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A Composition-Based Approach for Predicting Hanford Tank Waste Liquid Viscosity

April 2018

RC Daniel
AJL Fuher
MS Fountain

U.S. DEPARTMENT OF
ENERGY

Prepared for the U.S. Department of Energy
under Contract **DE-AC05-76RL01830**

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Executive Summary

Liquid viscosity is an important Hanford waste physical property that governs, in part, the performance of key Hanford flowsheet unit operations and processes, including waste filtration, ion exchange, pumping and transport, and mixing. Evaluation and optimization of these processes rely on liquid viscosity correlations subject to substantial error (at least ±60%) that can lead to overly conservative, and sometimes physically unachievable, limits for validation and operation of these unit operations. The current liquid viscosity correlations used for the Hanford flowsheet attempt to capture the effects of specific waste chemistry (namely, the speciation of various salts) on liquid viscosity using liquid density alone. It is postulated that the ±60% or greater error associated with these "density-based" liquid viscosity predictions is driven in part by the inability of waste density to capture the full impact of waste chemistry on liquid viscosity, and that improved prediction accuracy could be achieved by implementing a composition-based approach to evaluating liquid viscosity for Hanford wastes. Recent publications, namely those of Lencka et al. (1998), Hu (2004), and Laliberté (2007a), provide correlations and comprehensive, consolidated databases of single-salt solution viscosity that enable composition-based predictions for Hanford-type liquids (i.e., concentrated multicomponent aqueous electrolyte solutions).

In the current study, the viscosities of Hanford wastes and waste simulants were predicted using a composition-based model developed by Laliberté (2007a) (hereafter referred to as the "Laliberté viscosity model") to evaluate its accuracy relative to the current density-based models used to predict waste viscosity for engineering applications at the Hanford Site. A viscosity database that captured the composition and viscosity of wastes and waste simulants was developed to support this evaluation. To facilitate application of the Laliberté viscosity model, waste and waste simulant compositions were converted to an equivalent salt recipe composed of salts with known viscosity coefficients using a number of simplifying assumptions that have the potential to impact the fidelity of the model prediction. Despite these simplifications, the Laliberté viscosity model was able to predict viscosity more accurately than the density-based correlations currently available for Hanford flowsheet use, such as that proposed in RPP-RPT-51652. The use of composition-based viscosity models, like that proposed by Laliberté (2007a), shows promise for leading to improved prediction of liquid waste viscosity. As implemented in this study, application of the Laliberté viscosity model could lead to a decrease in the uncertainty associated with liquid viscosity prediction by as much as a factor of two, allowing for reduction in unit operation design conservatism and for the more realistic selection of test simulants for flowsheet process evaluation and optimization, all of which could potentially reduce flowsheet design margins, lower costs and reduce duration of the Hanford mission, and reduce Hanford flowsheet risks.

Acknowledgments

The authors thank Jacob Reynolds and Stuart Arm of Washington River Protection Solutions for their technical feedback on and support of this report and the analyses it presents. In addition, the authors thank Carolyn Burns, Philip Schonewill, and Jason Serkowski for their detailed and careful reviews of the report and the calculations that underpin its technical basis. The authors also acknowledge Chrissy Charron and Veronica Perez for help with capturing project documentation and for their critical guidance on project standards and execution of work.

Acronyms and Abbreviations

BBI	best-basis inventory
DS	dissolved solids
FMP	Flowsheet Maturation Plan
IC	ion chromatography
ICD	Interface Control Document
ICP	inductively coupled plasma
ICP-OES	inductively coupled plasma optical emission spectrometry
LAW	low-activity waste
LAWPS	Low-Activity Waste Pretreatment System
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
RPP	River Protection Project
SRNL	Savannah River National Laboratory
TOC	total organic carbon
TWINS	Tank Waste Information Network System
UDS	undissolved solids
WRPS	Washington River Protection Solutions, LLC
WSRC	Westinghouse Savannah River Company
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

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1.0 Introduction

Knowledge of the viscosity of Hanford tank waste liquids enables improved understanding and optimization of waste-handling operations such as cross-site and in-process pipeline transfers, filtration, and tank corrosion control. The current method of estimating Hanford waste liquid viscosity relies on an empirical correlation developed from 242-A Evaporator boildown and slurry samples (RPP-19221). Subsequent revisions of the Hanford waste liquid viscosity model have been proposed by Poloski et al. (2007), Wells et al. (2011), and RPP-RPT-51652. The Hanford waste liquid viscosity correlations proposed in each of these reports share the same functional form: viscosity is expressed as a function of temperature and density that are correlated using a set of arbitrary constants whose values are determined through least-squares regression of existing Hanford liquid waste viscosity data. These correlations enable prediction of waste viscosity from knowledge of waste liquid density and temperature alone, eliminating the need to fully understand the composition of the waste being considered; however, their predictions are also subject to significant uncertainty—comparison of predicted to measured waste viscosities found relative differences as large as ±60% (RPP-RPT-51652). Likewise, evaluation of 95% confidence bands leads to bounding liquid viscosity limits that fall nearly a factor of 2 above and below the predicted value.

Large uncertainty in viscosity can dictate unrealistic or grossly conservative design criteria that are difficult or impossible achieve (when developing representative test materials and simulants) or that lead to the overdesign of waste-handling systems (e.g., transfer pumps and tank mixing systems). With respect to the latter, overdesign can lead to generation of additional effluents when feed waste requires unplanned (and potentially unnecessary) conditioning to bring waste liquid viscosity into acceptable bounds as documented in Interface Control Documents (ICDs) (e.g., 24590-WTP-ICD-MG-01-019 and 24590-WTP-ICD-MG-01-030). Improved viscosity model accuracy and reduced model uncertainty could help avoid overdesign and reduce costs associated with waste processing and design maturation. Two approaches for achieving improved accuracy and/or reduced uncertainty are 1) the evaluation of alternate waste composition-based models and 2) recasting of current models with a more tightly controlled set of waste liquid viscosity samples.

The current report explores the former option, namely the use of an alternate composition-based liquid viscosity model like that developed by Laliberté (2007a) for predicting the viscosity of multicomponent concentrated electrolyte solutions. Here, the end goal sought by use of this model is improvement in the accuracy of waste liquid viscosity prediction by explicitly incorporating waste composition (rather than indirectly incorporating it through density) and by reducing the reliance on historical waste liquid viscosity measurements. To support this evaluation, a literature review was performed to support selection of an appropriate viscosity model and to support development of a limited Hanford waste and waste simulant composition and viscosity database on which to evaluate model performance.

It should be noted that the current work fulfills Task 1 of the flowsheet maturation plan (FMP), FMP-WASTE-12, "Liquid Rheology" (RPP-PLAN-58003), and supports Pacific Northwest National Laboratory's (PNNL's) efforts to provide Washington River Protection Solutions, LLC (WRPS) baseline technical support to the One System River Protection Project (RPP) Integrated Flowsheet team. This work also supports PNNL's broader mission to help identify and close flowsheet model and operations gaps and realize opportunities to reduce the waste treatment mission cost, schedule, and technical risk associated with the One System RPP Integrated Flowsheet. Gaps and opportunities are documented in the *One System River Protection Project Integrated Flowsheet Maturation Plan* (RPP-PLAN-58003), and solution approaches are proposed and declared in associated FMPs contained in its appendices.

2.0 Quality Assurance

This work was conducted with funding from WRPS under PNNL project 67116, contract 36437-171, and under PNNL project 71351, contract 36437-239, both with the title "Tank Waste Disposition Integrated Flowsheet Support."

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*, 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*, and NQA-1a-2009, *Addenda to ASME NQA-1-2008*, 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 "Basic Research" and planned, performed, documented, and reported in accordance with procedure QA-NSLW-1101, *Scientific Investigation for Basic Research*. All staff members contributing to the work received appropriate technical and QA training prior to performing quality-affecting work.

3.0 Background and Approach

Liquid viscosity is an important waste-handling parameter that affects crossflow filtration performance, tank mixing, transfer-line fluid dynamics, mixer and transfer pump design, critical velocity determinations, and predictions of sodium hydroxide needs in the corrosion management program for the Hanford double-shell tank farms (Daniel et al. [2009], TFC-ENG-STD-26, OSD-T-151-00007). The Low-Activity Waste Pretreatment System (LAWPS) and the Hanford Tank Waste Treatment and Immobilization Plant (WTP) Low-Activity Waste (LAW) Facility currently limit the incoming tank waste feed to a 15 mPa·s slurry viscosity, imposed as a waste acceptance criterion, to mitigate potential waste-handling complications due to viscosity (RPP-RPT-58649; 24590-WTP-ICD-MG-01-030). Not only are viscosity predictions key to design and operational performance, anticipating and predicting liquid waste viscosity to successfully meet facility waste acceptance criteria is a mission requirement within the RPP Reference Integrated Flowsheet (RPP-RPT-57991). The discussion that follows provides some history of tank waste viscosity data, the origins of various liquid viscosity predictions, and their applications at Hanford. This is followed by a detailed description of a waste-composition-based approach used in this work to attempt to improve prediction of Hanford liquid waste viscosity.

No single, concerted effort has been undertaken to sample and measure the liquid viscosity of Hanford tank wastes to date. Rather, characterization efforts have largely been limited to single tanks or have been based on waste composites recovered from archived waste samples. In addition, no single Hanford Site contractor or set of research staff has performed waste liquid viscosity measurements for samples representative of the entire volume of Hanford tanks, and studies have been performed using different equipment (with different accuracies and performance ranges) across several decades. Only within the past 10 years have efforts been undertaken to consolidate existing waste viscosity measurements (see Poloski et al. 2007; Wells et al. 2011; and RPP-RPT-51652) to provide a more complete picture of the range and magnitude of Hanford waste viscosities that will be encountered during waste processing. These and earlier reports also sought to address the need for predictive liquid viscosity tools, because changes in the chemistry associated with waste aging during long-term storage at Hanford and mixing and conditioning during retrieval for waste processing may lead to waste chemistries different from what existed in the tank when the samples for waste liquid viscosity were measured. To ease implementation of these tools, prediction was based on waste liquid density, which is easy to measure and is suggestive of waste salt concentration and composition. These and similar efforts have led to the development of correlations that allow prediction of waste liquid viscosity from waste density (and temperature).

An early waste liquid viscosity correlation (Equation **Error! Reference source not found.** below) was derived and documented from 242-A Evaporator boildown and slurry samples (Reynolds 1988). The correlation has the form

$$\mu_L = -35.82 - 0.3850T + 42.65s_L, \tag{3.1}$$

where μ_L is the liquid viscosity (in mPa·s), s_L is the liquid's specific gravity, and T is temperature in °C. Equation **Error! Reference source not found.** is applicable for solutions that have no solids and for which $s_L < 1.35$. Equation **Error! Reference source not found.** is cited in RPP-19221, which is the required critical velocity calculation methodology called out in TFC-ENG-STD-26.

