_2O$, $Na_3PO_4.0.25NaOH{\cdot}12H_2O$); 1.17 g/mL liquid, pH 12.1	C-109	38 vol% TFeCN (ferrocyanide sludge), 36% CWP1 (PUREX cladding waste)	High Al (boiling) [GC 2]	DI water; 1:1	3.5%	1.0×10^{-6}
				DI water; 3:1	2.2%	1.0×10^{-5}

Table A.3. Sludge waste composition and settling information (For Information Only).

Solids composition for major constituents only, wt%*; liquid properties are pH (or OH concentration) and density	Tank or M12 Group	Waste Type	Dominant Species [General Category]	Dilution	Initial Solids (vol%)	"Fast" Interface Settling Velocity (m/s)
Modeled 7% $Al(OH)_3$, 17% dawsonite, 11% FeOOH, 16% $Na_2U_2O_7$, 15% $Ca_5OH(PO_4)_3$, 6% $Ni(OH)_2$, 23% salt ($Na_4P_2O_7 \cdot 10H_2O$); 1.17 g/mL liquid, pH 10.4	C-112 composite	69 vol% TFeCN	Uranium [GC 6]	DI water; 1:1	5.9%	4.6×10^{-7}
				DI water; 3:1	2.2%	5.0×10^{-6}
Measured: Ferrocyanide waste (Fiskum et al 2009): solids after washing with 0.01M NaOH were 12% U (in $Na_2U_2O_7$, $Na_4(UO_2)(CO_3)_3$, possibly U_3O_8), 11% Fe (in Fe_2O_3, $Na_2Al_{0.5}Fe_{9.5}O_{15}$), 9% Al (in $Al(OH)_3$, Na aluminosilicate), 6% Ca (in $Ca(SO_4)(H_2O)_{0.5}$, CaP_4O_{11}), 5% Na, 4% Sr (in $Sr(H_2PO_3)_2$), 4% P, 4% Ni (no identified compound); reconstituted liquid @ 1.15 g/mL, free OH 4975 ug/mL	M12 Group 8	high-Fe PFeCN (ferrocyanide sludge)	Uranium [GC 6]	None	5.6%	1.5×10^{-6}
					5.2%	5.3×10^{-6}
					5.0%	3.0×10^{-6}
Modeled: 60% AlOOH, 36% salt ($NaNO_3$); 1.37 g/mL liquid, pH 13.5	S-104 Seg. 2	47 vol% R saltcake, 43% R1 (boiling) (R wastes are REDOX high-level waste)	High Al (boiling) [GC 2]	DI water; 1:1	8.7%	3.1×10^{-7}
				DI water; 3:1	2.8%	2.3×10^{-6}
	S-104 Seg. 4			DI water; 3:1	2.3%	9.0×10^{-7}
Measured: TBP U-recovery waste (Edwards et al 2009): solids after washing with 0.01 M NaOH were 16% Fe (possibilities include FeOOH and Fe_2PO_5), 15% Na, 13% U (possibly UO_2 phosphates or dihydrogenphosphates), 12% P, 1.6% Al (possibly $Al(OH)_3$, Na aluminosilicate, or Al U phosphates; reconstituted liquid @ 1.21 g/mL, free OH < 597 ug/mL	M12 Group 7	TBP (tributyl phosphate waste)	Uranium [GC 6]	None	7.9%	8.5×10^{-8}
					7.7%	3.2×10^{-7}
					4.5%	7.6×10^{-8}
	M12 Group 4			None	19%	1.4×10^{-5}

Table A.3. Sludge waste composition and settling information (For Information Only).

Solids composition for major constituents only, wt%[*]; liquid properties are pH (or OH concentration) and density	Tank or M12 Group	Waste Type	Dominant Species [General Category]	Dilution	Initial Solids (vol%)	"Fast" Interface Settling Velocity (m/s)
Measured: REDOX cladding waste (Snow et al 2009): solids after washing with 0.01 M NaOH were 91% $Al(OH)_3$, 1.5% Na aluminosilicate; reconstituted liquid @ 1.16 g/mL (approximately 3 M Na), free OH 1760 ug/mL		high-Al CWR (REDOX cladding waste)	High Al (non-boiling) [GC 1]		18%	1.5×10^{-5}
					18%	1.5×10^{-5}

The source for composition information, unless otherwise noted, is the modeled tank-average waste composition listed in Table C.1 (solids) and Table A.1 (liquid) of Wells et al. (2011).

