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Simulant Development for LAWPS Testing

RL Russell
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CA Burns

May 2017

U.S. DEPARTMENT OF
ENERGY

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

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Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

The Direct Feed Low-Activity Waste (DFLAW) process has been proposed to support early production of immobilized low-activity waste (ILAW). In the DFLAW process, Hanford tank waste supernatant is sent to the Low-Activity Waste Pretreatment System (LAWPS) for filtration and cesium removal. The resultant treated waste is delivered to the Hanford Tank Waste Treatment and Immobilization Plant (WTP) Low-Activity Waste (LAW) Vitrification Facility for immobilization. The conceptual design and ongoing technology maturation of the LAWPS facility are being conducted by Washington River Protection Solutions, LLC (WRPS), but the DFLAW process also necessitates interfaces between WRPS and Bechtel National, Inc. to deliver the treated LAW from the LAWPS facility to the WTP for vitrification.

This report describes simulant development work that was conducted to support the technology maturation of the LAWPS facility. Desired simulant physical properties (density, viscosity, solids concentration, solids particle size), sodium concentrations, and general anion identifications were provided by WRPS. The simulant recipes, particularly a “nominal” 5.6M Na simulant, are intended to be tested at several scales, ranging from bench-scale (500 mL) to full-scale (upwards of 6,000 gallons). Each simulant formulation was selected to be chemically representative of the waste streams anticipated to be fed to the LAWPS system, and used the current version of the LAWPS waste specification as a formulation basis. After simulant development iterations, four simulants of varying sodium concentration (4.0M, 5.6M, 6.0M, and 8.0M) were prepared and characterized. The formulation basis, development testing, and final simulant recipes and characterization data for these four simulants are presented in this report.

All of the simulants described in this report fall within the physical property target ranges specified for processing in the LAWPS, but they do not span the entire range of specified physical properties. Simulants that are bounding with respect to a particular physical property or result in specific processing performance would have to be adjusted from these recipes or developed separately.

Acknowledgements

The authors would like to thanks Pacific Northwest National Laboratory staff members who contributed to the completion of this report. Experimental and analysis support staff included Margaret (Peggy) Smoot, Diana Linn, Nathan Canfield, Jared Kroll, Viviana Gervasio, Ian Leavy, Steven Baum, John Stephenson, and Michelle Snyder. The authors are also grateful for the technical discussions and support provided by Scot Rassat, Lenna Mahoney, Rick Shimskey, and Richard Daniel. The report was greatly improved due to the technical review of Sandy Fiskum, the editorial review of Matthew Wilburn, and the quality support provided by Bill Dey.

The work discussed in this report was funded by Washington River Protection Solutions, LLC, and many of their staff were also helpful in shaping this document. Special thanks to Matt Landon, Kevin Ard, and Jacob Reynolds of Washington River Protection Solutions for their support during the initial phase of this work. Other reviewers have provided helpful comments or suggestions along the way, and the authors are appreciative of their input:

- Peter Benson (AECOM – Waste Treatment Completion Company)
- Clark Carlson (Pacific Northwest National Laboratory)
- Dave Herman (Savannah River National Laboratory)
- William King (Savannah River National Laboratory)
- Rose Russell (Washington River Protection Solutions)
- Sahid Smith (Department of Energy – Office of River Protection)

Acronyms and Abbreviations

CD	Critical Decision
CFF	cross-flow filtration
DFLAW	Direct Feed Low-Activity Waste
DOE-ORP	U.S. Department of Energy Office of River Protection
FIO	For Information Only
HTWOS	Hanford Tank Waste Operations Simulator
ILAW	immobilized low-activity waste
LAW	low-activity waste
LAWPS	Low-Activity Waste Pretreatment System
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
SOW	statement of work
sRF	spherical resorcinol-formaldehyde
TC	total carbon
TIC	total inorganic carbon
TOC	total organic carbon
WRPS	Washington River Protection Solutions, LLC
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XRD	X-ray diffraction