A more recent liquid viscosity model was developed by Poloski et al. (2007) and subsequently updated by Wells et al. (2011) and RPP-RPT-51652. As implemented in RPP-RPT-51652, liquid viscosity correlation is:

$$\mu_L = \exp\left\{a(\rho_L - f) + b(\rho_L - 1) + \left[\frac{c(\rho_L - 1) + d}{T}\right]\right\} \tag{3.1}$$

where μ_L is the liquid viscosity (in mPa·s), ρ_L is the liquid density (in g/mL), T is liquid temperature in K, a, b, c, and d are best-fit constants (determined by linear regression against measured waste viscosity data), and f is 1.42. Recent technical evaluations of slurry transfer-line flushing (RPP-RPT-59600) and critical velocity assessments (RPP-RPT-59585) recommended the replacement of Equation **Error! Reference source not found.** by Equation (3.1) for predicting slurry transfer operational parameters currently guided by TFC-ENG-STD-26. The viscosity correlations proposed by Poloski et al. (2007) and Wells et al. (2011) use a similar form:

$$\mu_L = a\exp\left\{b(\rho_L - 1) + \left[\frac{c(\rho_L - 1) + d}{T}\right]\right\} \tag{3.2}$$

As before, a, b, c, and d are best-fit constants determined by linear regression. In both Poloski et al. (2007) and Wells et al. (2011) density-based viscosity correlations, density is input in g/mL, temperature is input in K, and viscosity is in mPa·s. Table 3.1 lists the best-fit constant used in Equations (3.1) and (3.2).

Table 3.1. Best-fit Constants for Hanford Density-Based Viscosity Correlations Equations (3.1) and (3.2)

Constant	Poloski et al. (2007)	Wells et al. (2011)		RPP-RPT-51652
		ρ_L < 1.41 g/mL	ρ_L ≥ 1.41 g/mL	
a	0.00216	0.101	0.000125	5.29
b	-6.69	-6.06	0.816	-18.29
c	3700	3490	3890.0	7103.79
d	1810	746	1590.0	54.36

Both Equations **Error! Reference source not found.** and (3.1) (and their analogs in Poloski et al. [2007] and Wells et al. [2011]) facilitate prediction of the viscosity of liquid tank waste as a function of waste temperature and liquid density; inputs for both equations are determined from direct sampling and characterization of Hanford waste, estimates, and/or tank monitoring. Although density-based models require few inputs when determining viscosity, the result appears to be subject to significant uncertainty. For example, the Wells et al. (2011) viscosity model, for a 1.3 g/mL liquid waste at 20 ˚C, predicts a viscosity of approximately 7 mPa·s. From Figure 3.5 in Wells et al. (2011), this predicted 7 mPa·s viscosity has an estimated uncertainty (95% confidence bands) of ±5 mPa·s. Application of conservative bounds (i.e., 2 or 12 mPa·s for 95% confidence in the example above) may lead to difficult-to-meet or unrealistic design verification targets for waste feed processing like those encountered in recent efforts to develop a 15 mPa·s simulant that met a 6M Na target for crossflow filter testing.[1] The large error bands do not necessarily result entirely from artifacts of the model fits or its inability to capture composition-specific viscosity trends, but may also result, in part, from the varied methods and processes through which waste liquid viscosity has been measured at Hanford over the course of multiple decades. For example, direct measurement of tank waste samples may occur in hot-cell environments where the

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[1] Burns CA, RC Daniel, SD Hoyle, and PP Schonewill. 2017. *High Viscosity Simulant Recommendation for Integrated Testing*; attachment to LTR-67535-0015, "Electronic Transmittal of High-Viscosity Simulant Recommendation for Integrated Testing." PP Schonewill (PNNL) to MR Landon (WRSP), dated July 24, 2017. Pacific Northwest National Laboratory, Richland, Washington.

robustness of viscosity measurement equipment may take precedence over instrument precision and sensitivity. The hazards and required safeguards associated with rheological measurements of Hanford waste may in this way further obfuscate an inherently difficult-to-measure physical property.

When the density-based liquid viscosity models referenced above were developed, "developing a liquid-viscosity model as a function of temperature and composition was not possible because the data used to develop the model did not have sufficient compositional analyses" (RPP-RPT-51652). It was further recognized that liquid density alone was considered an "imperfect representative" of the effect of the composition of dissolved solids in waste liquid (RPP-RPT-51652). Although detailed chemical information is not available for all tanks, some characterization studies provide sufficient chemical speciation information for individual tanks or waste composite samples to estimate liquid waste composition in terms of individual salts. Examples include Fiskum et al. (2008), Lumetta et al. (2009), Edwards et al. (2009), and Fiskum et al. (2009). Furthermore, efforts have been made to develop chemical simulants that mimic the processes that led to the generation of Hanford sludge and saltcake wastes, and the composition of these simulants (at least in terms of the components, their order of addition, and the intended products). As such, there may be a limited set of tanks and simulants that have sufficient information to estimate liquid viscosity based on waste composition alone. Assessment of such a model then requires two basic elements: 1) identification of a composition-based liquid viscosity model suitable for use with concentrated, multicomponent electrolyte solutions and 2) collection of waste/simulant compositional data.

The purpose and approach of this work was to identify and evaluate an existing composition-based liquid viscosity model from literature and benchmark its predictive performance against previously developed density-based models by Poloski et al. (2007), Wells et al. (2011), and RPP-RPT-51652. From this application, gaps and limitations of composition-based model performance were identified and recommendations for improvement provided. To achieve this end, a review of scientific literature was conducted to select the most applicable existing model and a database of measured liquid viscosity from well-characterized Hanford tank waste and liquid simulant data was constructed. Using data from the liquid viscosity database, the predictive performance of the composition-based liquid viscosity model and the previous density-based models were then compared.

4.0 Selection of the Liquid Viscosity Model

A review of scientific literature was performed to identify and capture models that had been recently developed through empirical, semi-empirical, or first-principles approaches to modeling liquid viscosity. This literature review identified more than one dozen potentially applicable composition-based viscosity models that were developed in the previous two decades. Many of these models were developed to predict the viscosity of binary-salt solutions (i.e., one salt and water), and few looked at more than one salt component at a time. Given the complexity of Hanford tank waste supernatants, models that are only capable of predicting binary-salt solution viscosity are not viable. The completed literature survey identified models introduced by Lencka et al. (1998), Hu (2004), and Laliberté (2007a) as being most applicable to multicomponent electrolyte solutions.

The Lencka et al. (1998) model was developed to predict multicomponent (multi-salt) electrolyte solution viscosity from empirically obtained data for single-solute systems. The model incorporates the effects of long-range electrostatic interactions solved for using the Onsager-Fuoss solution and the contributions from individual and species-species interactions using Jones-Dole coefficients (Lencka et al. 1998). The Lencka et al. (1998) model requires the salt speciation for the system of interest in both single- and multicomponent electrolyte solutions. Lencka et al. (1998) compare the developed model against single- and multicomponent electrolyte solutions. Results for a limited number of single-component systems show excellent agreement for concentrations up to 30 molar. The salt speciation of multi-component systems was determined using thermodynamic modeling software developed by OLI Systems, Inc., Cedar Knolls, New Jersey. The multicomponent systems demonstrated excellent agreement between predicted and measured values of liquid viscosity but were composed of only two salts with a peak concentration of 3 molar. The model requires the determination of binary-salt "interaction" coefficients for individual salt ions that must be acquired or extrapolated from unique multicomponent salt systems for which there is not a sufficiently comprehensive database to make the model readily applicable to Hanford wastes. Therefore, application of the Lencka et al. (1998) model was not practical within this scope of work.

The Hu (2004) model is based, in part, on the concept that binary electrolyte solutions of equal ionic strength will mix ideally. Hu (2004) concludes the "mixing process of viscosity at constant ionic strength shows very simple mixing behavior" and viscosities of "mixed electrolyte solutions can be well predicted only by using the additive contribution from the viscosities of binary solutions at constant ionic strength." Similar to Lencka et al. (1998), the Hu (2004) model is extendible to multicomponent systems upon determination of salt-specific coefficients empirically obtained from binary solution data. Results presented by Hu (2004) demonstrate excellent agreement between the predicted and measured viscosity values of the multicomponent system of KCl-$CaCl_2$-H_2O in the concentration range of 0 to 6 molar. However, Hu (2004) only studied a limited number of salts and further experimentation on many additional binary solutions would be required to extend the model to Hanford wastes.

The Laliberté (2007a) model allows for extension of single-salt solution data to multicomponent salt systems similar to the models of Lencka et al. (1998) and Hu (2004). The Laliberté model also uses a mixing rule, reminiscent of the work by Hu (2004), incorporating two separate terms determined through two separate viscosity formulas developed for pure water and solutes (salts), respectively. While the Laliberté (2007a) model requires the determination of six salt-specific parameters that must be empirically determined, Laliberté (2007a,b) generated these parameters for 74 different solutes, many of which are applicable to Hanford waste. This extensive library of coefficients makes the Laliberté (2007a,b) model more complete than the Hu (2004) model. A subsequent study by Laliberté concerning complex electrolyte solution heat capacity also included a revised set of viscosity coefficients for 96 unique salts (Laliberté 2009). Solution viscosity, as predicted by the Laliberté (2007a) model for an arbitrary number of salts is:

$$\eta = \eta_w^{w_w} \prod_i \eta_i^{w_i} \tag{4.1}$$

where w_i is the weight fraction of salt i in solution, w_w is the weight fraction of water, η_i is the pure solute viscosity for salt i, and η_w is the viscosity of water. The pure solute viscosity η_i and the viscosity of water η_w are given by:

$$\eta_i = \frac{\exp\left[\frac{v_{i,1}(1-w_w)^{v_{i,2}} + v_{i,3}}{v_{i,4}T + 1}\right]}{v_{i,5}(1-w_w)^{v_{i,6}} + 1} \tag{4.2}$$

$$\eta_w = \frac{T + 246}{(0.05594T + 5.2842)T + 137.37} \tag{4.3}$$

Here, T is the solution temperature in °C. As shown by Equation (4.2), the pure solute viscosity η_i for salt i incorporates six salt-specific viscosity coefficients denoted by $v_{i,(1-6)}$ and determined through empirically measured viscosity data (either as a single-salt solution or as a mixture with other salts whose viscosity coefficients are known).