[*] Because the compositions include only the major constituents, they do not sum to 100 wt%.

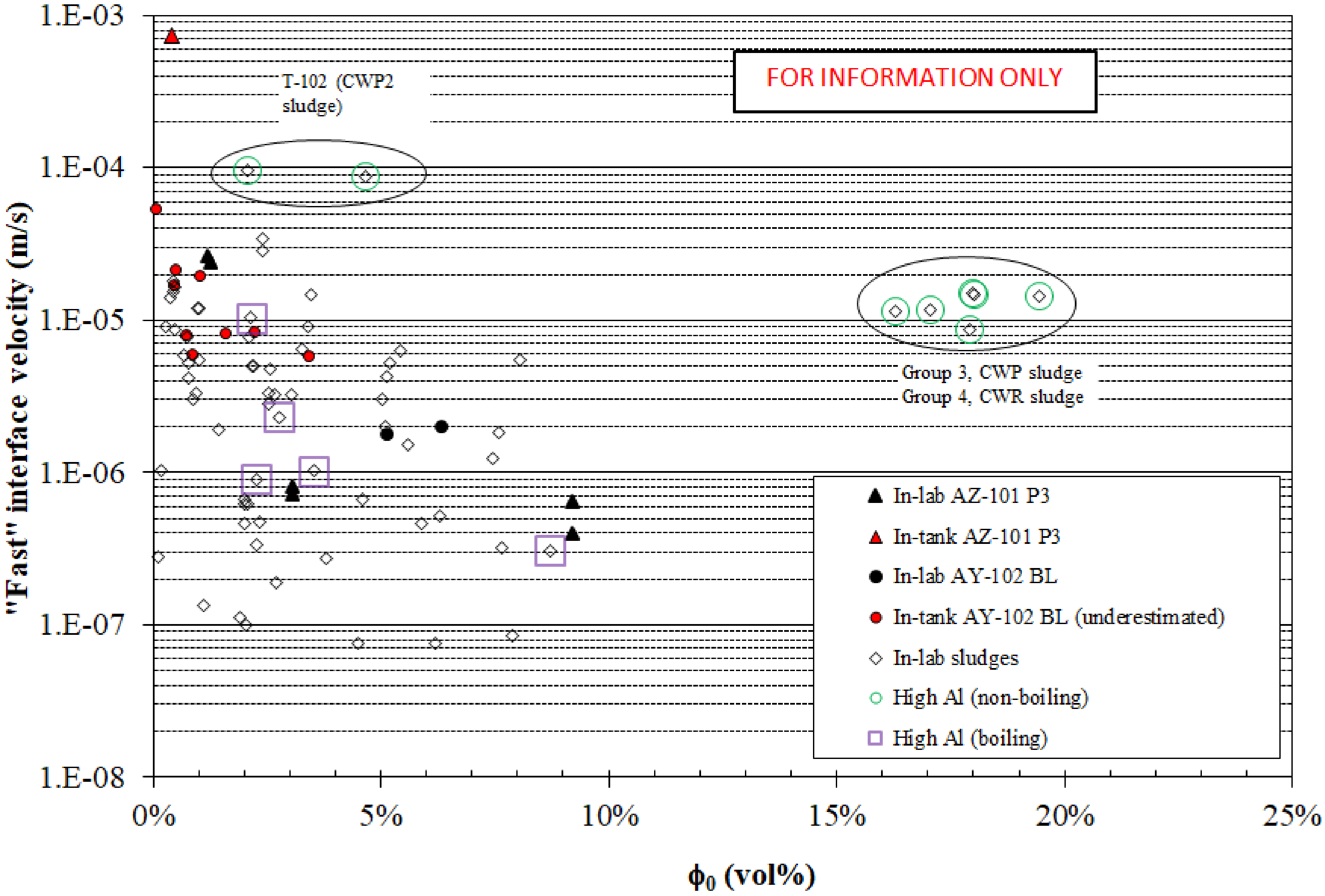

Figure A.1. High-aluminum (GC 1 & 2) waste settling.