The models proposed by Lencka et al. (1998), Hu (2004), and Laliberté (2007a) all allow prediction of viscosity for multicomponent concentrated electrolyte solutions. That is, all three models express viscosity in terms of individual component contributions (i.e., salts plus water). Furthermore, all require knowledge of single-salt data, either as raw inputs or to develop model coefficients for single-salt viscosity correlations, to underpin extension of single-salt data to multicomponent systems. However, both Lencka et al. (1998) and Hu (2004) require additional "interaction" coefficients to describe interactions between pairs of salt species. In its current state, the "interaction" coefficients proposed by Hu (2004) must be regressed from two-salt electrolyte solution viscosity data. In contrast, Lencka et al. (1998) and Laliberté (2007a) provide a method for extension of single-salt data to multicomponent systems without the need to derive "interaction" coefficients (although Lencka et al. [1998] require determination of ion-ion "interaction" coefficients from single-salt data). From an end-use perspective, both Lencka et al. (1998) and Laliberté (2007a) viscosity models serve as suitable platforms for a composition-based analysis of waste viscosity. However, from a practical perspective, Laliberté (2007a,b) and Laliberté (2009) provide viscosity model coefficients for 96 salt systems (including acids and bases). While Lencka et al. (1998) suggest a similar database of at least 17 salts, the original article does not provide the necessary ion "interaction" coefficients underlying Jones-Dole coefficients needed to implement the model independently of the OLI Systems implementation (i.e., "OLI Flowsheet: ESP" software).[1] Assessment of literature citing Lencka et al. (1998) finds limited model implementation and few model coefficients.

Based on the discussion in the preceding paragraph, the current effort selected the Laliberté (2007a) viscosity model for use in composition-based analysis of Hanford waste liquid viscosity. The Laliberté (2007a) model (hereafter referred to simply as the "Laliberté viscosity model") is suitable for complex electrolyte solutions, and moreover, has regressed model coefficients for a large number of salts relevant to Hanford wastes. This choice is inherently one of convenience, because 1) the two models are similar in implementation and outcome (although they differ in the functional form of the viscosity model) and 2) the peer-reviewed literature does not appear to provide sufficient information to quickly implement the model of Lencka et al. (1998) within the budget and scope of the current study.

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[1] Software description available (as of March 2018) at "https://www.olisystems.com/flowsheet-esp".

5.0 Key Constituents and Database Development

To support evaluation of predictive accuracy for composition-based viscosity models, a key aspect of the current effort involved development of a Hanford-relevant database of waste and waste simulant viscosity and composition. First, Hanford waste composition data were compiled, reviewed, and documented to identify the major chemical components. Identification of the major chemical components within Hanford waste enabled informed decisions about how to charge balance and create equivalent salt-soluble chemical compounds from data within the liquid viscosity database. This is critical to the application of the Laliberté viscosity model because not all available waste composition data may be directly plugged into the model. The process of identifying major chemical components within the waste is described in Section 5.1 along with a table of key waste components down-selected from this work. Section 5.2 captures the methodology used to develop the liquid viscosity database, explains key data of interest to this work, and summary tables show a portion of the data collected.

5.1 Down-Selection of Major Chemical Components in Hanford Tank Waste

The major chemical components within Hanford waste were identified from the Tank Waste Information Network System (TWINS) best-basis inventory (BBI) summary based on relative weight percent (wt%) and molar concentration. The TWINS BBI summary maintains a record of sample-based information that is used to “develop and maintain 25 chemical and 46 radionuclide components for 177 underground storage tanks” (RPP-7625). As part of this work, the 46 radionuclide components of the waste were ignored, because the bulk of these radionuclides are contained within the insoluble sludge fraction of Hanford waste and would therefore have minimal impact on the rheology of waste liquid (Wells et al. 2011). Therefore, further down-selection of only the 25 chemical components of the TWINS BBI summary report was necessary.

The TWINS BBI summary report was downloaded from the TWINS website (twinsweb.labworks.org) in a Microsoft Excel-viewable format (.CSV). The mass (in kg) for each of the 25 chemical components was reported within each of the 177 underground tanks, often from sample-based information that includes saltcake and sludge. The BBI summary report also contains a column for tank-by-tank summation of the mass of each chemical component. This summation was used to determine the relative wt% of each chemical component within the tanks. To further narrow the selection, only those chemical components that composed either greater than 0.5 wt% or greater than 0.5% by molar concentration were further considered by this work. Table 5.1 lists the 14 major chemical components, with their respective wt% and molar concentration (in %) relative to all 25 chemical components from the TWINS BBI summary. Figure 5.1 is used to further illustrate how the 11 eliminated chemical components make up a small fraction of tank waste.

Table 5.1. 14 Major Chemical Components

c

Chemical Name	Formula	wt%	Molar Conc. (%)
Aluminum	Al	5.68	7.78
Carbonate	CO_3	6.63	4.08
Sodium	Na	31.64	50.80
Nitrite	NO_2	7.83	6.28
Nitrate	NO_3	35.55	21.16
Phosphate	PO_4	3.28	1.27
Sulfate	SO_4	2.39	0.92
Fluorine	F	0.82	1.60
Total Organic Carbon	TOC	0.82	2.53
Potassium	K	0.64	0.61
Silicon	Si	0.51	0.67
Chlorine	Cl	0.54	0.56
Iron	Fe	0.82	0.54
Oxalate	C_2O_4	0.97	0.41
All Others	NA	0.24	0.30

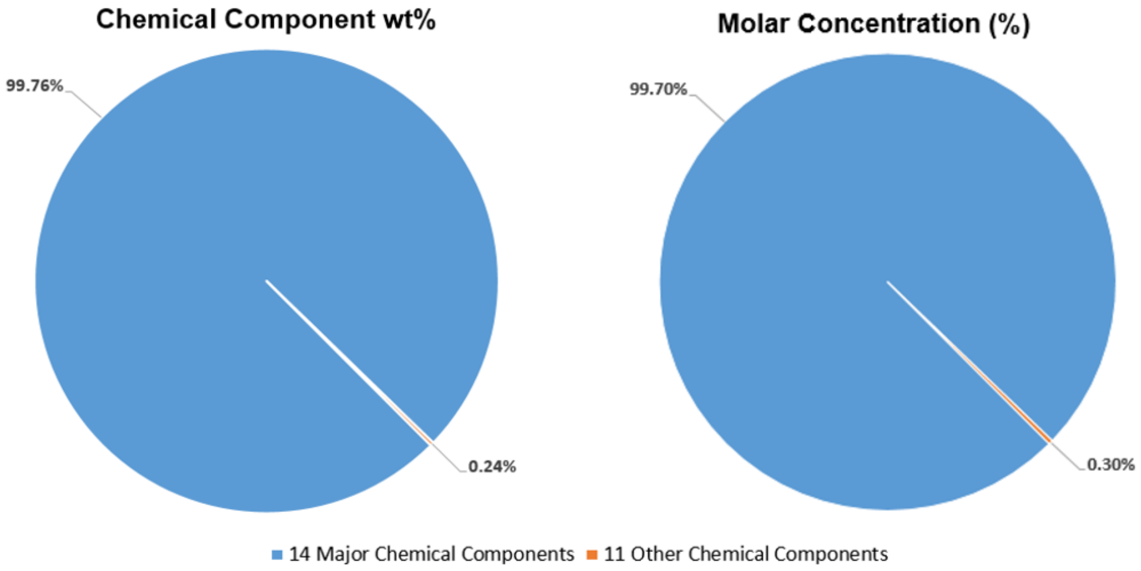

Figure 5.1. Comparison of Contributions from the 14 Retained and 11 Eliminated Chemical Components.

Key observations drawn from Table 5.1 and Figure 5.1 include the following:

- More than 99.7 wt% of Hanford waste may be represented by 14 major chemical components.
- Three-fourths of the mass within the tanks may be accounted for by sodium, nitrite, and nitrate alone, all of which are known to cause increased rheology at higher concentrations.
- With the exception of oxalate, all 14 major chemical components found in excess of 0.5 wt% also had a molar concentration within the tank of greater than 0.5%.
- Most of the 25 chemical components tracked by BBI are present in mass fractions of less than 1 wt%.

These observations will, in part, inform decisions about charge balancing and equivalent chemical compounds when applying data from the liquid viscosity database discussed in Section 5.2.

5.2 Development of the Liquid Viscosity Database

A liquid viscosity database was constructed based on single- and multicomponent salt solution data as a function of salt concentration, salt speciation, and solution temperature, among other parameters. Within the peer-reviewed literature, and Hanford technical reports and characterization effort literature, there are numerous studies of concentrated electrolyte viscosity. Although the focus is primarily on single-salt solutions, there are also numerous measurements of two- and three-salt systems. However, viscosity measurements for electrolyte solutions relevant for Hanford wastes are limited. Indeed, the most relevant systems are direct measurements of waste viscosity and composition in Hanford waste characterization reports and through reports documenting Hanford waste simulant development. With respect to Hanford waste and simulant literature, the studies are constrained even further by the requirement that both viscosity and composition be available for the same (or similar) waste materials to facilitate not only prediction of waste viscosity but validation of model-predicted viscosity against actual measurement.

As few relevant viscosity measurements may be found in literature, and Hanford technical reports that also include full compositional analysis, characterization data of Hanford liquid tank waste samples were given in terms of elemental composition rather than salt speciation. This recorded elemental composition was provided in laboratory analysis reports from waste characterization using inductively coupled plasma optical emission spectrometry (ICP-OES) and ion chromatography (IC), and the database omitted any concerning flagged ICP/IC data. Data sets that did include salt speciation and concentration came from characterized Hanford liquid waste simulants. These two forms of data were the only two data types available to populate the liquid viscosity database.

The liquid viscosity database includes the elemental composition for characterized liquid tank waste (in μg/mL) and the salt composition of characterized Hanford liquid waste simulants (in μg/mL). These data are essential to charge balancing, creating equivalent salt solution recipes based on elemental composition, and applying the Laliberté viscosity model. Other characterization data collected for each sample include viscosity (and the associated temperature at which it was measured), density, undissolved solids (UDS) concentration, and dissolved solids (DS) concentration. The sample density allows comparison of calculated viscosity values using Laliberté (2007a) against current density-based methods (i.e., those of Poloski et al. [2007], Wells et al. [2011], and RPP-RPT-51652) to gauge the overall improvement (if any) that a composition-based viscosity model offers. The UDS concentration ensures that the data provided by characterization of the sample are for a liquid waste with no or very minimal solids. To broaden the number of points gathered within the liquid viscosity database, samples with up to 1.2 wt% UDS were still considered as liquid waste and many tank waste samples had either trace or no solids. The sodium molarity was also included where available. Table 5.2 shows the summarized data for characterized chemical simulant samples and Table 5.3 shows summarized data for characterized tank waste samples.

Table 5.2 and Table 5.3 have data sourced from PNNL, WRPS, Westinghouse Savannah River Company (WSRC), and Savannah River National Laboratory (SRNL) reports. Densities ranged from 1.086 to 1.34 g/mL. Dissolved solids concentration increased with increasing density from values of 12.1 to 38.9 wt%. Measured viscosities ranged from 1.1 to 7.33 mPa·s and were collected from temperatures as low as 20 C to as high as 80°C. These conditions span a significant portion of the liquid physical properties and operating ranges expected in Hanford waste processing, and as such, serve as a suitable test set against which to validate performance of the composition-based viscosity model.

There were several challenges in collecting complete information for the liquid viscosity database, and some liquid viscosity data sets were omitted from the database based on screening criteria described previously (namely, characterized samples with anything above 1.2 wt% UDS concentration or when reports did not include density, chemical composition, or dissolved solids concentration). Simulants were required to be chemically produced, without the aid of artificial thickeners (e.g., glucose, glycerin) to increase liquid viscosity. The majority of density measurements were also only taken at one temperature (e.g., room temperature) and not necessarily performed at temperatures that mirrored viscosity measurements. Additionally, less than half of reports include associated errors in measurement of either density or viscosity.

Finally, it is worth noting that Table 5.2 and Table 5.3 are both summary tables providing only a portion of the data collected within the liquid viscosity database. The database contains over 280 data points for the salt composition of simulants and over 550 points of data for the elemental composition of sampled tank waste. Additional information recorded in the database, where available, includes the viscosity measurement instrument, reported temperature of density measurement, waste conditioning, date of sample, date of analysis, and reported error in density and viscosity.

Table 5.2. Physical Properties of Characterized Chemical Simulant Samples

Unique ID[(a)]	Reference Source[(b)]	UDS (wt%)	Dissolved Solids Concentration (g solids/g supernate)	Temperature of Density Measurement (°C)	Density (g/mL)	Temperature of Viscosity Measurement (°C)	Viscosity (mPa·s)	Sodium Molarity (M)
1.20	PNNL-26165	0.14	0.226	20±5	1.19	20	2.64	4.0
1.25	(Russell et al. 2017)					25	2.38	
1.45						45	1.97	
2.20	PNNL-26165	1.1	0.306	20±5	1.27	20	4.09	6.0
2.25	(Russell et al. 2017)					25	3.70	
2.45						45	2.29	
3.20	PNNL-26165	0.45	0.298	20±5	1.26	20	3.82	5.6
3.25	(Russell et al. 2017)					25	3.41	
3.45						45	2.20	
4.20	PNNL-26165	0.24	0.389	20±5	1.34	20	7.33	8.0
4.25	(Russell et al. 2017)					25	6.25	
4.45						45	3.81	
5.25	WTP-RPT-057	0.33	0.333	na	1.256	25	3.5	4.8
5.40	(Russell et al. 2003)					40	2.5	
5.50						50	2.1	
5.60						60	1.8	
6.23	WHC-SD-WM-TI-624	0.63	0.344	23	1.31	23	3.60	6.0

(a) The unique ID for each table entry is established by PNNL to differentiate each unique simulant/waste composition and temperature combination in the database. The ID is of the form [N].[T], where N identifies a unique simulant/waste and T is the temperature at which viscosity is measured (in °C).

(b) Reference sources are identified by both the method used in the viscosity database and (in square brackets if different) in Section 10.0 of this report.

na Temperature for density measurement unavailable or not provided by reference source. Assumed 20°C when evaluating densities for liquid viscosity.

Table 5.3. Physical Properties of Characterized Tank Waste Supernate Samples

Unique ID[a]	Reference Source[b]	UDS (wt%)	Dissolved Solids Concentration (g solids/g supernate)	Temperature of Density Measurement (°C)	Density (g/mL)	Temperature of Viscosity Measurement (°C)	Viscosity (mPa·s)	Sodium Molarity (M)
7.25	WTP-RPT-022	na[h]	0.316	n/a	1.258	25	4.5	4.7
7.35	(Goheen et al. 2002)					35	4.4	
7.50						50	2.7	
7.80						80	3.0	
8.25	WTP-RPT-069	na[h]	0.312	na	1.260	25	3.47	na[c]
8.40	(Baldwin et al. 2003)					40	2.36	
9.25	WTP-RPT-095	0	0.121	25	1.095	25	1.4	1.75
9.40	(Poloski et al. 2003)			40	1.086	40		
10.25	WTP-RPT-095	0	0.179	25	1.150	25	1.8	2.75
10.40	(Poloski et al. 2003)			40	1.137	40	1.4	
11.25	WTP-RPT-095	0	0.231	25	1.203	25	2.4	3.75
11.40	(Poloski et al. 2003)			40	1.187	40	1.7	
12.25	WSRC-TR-2000-00352[d]	0.1	0.304	na	1.26	25	3.2	5.25
12.50						50	2.5	
13.25	WSRC-TR-2000-00352[e]	1.2	0.161	na	1.15	25	3.7	2.8
13.50						50	2.4	
14.25	WSRC-TR-2000-00352[f]	0	0.373	na	1.33	25	2.7	6.4
14.50						50	2.0	
15.25	WSRC-TR-2000-00352[g]	0	0.315	na	1.23	25	4.2	4.9
15.50						50	2.8	

(a) The unique ID for each table entry is established by PNNL to differentiate each unique simulant/waste composition and temperature combination in the database. The ID is of the form [N].[T], where N identifies a unique simulant/waste and T is the temperature at which viscosity is measured (in °C).

(b) Reference sources are identified by both the method used in the viscosity database and (in square brackets if different) in Section 10.0 of this report.

(c) composite supernate

(d) Waste composition from BNF-003-98-0248

(e) Waste composition from BNF-003-98-0249

(f) Waste composition from BNF-003-98-0250

(g) Waste composition from WSRC-TR-2000-00420

(h) UDS not directly measured; visual inspection observed no solids. UDS for these samples is assumed minimal.

na UDS or temperature unavailable or not provided by reference source. Missing temperatures are assumed 20°C when evaluating densities for liquid viscosity.

6.0 Application of Laliberté Model to Predict Viscosity

Tank waste and simulant characterization data from the liquid viscosity database described in Section 5.0 of this report were used to benchmark the predictive performance of the composition-based Laliberté viscosity model against actual viscosity measurements and compared to the density-based models developed by Poloski et al. (2007), Wells et al. (2011), and RPP-RPT-51652. The application of the Laliberté viscosity model requires specification of an aqueous solution in terms of salt species (e.g., Na_2CO_3, NaOH, Na_2SO_4, etc.), rather than the concentration of salt anions or chemical constituents that are supplied from ICP/IC-based tank waste characterization data. Conversion of this chemical data to equivalent salt components must therefore be performed for Hanford tank waste. A similar procedure must be executed when evaluating viscosity for Hanford waste simulants (whose chemistry is specified in terms of the masses of reactants used to prepare the simulant rather than the resulting products and their concentrations) that accounts for changes in the simulant chemistry that occur during preparation of Hanford simulants (namely through precipitation and re-dissolution of metal hydroxides upon addition of sodium hydroxide to the initial mixed metal nitrate salt solution).

The first step in applying the Laliberté model is to convert the waste ICP/IC data or simulant recipe into an equivalent solution of salts (e.g., for simulants, aluminum nitrate [$Al(NO_3)_3$] reacts with sodium hydroxide [NaOH] to form aluminate [$NaAl(OH)_4$]). Once an equivalent solution of salts is created, the second step is to identify and fill (if possible) any gaps in the Laliberté data or in the implementation of the model. General considerations and assumptions made while converting source composition data to an equivalent salt basis for use in the Laliberté viscosity model included the following:

- Insoluble solids and solid products are not considered in the viscosity correlations.
- For exact simulant recipes, organics other than sodium acetate, sodium formate, and sodium oxalate were ignored.
- For Hanford waste compositions (based on ICP/IC data), three organic salts, namely sodium acetate, sodium formate, and sodium oxalate, were treated explicitly and their contribution to total organic carbon (TOC) concentrations removed. Any remaining TOC is treated as sodium oxalate.
- Sodium nitrite is not one of the 96 solutes with viscosity model coefficients generated by Laliberté (2007a, 2009). Viscosity coefficients for $NaNO_2$ were generated by regression of $NaNO_2$ viscosity data from Kutsenko et al. (1978), Shurdumov et al. (1983), Mauss (1985), and Protsenko et al. (1970) against Eq. (4.2).

Once conversions are finalized, the Laliberté viscosity model may be used to provide predictions of liquid waste viscosity, which may then be compared to actual viscosity measurements and density-based correlations. The solution chemistry of Hanford wastes and their simulants is complex; the composition conversion process that facilitates application of the Laliberté viscosity model to simulant and waste systems is subject to an unquantified error and uncertainty introduced by the simplifying assumptions that underpin composition conversion. Further work may be able to quantify these uncertainties and build upon initial work. Sections 6.1 and 6.2 account for application constraints and conversions specific to liquid simulants and waste supernates, respectively.

6.1 Conversion of Simulant Data to Equivalent Salt Components for Application of the Laliberté Model

The simulant composition data available from the liquid viscosity database are considered of good quality because the amounts of base salts added to the simulant could be measured with high precision. However, the solution “make-up” does not reflect the final chemical composition to the same level of precision. The simulant undergoes further chemical changes with the addition of all base salt components. The following considerations and assumptions were made when converting liquid waste simulant data:

- Soluble species added in trace amounts were neglected.
- When the nitrate salt of an insoluble mineral was encountered, sodium hydroxide was consumed, and sodium nitrate was produced. The insoluble mineral left from the reaction was then removed from further analysis.
- The nitrate salts of soluble minerals were assumed to go into solution.
- Soluble salts were assumed to go into solution.
- Insoluble salts and oxides were ignored in the analysis because they were truly insoluble.
- Phosphates were converted to eliminate intermediate species that may be more prevalent at lower pH (e.g., $Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$ and $NaH_2PO_4 + 2NaOH \rightarrow Na_3PO_4 + 2H_2O$).

Throughout the conversion and substitution process, major species were tracked and added or subtracted from the total simulant solution as appropriate.

6.2 Conversion of Waste Supernates Data to Equivalent Salt Components for Application of the Laliberté Model

The Laliberté (2007a) model requires the input of salt species and not elemental waste composition. The conversion of elemental waste composition requires that a number of assumptions be made to simplify the process. These considerations and assumptions for liquid tank waste data included the following:

- Several analytes were considered duplicates (or considered to contain duplicate information); namely P and PO_4, total inorganic carbon and CO_3, Al and AlO_2, and S and SO_4. Duplicate analyte pairs (e.g., P and PO_4) were converted to the same mass basis (e.g., PO_4 for P and PO_4) and only the maximum concentration from the converted pair was retained for analysis.
- Ca, K, and NH_3 (as NH_4^+) were assumed to derive from soluble nitrate salts.
- Aluminum (Al) and aluminates (AlO_2) from ICP/IC-based analysis were converted to sodium aluminate [$Al(OH_4)^-$].
- Oxalate (C_2O_4), acetate ($C_2H_3O_2$), and formate (CHO_2) were all treated as sodium salts and their contributions removed from measured TOC.
- TOC remaining after exclusion of oxalate (C_2O_4), acetate ($C_2H_3O_2$), and formate (CHO_2) was treated as sodium carbonate.[1]
- Cl, CO_3, F, NO_3, PO_4, SO_4, and OH were treated as their equivalent sodium salts (e.g., NaCl).
- Reported OH was assumed to be free hydroxide.
- Charge balance was accomplished by treating excess Na as $NaCO_3$ and ignoring NO_3 and Na deficiencies.