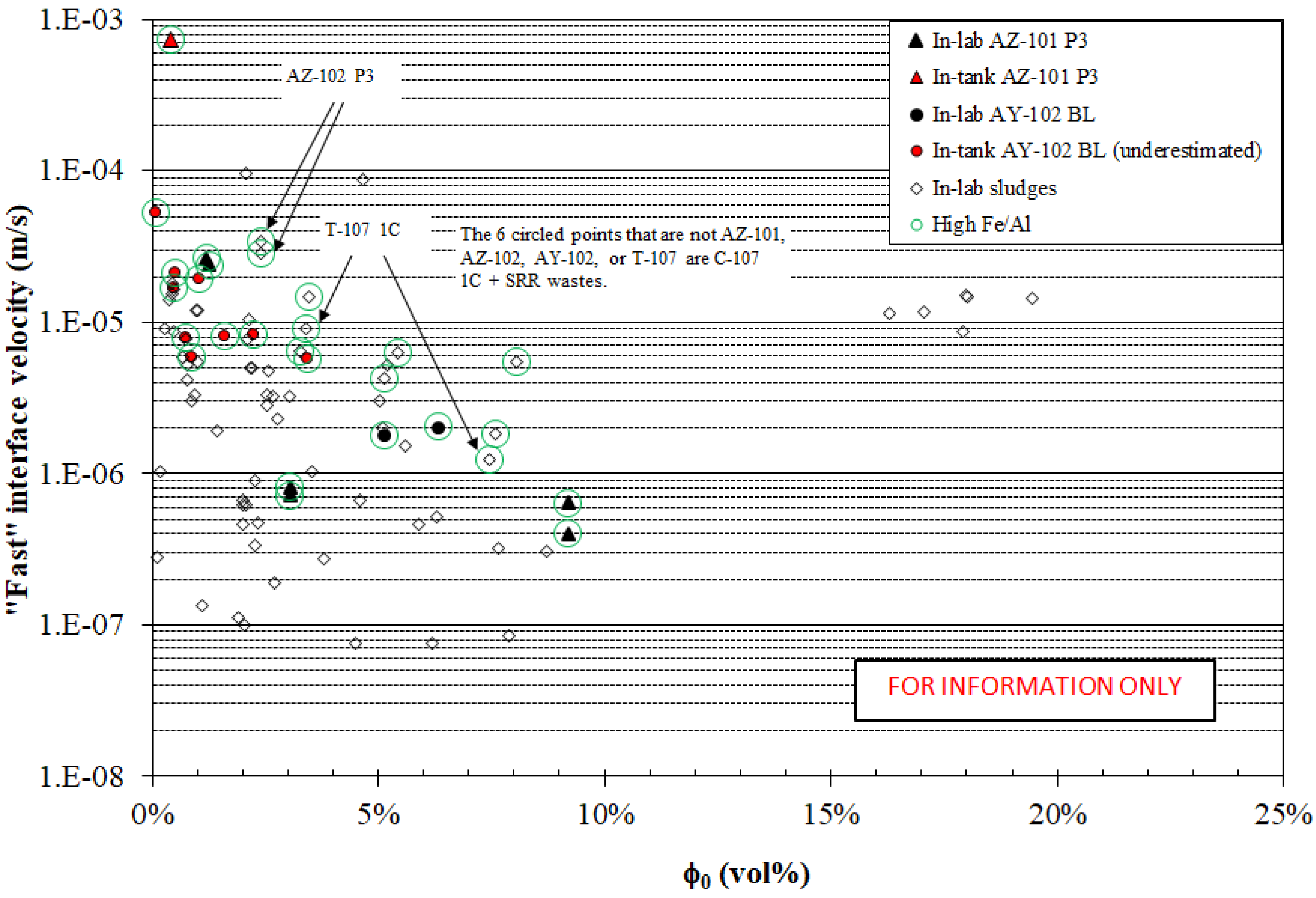

Figure A.2. Iron-aluminum (GC 3) waste settling.