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[1] Assignment of TOC to a single- or pre-defined mixture of organic compounds whose viscosity coefficients are known (such as sodium acetate, sodium formate, and sodium oxalate) was evaluated and found to produce a lower-quality fit (see Appendix A).

Similar to the simulant conversion, major species were tracked and were added to or subtracted from the total solution as appropriate.

7.0 Results and Discussion

This section presents model results from initial data collected in the liquid viscosity database that will present the potential viability of composition-based viscosity models for use with Hanford waste liquids. Discussion of these results highlights advantages, deficiencies, and identifies current data and model gaps in the composition-based approach.

Laliberté (2007a) liquid viscosity model predictions using simulant and liquid tank waste data are compared against actual measured viscosity values in Figure 7.1. The plot presented in Figure 7.1 is a parity plot with values predicted by the Laliberté (2007a) model on the Y-axis and measured viscosity values on the X-axis. The blue circular points correspond to viscosity for chemically produced liquid simulants (hereafter termed the “simulant” case analyses), and the orange upside-down triangles correspond to viscosity for tank waste data (hereafter referred to as the “waste” case analyses). The parity line that runs diagonally represents a one-over-one match between the calculated and measured viscosity values. The total root mean square error of the prediction (E), termed the parity error, is shown in the figure legend and is defined as

$$E = \sqrt{\frac{1}{N}\sum_{j}^{N}\left(\eta_j^{(c)} - \eta_j^{(m)}\right)^2} \tag{7.1}$$

where N is the number of test cases (i.e., viscosity database entries) and $\eta_j^{(c)}$ and $\eta_j^{(m)}$ are the predicted (calculated) and measured viscosity for the j^{th} test case, respectively. For the simulant data (i.e., blue circular points), the Laliberté model predicts viscosities that are generally quite close and in many cases near identical to measured values (with a parity error of 0.400 mPa·s). The best agreement for the simulant cases is observed for the mid-range viscosities (3 to 5 mPa·s). At low viscosity (1 to 3 mPa·s), the Laliberté viscosity model (as applied herein) appears to slightly under-predict viscosity, whereas at high viscosity (5 to 8 mPa·s), the model appears to slightly over-predict viscosity. In contrast, the predictive performance of the Laliberté model and/or the approach used to determine the equivalent salt basis for the waste cases (parity error of 0.867 mPa·s) is not as good as that for the simulant cases. While predictive performance for the wastes is similar to that of simulants at low viscosity (1 to 2.5 mPa·s), the mid-range viscosity (2.5 to 5 mPa·s) falls off the parity line for most cases considered. In this range, an equal number of cases appear to fall above and below the parity line; however, the magnitude of error appears to weight toward the model under-predicting liquid viscosity.

Figure 7.1 provides a limited assessment of predictive performance of the Laliberté viscosity model and the analytical data/salt recipe conversion models implemented herein. A more complete assessment of predictive performance, that evaluates the Laliberté model against Hanford Site liquid viscosity models (namely those of Poloski et al. [2007], Wells et al. [2011], and RPP-RPT-56152) is provided in Figure 7.2. In Figure 7.2, the purple squares represent the predictions of the Poloski et al. (2007) liquid viscosity model, the green triangles represent the predictions of the Wells et al. (2011) model, and the blue diamonds represent the predictions of the RPP-RPT-56152 (Meacham) model. These three liquid viscosity models are all a function of measured density and temperature for liquid simulant or Hanford tank waste supernate. Again, predicted/calculated values of viscosity are on the Y-axis and actual measured values are on the X-axis, with the parity line running diagonally across the plot and representing a one-over-one match. As before, the legend includes an assessment of parity error for each of the viscosity models. It should be noted that although the legend and plot still differentiate between simulant and waste cases for the Laliberté model, the parity error for these two cases has been lumped together to allow direct comparison of the overall performance of this model with the three density-based models. For this reason, the parity errors for the Laliberté simulant and waste cases are identical.

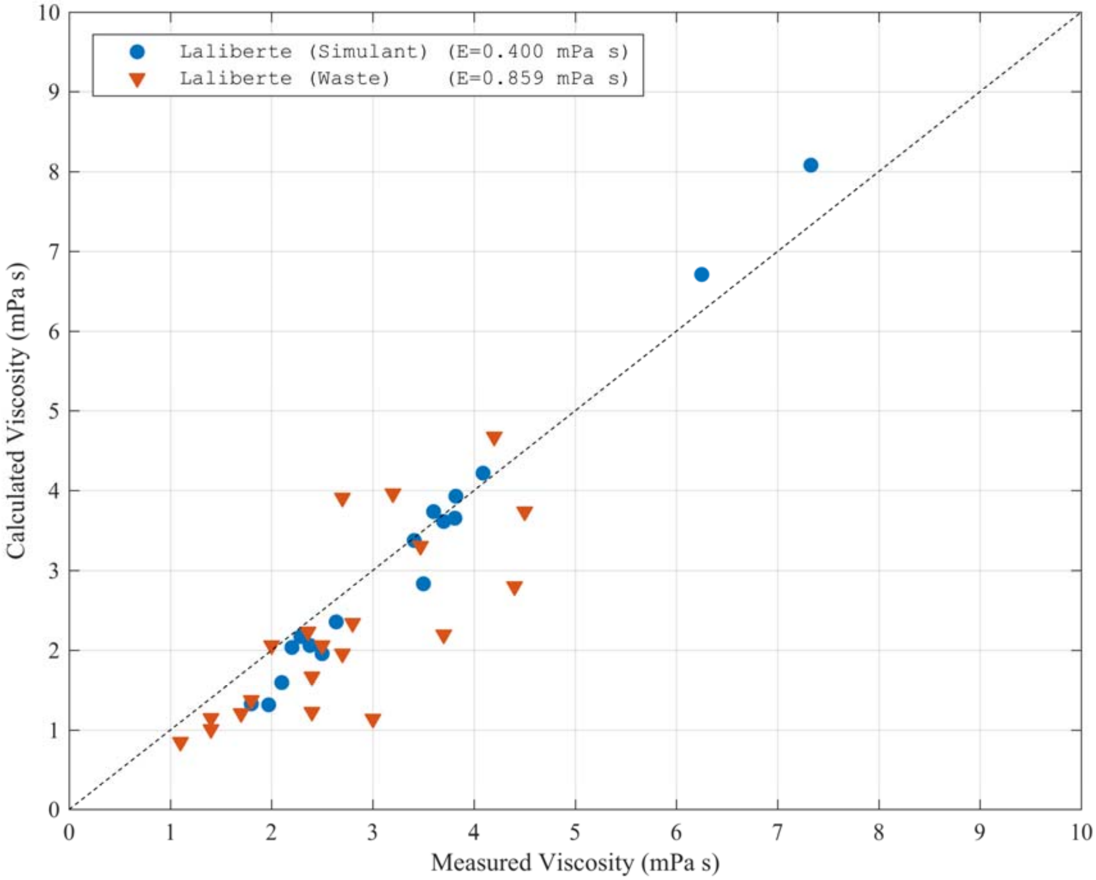

Figure 7.1. Laliberté (2007a) Model Compared to Actual Measured Viscosity

Figure 7.2 shows that the composition-based Laliberté viscosity model (as implemented herein) provides viscosity predictions that are, when considering the entire data set, more accurate than the density-based models of Poloski et al. (2007), Wells et al. (2011), and RPP-RPT-51652 (Meacham). That is not to say that the Laliberté viscosity model is superior for all cases. Indeed, for the current data set, there are many cases, especially in the 1 to 3 mPa·s range, where the Poloski et al. (2007) model provides a more accurate prediction of viscosity relative to all available viscosity models. However, the accuracy of the Poloski et al. (2007) model appears to diverge above 3 mPa·s, producing several viscosity predictions that fall well above the parity line (such as the 6.2 mPa·s calculated viscosity with a corresponding 2.8 mPa·s measured viscosity). For most cases, the Wells et al. (2011) and RPP-RPT-51652 (Meacham) correlations appear to over-predict viscosity (for the current data set) and are subject to significant scatter and divergence for mid-range viscosities. In general, the Poloski et al. (2007) model provides the most accurate density-based viscosity predictions and best span (e.g., balance of high and low viscosities) of the parity line. While the Laliberté viscosity model appears to under-predict at low viscosities and over-predict at high viscosities, the model also provides the closest grouping of viscosities to the parity line. Thus, while the Poloski et al. (2007) model provides a more accurate assessment of viscosity for some cases, its overall performance is not as good as the Laliberté model.

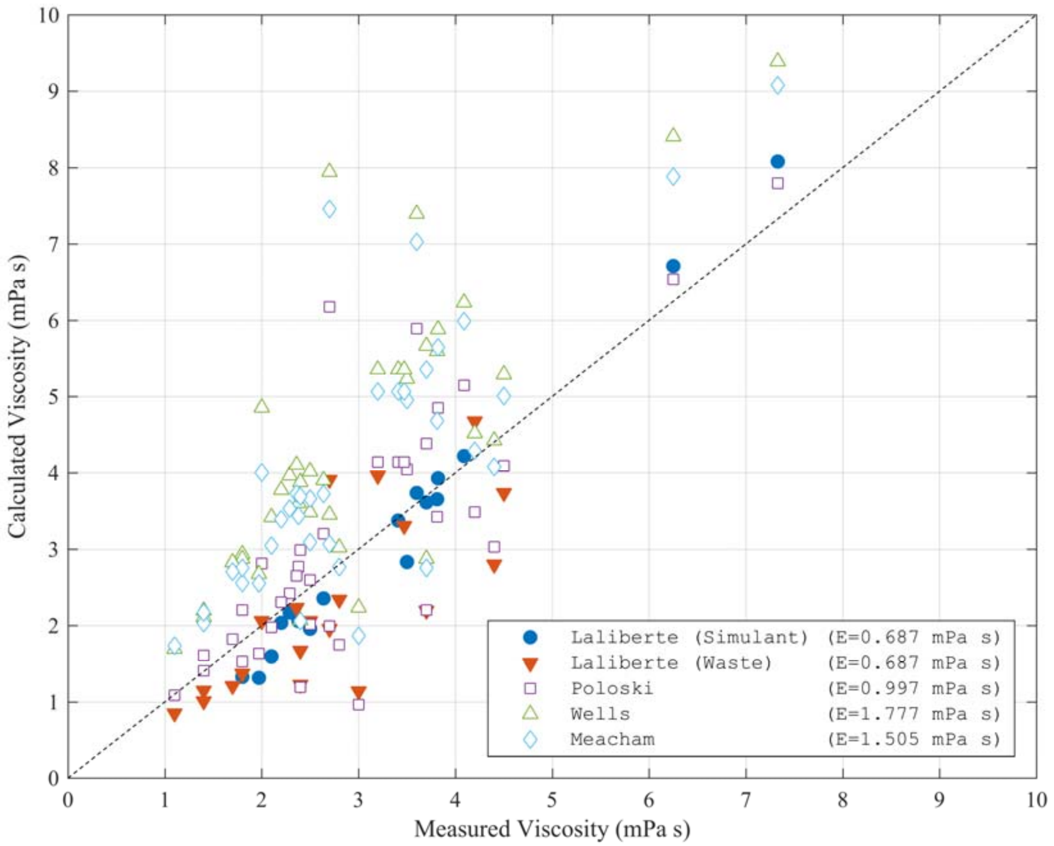

Figure 7.2. Density-Based Models and Laliberté Model Compared to Actual Measured Viscosity