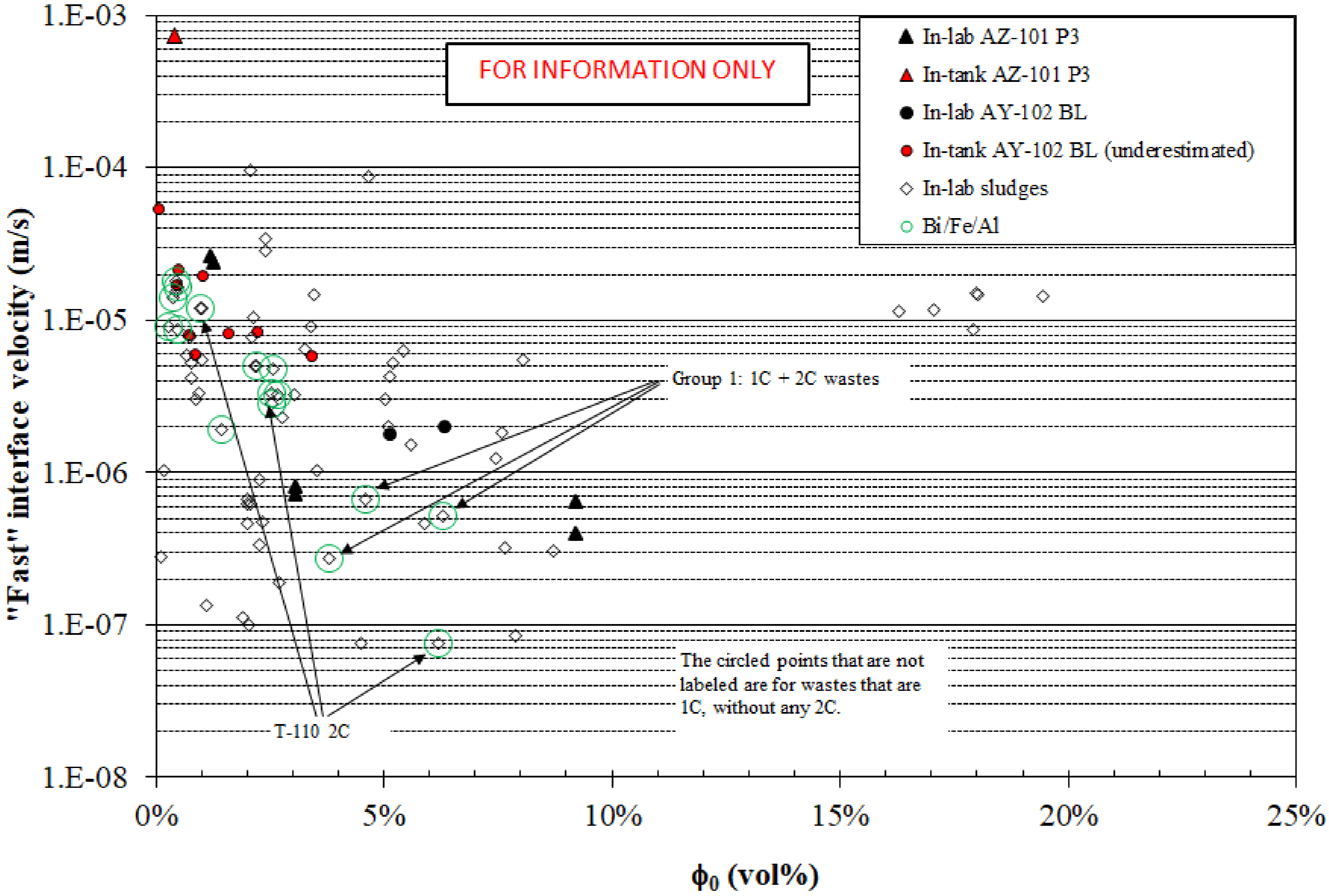

Figure A.3. Bismuth-iron-aluminum (GC 4) waste settling.