Table 7.1. Relative Error of Each Viscosity Model

Liquid Viscosity Model	Simulant Error (mPa·s)	Waste Error (mPa·s)	Combined Error (mPa·s)
Laliberté (2007a)	0.400	0.859	0.687
Poloski et al. (2007)	0.762	1.161	0.997
Wells et al. (2011)	1.882	1.683	1.777
RPP-RPT-56152 (Meacham)	1.555	1.460	1.505

The preceding discussion is based primarily on visual inspection of Figure 7.2. To provide a more quantitative measure of model performance, the parity error associated with each correlation is evaluated for the simulant test cases, the actual waste test cases, and the combined overall simulant and waste viscosity data set. Table 7.1 presents the breakdown of parity errors for each test case and viscosity model combination. It should be noted that the Table 7.1 analysis does not break test cases down into distinct viscosity ranges, but rather considers the model's performance against the entire data set of viscosity ranges. As suggested previously, the Laliberté model significantly outperforms the density-based correlations for both simulant and actual waste test cases. As stated in the previous paragraph, Laliberté's model is most accurate for simulant cases. This also appears to be the case for the Poloski et al. (2007) density-based viscosity correlation, where prediction for simulant recipes is much better than for actual

Hanford waste data. This is not surprising, because better-quality composition and physical property data are expected when preparing and evaluating well-defined, nonradioactive simulants in a standard laboratory setting. In contrast, both Wells et al. (2011) and RPP-RPT-51652 (Meacham) density-based models show slightly worse performance for simulant relative to actual waste cases, which is suggestive of a systematic error when quantifying viscosity with these models.

In general, no single factor appears to influence the parity errors shown in Table 7.1. Wells et al. (2011) and RPP-RPT-51652 (Meacham) over-predict viscosity for the vast majority of test cases, and as such, the large parity error for these two models is driven primarily by a systematic over-prediction of viscosity relative to measurement. The viscosities predicted by the Poloski et al. (2007) model appear to fall more evenly above and below the parity line, and as such, the parity error could result from poor correlation of composition-based effects, random error in the measured viscosities, or some combination thereof. The Laliberté model viscosities tend to fall more frequently below the parity line, indicating that parity error could be driven by systematic failure to appropriately account for component-based effects (either as a result of flaws in the Laliberté model or in the methods used to develop the equivalent salt recipe for simulants and wastes). The improved predictive performance of the Laliberté viscosity model relative to all density-based models is driven largely by an overall reduction in differences between measured and predicted viscosities in the intermediate viscosity range from 2.5 to 5 mPa·s.

The observations made in the preceding paragraphs allow development of a tentative set of Laliberté multicomponent viscosity model performance conclusions:

- Although density-based viscosity models (namely that of Poloski et al. 2007) offer better accuracy for some of the test cases evaluated herein, the composition-based Laliberté viscosity model provides the most accurate overall assessment of liquid viscosities reported herein, regardless of whether that prediction derives from a simulant recipe or ICP/IC-derived actual waste. Indeed, the performance of the Laliberté viscosity model for the current data set is substantially more accurate than that provided by the most current density-based viscosity model (RPP-PRT-51652 [Meacham]).
- The performance of the Laliberté (2007a) viscosity model using converted waste ICP/IC data is poor relative to its performance with well-characterized simulants but is still better than that of even the best-performing density-based viscosity model for the test cases considered (i.e., that of Poloski et al. 2007).

Although, the first conclusion should be moderated by the relatively limited set of waste and simulant data used to evaluate the Laliberté viscosity model, it highlights the potential of composition-based models for improving the accuracy of liquid viscosity predictions beyond that currently obtainable using density-based correlations.

The current work also highlights that the Poloski et al. (2007) density-based correlation can predict liquid viscosity with good accuracy (relative to all the models evaluated herein). Relative to the Laliberté viscosity model, implementation of the Poloski correlation is simple, as its use requires only knowledge of liquid density. On the basis of this study alone, the Poloski correlation could be concluded to provide a "reasonable" balance between ease of implementation and accuracy. However, Poloski et al. (2007) model has been superseded by the two models that over-predict viscosity in this study and would not be the first recommended choice for predicting liquid viscosity of the density-based correlations currently available. From an end-use standpoint, the performance of the Poloski et al. (2007) model is undercut by the poor performance of the two other density correlations, because it does not agree with density-based correlations fit to a larger set of density/viscosity data. Even though the Laliberté model predicts viscosity lower than Wells et al. (2011) and RPP-PRT-51652 (Meacham), it is fundamentally underpinned by the accuracy of the source composition and single-salt viscosity data. And, given accurate source data, such as waste simulant compositions, the fidelity of the Laliberté model (and the formulation used to arrive at the equivalent salt recipe) is further underpinned by good parity with simulant viscosity measurements. While the level of information required to implement the Laliberté model viscosity model is substantial relative to density-based models, the viscosity model itself appears to provide a viable and potentially more accurate means of determining waste viscosity relative to existing recommended correlations.

The limited testing above does not provide clear reasons for deficiencies in performance of the Laliberté viscosity model for actual wastes (relative to simulants). Possible causes for reduced model performance include improper conversion from ICP/IC data, exclusion of key viscosity-determining analytes (likely unidentified organic compounds associated with TOC), and random or systematic error in actual waste composition or viscosity data. Improvement to the model could be achieved by adding rigor to the (as implemented currently) relatively simplistic methods for creating equivalent salt speciation from ICP/IC data, identifying and closing gaps in the Laliberté viscosity model and its underlying viscosity data, and through evaluating the removal of outliers in the source viscosity data set. The remainder of this report focuses on the second of these improvements, namely the identification of model gaps and opportunities for gap closure.

8.0 Gap and Opportunity Summary for Liquid Viscosity Model

A composition-based liquid viscosity model was applied using measured Hanford tank waste supernate and liquid simulant properties. Specifically, the predictive capabilities of the Laliberté composition-based liquid viscosity model were compared to actual measured liquid simulant and tank waste viscosities and to previously developed density-based viscosity models. This effort was supported by reviews of the peer- and Hanford-based literature as well as the development of a Hanford-relevant viscosity database. First, waste composition date were reviewed to identify the major soluble components (salts) in Hanford waste based upon relative concentration. Next, the scientific literature was reviewed to identify existing composition-based liquid viscosity models and recent developments in models for predicting viscosity of concentrated electrolyte solutions, leading to the conclusion that the Laliberté model was the best model for this study. Limitations in the range of applicability were found in the Laliberté viscosity model based upon salt concentration. A database of expanded single- and multicomponent salt solution data as a function of salt concentration, salt speciation, solution temperature, and many more parameters was generated from technical reports about Hanford wastes.

Furthermore, a large number of existing technical reports that may include additional relevant information were tabulated for possible future addition into the database. Limited data on the impact of Hanford-relevant organic waste components on viscosity were found beyond assessments for sodium oxalate, sodium formate, and sodium acetate, and key organics such as the sodium forms of HEDTA and EDTA did not have corresponding model coefficients within the Laliberté (2007a) model, thereby identifying that further work will have to be done with regard to organic waste components. Application of the Laliberté model demonstrated the ability to charge-balance equivalent salt compositions of simulants and liquid tank waste to predict liquid viscosity, from which initial results suggest that the agreement between predicted and actual measured values is better than that of previously developed density-based models (for the test cases considered herein). This is recognized as an encouraging result, considering the simplifying assumptions and substitutions made during the conversion of collected data.

In conclusion, the Laliberté viscosity model offers the ability to predict, with some uncertainty, the viscosity of multicomponent electrolyte solutions from single-salt solution data without any additional fitting parameters being necessary. The coefficients for many salts present in Hanford waste are provided by Laliberté (2007a,b; 2009) and the extension of the model to unknown systems appears straightforward. From these conclusions, gaps and limitations encountered through this work are discussed in Section 8.1, and specific recommendations are provided in Section 8.2.

8.1 Liquid Viscosity Model Gaps

The generation of the liquid viscosity database and application of the composition-based Laliberté model identified several gaps and limitations. These gaps and limitations are provided below.

- Laliberté (2007a,b; 2009) does not include model coefficients for several key components, such as the sodium forms of EDTA and HEDTA and $NaNO_2$, in Hanford liquid waste and waste simulants; this gap could be closed to improve model relevance to Hanford wastes. For the current analysis, sufficient data were available to develop viscosity coefficients for $NaNO_2$, but not for the sodium forms of EDTA and HEDTA. A mass-equivalent addition of sodium oxalate was substituted for these latter two components. Other components for which viscosity coefficients are not available in the Laliberté (2007a,b; 2009) model include relatively minor components (such as $CsNO_3$) and larger organic molecules like EDTA.

- The influence of organic components on the liquid viscosity of Hanford wastes cannot be fully resolved from the available data and current state of the Laliberté viscosity model coefficient data. While ICP/IC data provide information about select organic components (e.g., acetate, format, oxalate), not all analytes evaluated have associated viscosity model coefficients (as is the case for glycolic acid, $C_2H_4O_3$). However, this gap can be addressed by development of analyte-specific coefficients from existing literature data or new viscosity measurements. A more severe limiting factor is that waste ICP/IC data only report TOC, such that an organic speciation must be assumed when treating TOC. For the current analysis, any TOC remaining after assignment of formate, oxalate, and acetate as sodium salts was assumed to be sodium carbonate. Without knowledge of the exact speciation of organic compounds, the impact of this assumption cannot be quantified from the current study. Unqualified scoping calculations (included in Appendix A) suggest that treatment of remaining TOC as either sodium oxalate or an equivalent mass mixture (by elemental carbon) of sodium formate, oxalate, and acetate leads to slightly poorer liquid viscosity predictions, with errors similar to that of the Poloski density-based correlation, for wastes. It is not clear if reduced performance derives from the selection of organic components to represent TOC or from the Laliberté model itself. As such, an improved basis for speciating TOC is an opportunity for improving model accuracy and strengthening its technical basis.