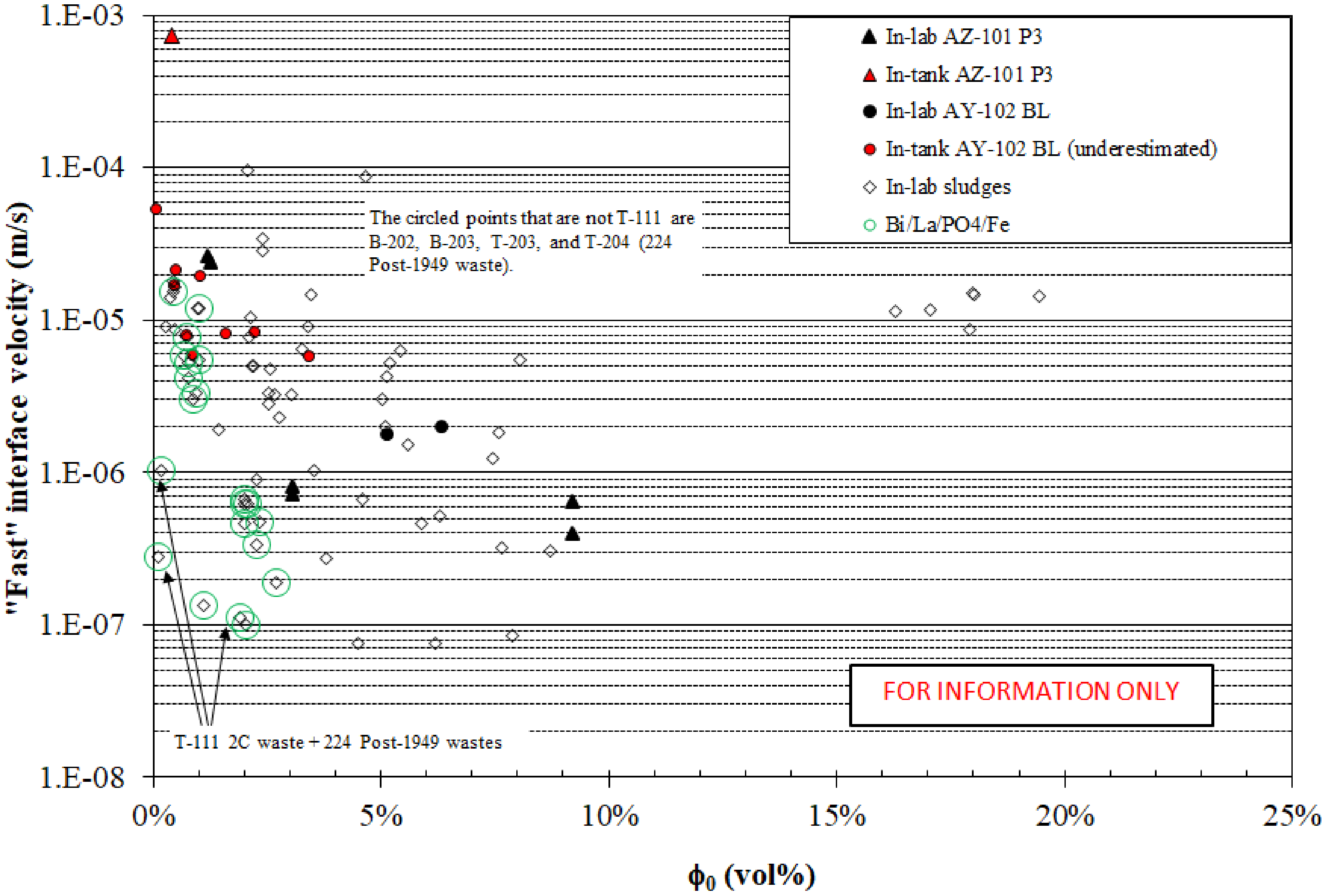

Figure A.4. Bismuth-lanthanum-phosphate-iron (GC 5) waste settling.

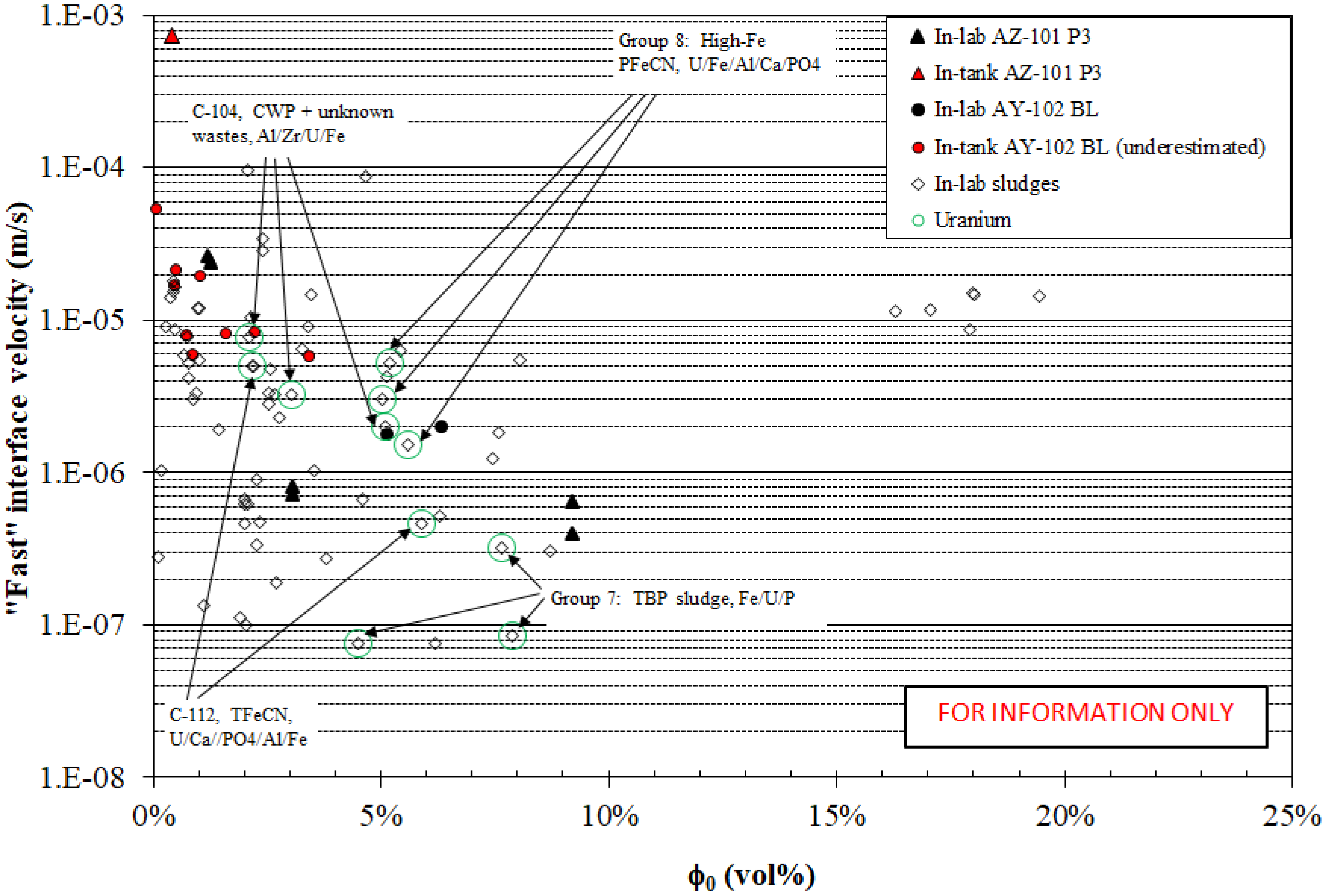

Figure A.5. Settling of otherwise uncategorized wastes all containing significant uranium (GC 6).

A.7 Appendix A References

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