- Most Hanford liquids are highly concentrated in dissolved salts and lead to extrapolations of single-salt component viscosity outside of the tested concentration range on which the Laliberté (2007a) viscosity coefficients are based. As shown in Equation (4.2), the solute viscosity for each component is predicted as a function of the total weight fraction of dissolved salts in water, denoted by $(1 - w_w)$, where w_w is the weight fraction of water. For certain salts, the viscosity coefficients are such that the pure component viscosity η_i can become negative at large $(1 - w_w)$, which leads to physically unrealistic (imaginary) total solution viscosities. Early assessments of the Hanford viscosity database encountered negative η_i for sodium carbonate; however, correction of equivalent salt recipe conversions and an update to the liquid viscosity coefficient database reported by Laliberté (2009) appears to have resolved the issue for the current calculations. Still, the maximum Na_2CO_3 concentration assessed by Laliberté (2009) for determination of viscosity coefficients is ~31-wt%, while the maximum dissolved solids concentration (i.e., $1 - w_w$) assessed herein was ~39-wt%, meaning that extrapolation of the model beyond its fitting range still takes place (but does not produce obviously flawed results). The issue, which is rooted in extrapolation, can be resolved by re-evaluation of sodium carbonate viscosity coefficients using viscosity measurements of admixtures of sodium carbonate with other salts at total salt concentrations relevant to Hanford wastes. Development of such data represents future work that could be done to address this gap.

- Composition-based models share two common limitations. First, to predict viscosity, there must be empirical data on the viscosity of each salt component to inform model coefficients. There are many salt components in Hanford waste that require this empirical analysis to be done in order to implement the component in the model. Second, analysis of the waste must include the full characterization of its chemical composition. Whereas previous, density-based models only required the density and temperature of waste to predict viscosity, composition-based models require increased physical characterization.

- A limitation in the application of the Laliberté viscosity model exists as a function of its being a composition-based model. As such, the composition in terms of specific salt speciation must either be known or determined through solution chemistry. In the current application, assumptions and simplifications are made throughout this process, which increases the uncertainty in model predictions of viscosity.

- A limitation exists in the application of the model due to the relatively limited amount of data in the liquid viscosity database. Finding liquid waste and simulant viscosity measurements that also include the full compositional characterization required to inform the Laliberté viscosity model is challenging. This limitation could be eased through the inclusion of additional simulant information; inclusion of peer-reviewed literature viscosities for complex, multicomponent electrolyte solutions that are not Hanford-relevant; and new waste or simulant viscosity and composition measurements from current or future waste characterization campaigns or simulant development. With respect to the latter, future campaigns should consider the need for high-quality data on both viscosity and composition to support these analyses.

8.2 Liquid Viscosity Model Opportunities for Improvements

As discussed in many of the gaps highlighted above, there are opportunities for improvement to the Laliberté viscosity model:

- Improvement to the Laliberté viscosity model will require that additional measurements be made for high-concentration salt viscosities for select systems. Components of particular interest are common Hanford salts, such as Na_2CO_3 at and above waste-relevant dissolved solids concentration (up to 40-wt%), and organic components such as EDTA.
- The liquid viscosity database should be expanded to include additional data points. The additional data will provide an increased body of evidence against which to gauge model performance in predicting liquid viscosity. More work should be done to resolve whether the chemical composition of viscosity data used in the density-based models can be found.
- More work should be done to fully assess and incorporate the relevant chemical reactions and products in the liquid waste and simulants. In the current approach, the complexity of simulant waste chemistry is avoided through application of highly simplified reactions, by neglecting or recasting certain soluble species that do not have corresponding model coefficients, and by only considering waste and simulant chemistry in terms of a limited subset of 23 salts. These simplifications were made to enable a “proof-of-concept” demonstration of composition-based model viscosity prediction capability. A more rigorous treatment of waste and waste simulant chemistry represents an opportunity to improve the accuracy of the Laliberté model (as applied to Hanford wastes) and the overall ability to predict liquid waste viscosity in general.

9.0 Conclusion

In the current study, the viscosities of Hanford wastes and waste simulants were predicted using a composition-based model developed by Laliberté (2007a) (the “Laliberté viscosity model”) to evaluate its accuracy relative to the current density-based models used to predict waste viscosity for engineering applications at the Hanford Site. A viscosity database that captured the composition and viscosity of wastes and waste simulants was developed to support this evaluation. To facilitate application of the Laliberté viscosity model, waste and waste simulant compositions were converted to an equivalent salt recipe composed of salts with known viscosity coefficients, using a number of simplifying assumptions that have the potential to impact the fidelity of the model prediction. Despite these simplifications, the Laliberté viscosity model was able to predict viscosity more accurately than the density-based correlations currently available for Hanford flowsheet use, such as that proposed in RPP-RPT-51652. The use of composition-based viscosity models, like that proposed by Laliberté (2007a), shows promise for leading to improved prediction of liquid waste viscosity. As implemented herein, application of the Laliberté viscosity model could lead to a decrease in the uncertainty associated with liquid viscosity prediction by as much as a factor of two, allowing for reduction in unit operation design conservatism and for the more realistic selection of test simulants for flowsheet process evaluation and optimization.

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Appendix A

Alternate Viscosity Model Test Cases

Appendix A

Alternate Viscosity Model Test Cases

In the liquid viscosity analysis presented in the main body of this report (see Section 6.0), conversion of waste inductively coupled plasma/ion chromatography (ICP/IC) data assigned any remaining total organic carbon (TOC) (namely that not already assigned to directly quantified acetate, formate, or oxalate anions) as sodium carbonate. Unqualified scoping calculations determined that assignment of the remaining TOC (or all TOC where acetate, formate, and oxalate were not quantified) to sodium carbonate, an inorganic salt, provides best agreement between measured and predicted viscosity. During scoping calculations, two other parametric variations were considered: 1) treating all remaining unassigned TOC as sodium oxalate or 2) treating all remaining TOC as an equal split (by elemental C mass) to sodium formate, acetate, and oxalate. In the two sections that follow, the results for each of these scoping cases are presented for reference. These calculations are adapted from the primary qualified calculation presented in the main body of this report but have not been formally reviewed for technical accuracy in accordance with the requirements of the applicable quality assurance program. For this reason, the results should be treated as "For Information Only" and have been marked accordingly.

A.1 Remaining TOC as Oxalate

The scoping calculation that treats any remaining TOC not assigned to acetate, formate, and oxalate (as determined by ICP/IC TOC data) as sodium oxalate is shown in Figure A.1, Figure A.2, and Table A.1. The results follow the same format as in the main body of the report, and as discussed in the introduction to this appendix, are unqualified and provided "For Information Only." Because treatment of TOC only applies to the conversion of actual waste ICP/IC data to its equivalent salt basis, simulant calculations are unchanged and match those provided in Section 7.0 of this report. As stated in the main body of the results, treatment of TOC as oxalate yields liquid viscosity results for actual waste that are poorer than those derived by treating remaining TOC as sodium carbonate. The increased error results from under-prediction of the waste viscosity when treating TOC as sodium oxalate. The overall parity error of waste prediction is equivalent to that of the Poloski et al. (2007) model.

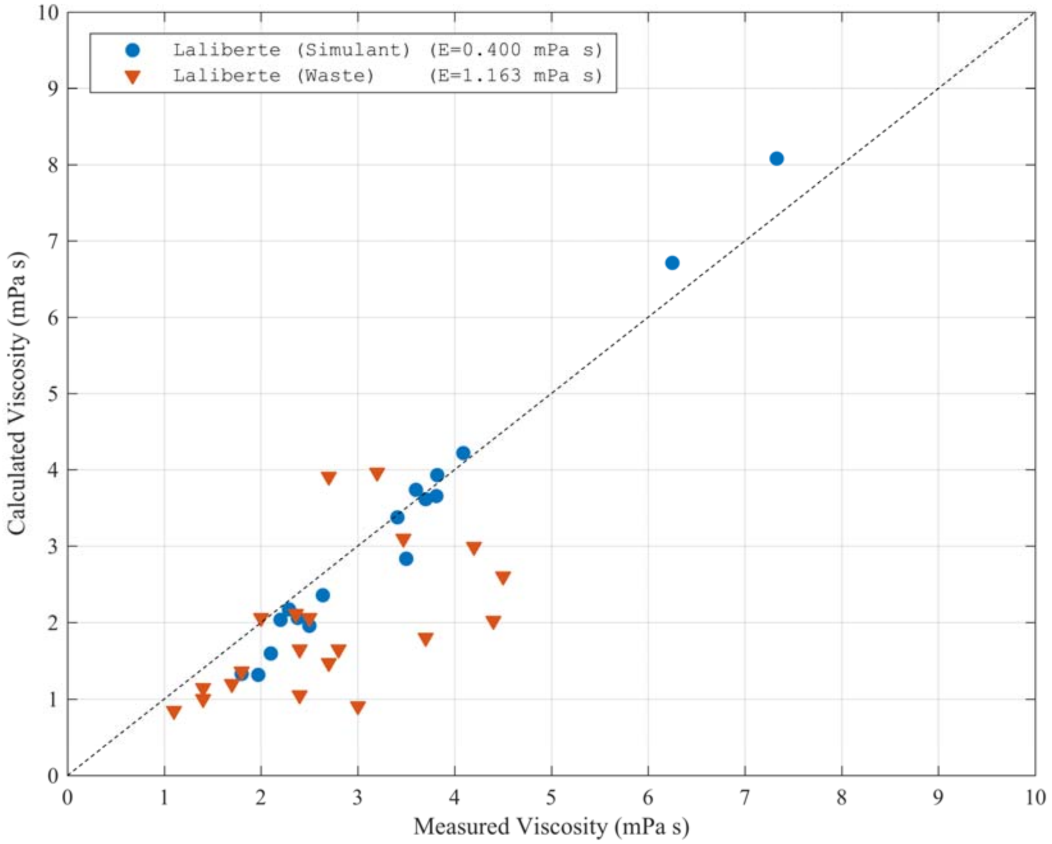

Figure A.1. Laliberté Viscosity Model Parity Chart for the Scoping Study Variant Where Remaining TOC Is Treated Entirely as Sodium Oxalate. Result is unreviewed and is "For Information Only."

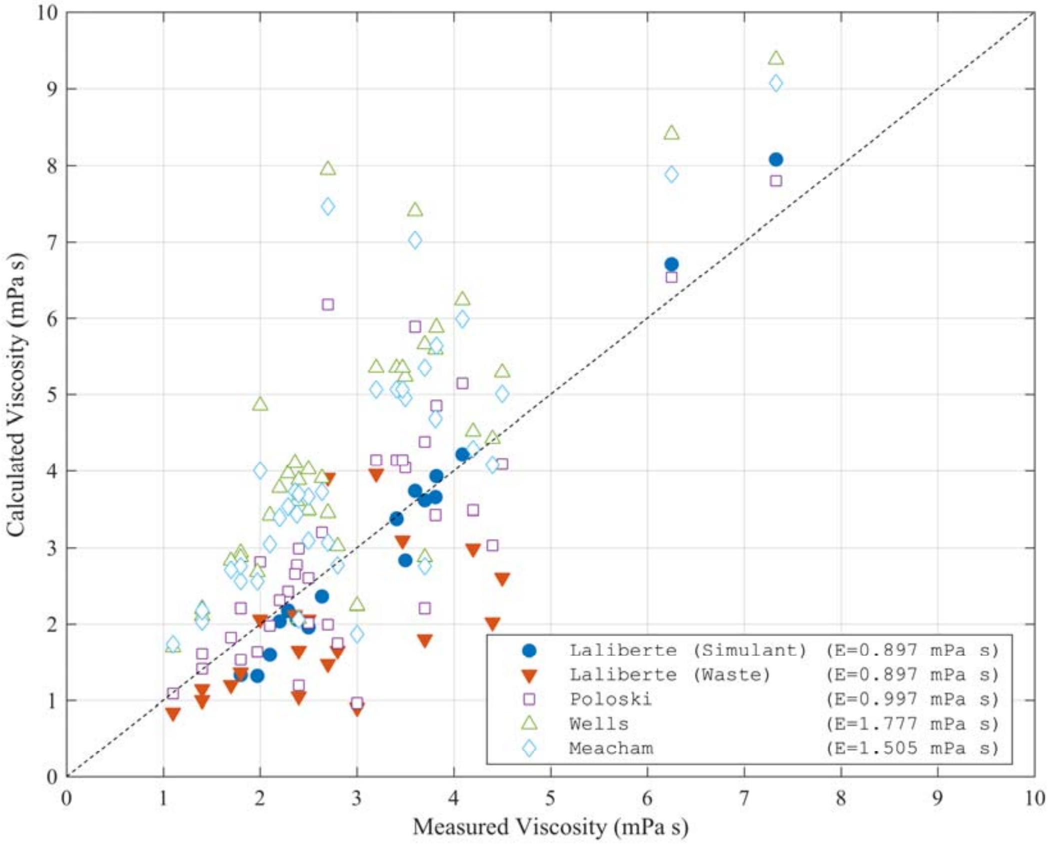

Figure A.2. Laliberté Model Parity Compared to the Density-Based Viscosity Correlations of Poloski et al. (2007), Wells et al. (2011), and Meacham et al. (2012). The Laliberté model calculation derives from a scoping study variant where remaining TOC is treated entirely as sodium oxalate. Result is unreviewed and is "For Information Only."

Table A.1. Relative Error of Each Viscosity Model. The Laliberté model result shown here corresponds to a scoping study variant where remaining TOC is treated entirely as sodium oxalate. Result is unreviewed and is "For Information Only."

Liquid Viscosity Model	Simulant Error (mPa·s)	Waste Error (mPa·s)	Combined Error (mPa·s)
Laliberté (2007a)	0.400	1.163	0.897
Poloski et al. (2007)	0.762	1.161	0.997
Wells et al. (2011)	1.882	1.683	1.777
RPP-RPT-51652 (Meacham)	1.555	1.460	1.505

A.2 Remaining TOC as Mixture of Acetate, Formate, and Oxalate

The scoping calculation that assigns any remaining TOC not assigned to acetate, formate, and oxalate (as determined by ICP/IC TOC data) to sodium acetate, formate, and oxalate (on an equal elemental carbon basis) is shown in Figure A.3, Figure A.4, and Table A.2. The results follow the same format as in the main body of the report, and as discussed in the introduction to this appendix, are unqualified and provided "For Information Only." Because treatment of TOC only applies to the conversion of actual waste ICP/IC data to its equivalent salt basis, simulant calculations are unchanged and match those provided in Section 7.0 of this report. The results are more-or-less equivalent to those found when treating all TOC as sodium oxalate. The overall agreement with measured liquid viscosity is not as good as that achieved when treating unassigned TOC as sodium carbonate.

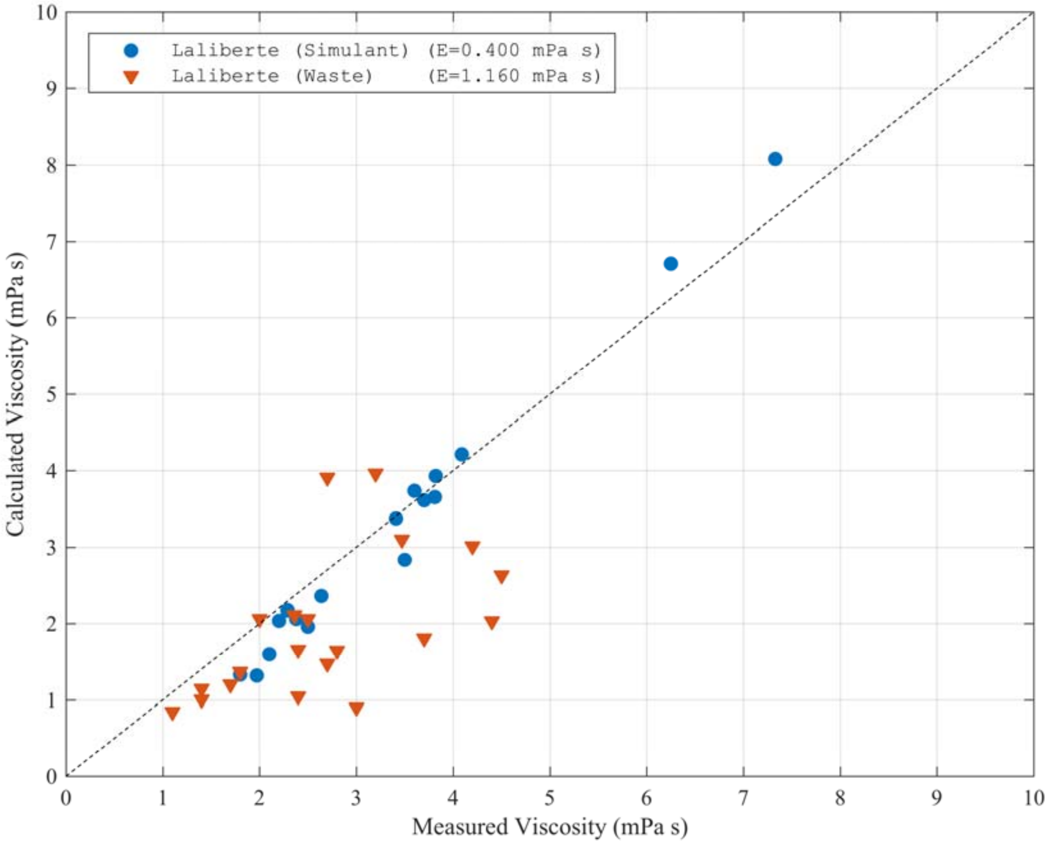

Figure A.3. Laliberté viscosity Model Parity Chart for the Scoping Study Variant Where Remaining TOC Is Treated as a Mixture of Sodium Oxalate, Acetate, And Formate (on an equal elemental carbon basis). Result is unreviewed and is "For Information Only."

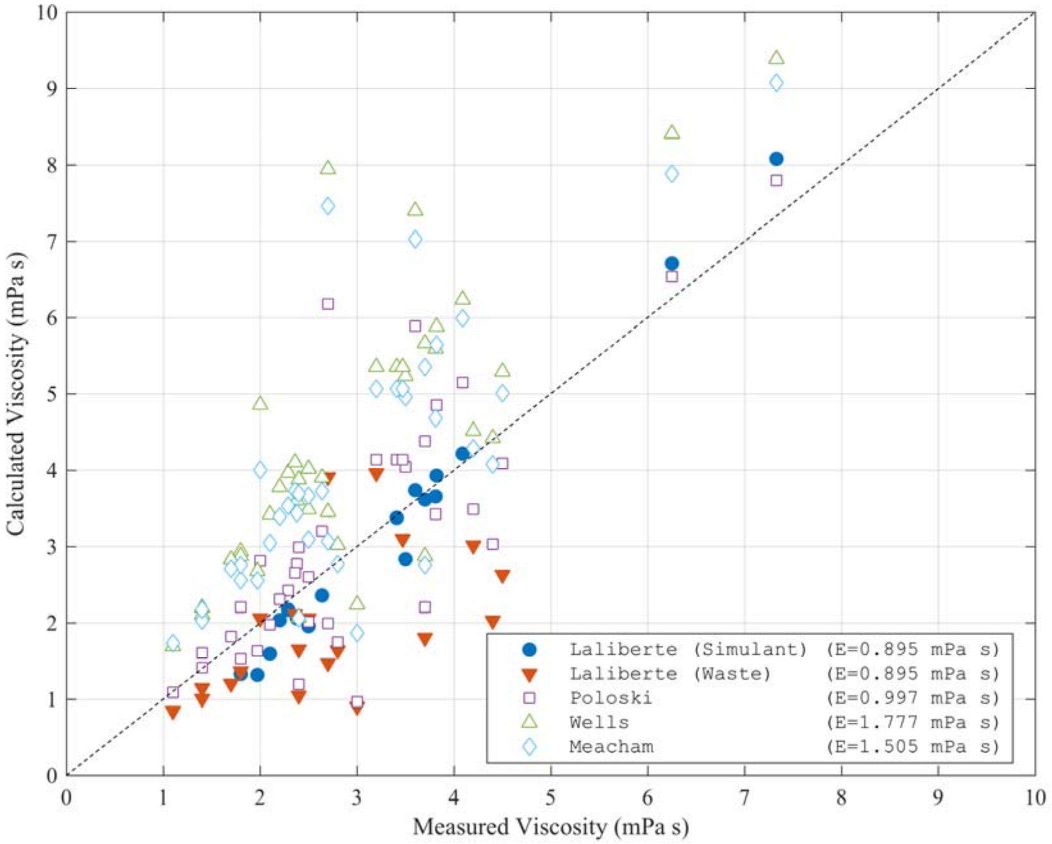

Figure A.4. Laliberté Model Parity Compared to the Density-Based Viscosity Correlations of Poloski et al. (2007), Wells et al. (2011), and RPP-RPT-51652 (Meacham). The Laliberté model calculation derives from a scoping study variant where remaining TOC is treated as a mixture of sodium oxalate, acetate, and formate (on an equal elemental carbon basis). Result is unreviewed and is “For Information Only.”

Table A.2. Relative Error of Each Viscosity Model. The Laliberté model result shown here corresponds to a scoping study variant where remaining TOC is treated as a mixture of sodium oxalate, acetate, and formate (on an equal elemental carbon basis). Result is unreviewed and is “For Information Only.”

Liquid Viscosity Model	Simulant Error (mPa·s)	Waste Error (mPa·s)	Combined Error (mPa·s)
Laliberté (2007a)	0.400	1.160	0.895
Poloski et al. (2007)	0.762	1.161	0.997
Wells et al. (2011)	1.882	1.683	1.777
RPP-RPT-51652 (Meacham)	1.555	1.460	1.505

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