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1.0 Introduction

The primary mission of the U.S. Department of Energy Office of River Protection (DOE-ORP) is to retrieve and process approximately 56 million gallons of radioactive waste from 177 underground tanks located on the Hanford Site. The Hanford waste tanks are currently operated and managed by Washington River Protection Solutions, LLC (WRPS). As part of tank farm operations, WRPS supports DOE-ORP's waste retrieval mission. An important element of the DOE-ORP mission is the construction and operation of the Hanford Tank Waste Treatment and Immobilization Plant (WTP). The WTP is tasked with separating the waste into low-activity waste (LAW) and high-level waste fractions and immobilizing these fractions by vitrification. The primary contractor supporting the construction of the WTP is Bechtel National, Inc.

To support early production of immobilized LAW, the Direct Feed Low-Activity Waste (DFLAW) process has been proposed. In the DFLAW process, LAW (supernatant) is sent to the Low-Activity Waste Pretreatment System (LAWPS) for filtration and cesium removal. The resultant treated waste is delivered to the WTP LAW Vitrification Facility for immobilization. The conceptual design and ongoing technology maturation of the LAWPS facility are being conducted by WRPS, but the DFLAW process also necessitates interfaces between WRPS and Bechtel National, Inc. to deliver the treated LAW from the LAWPS to the WTP for vitrification. Before the feed is transferred to the WTP LAW Vitrification Facility, tank supernatant waste will be pretreated in the LAWPS to meet the WTP LAW waste acceptance criteria. The key process operations for treating the waste include solids separation (by cross-flow filtration) and cesium removal (by ion exchange).

Figure 1.1 shows a general schematic of the anticipated process streams and unit operations.

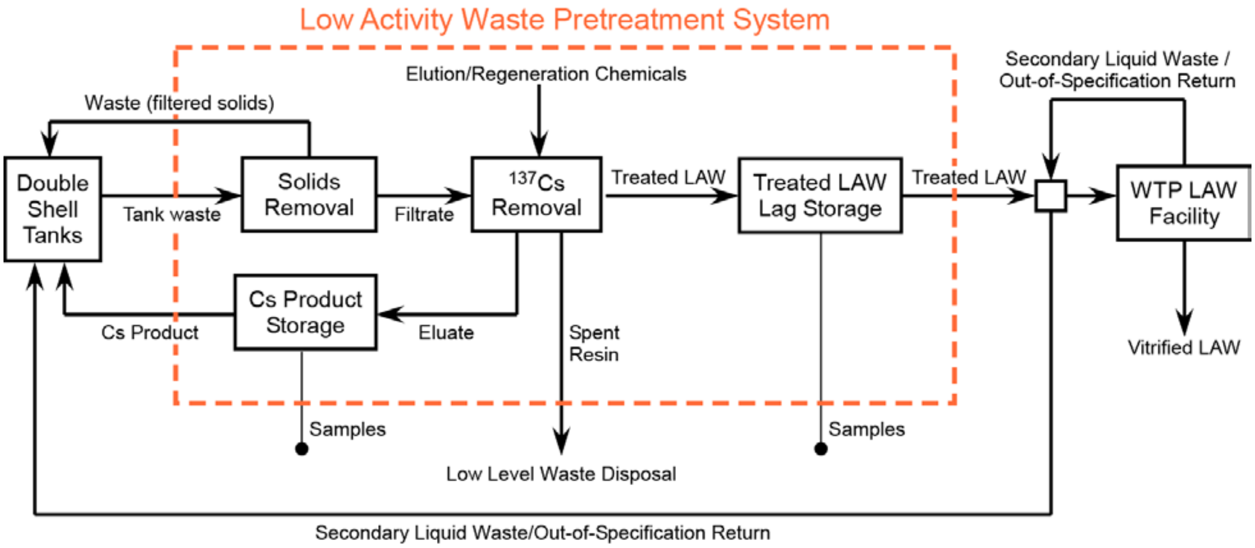

Figure 1.1. General Conceptual Schematic of the LAWPS Facility Unit Operations and Process Streams

To support LAWPS design selections prior to key project milestones (Critical Decisions[1]) and to improve the technology maturation level of the LAWPS, WRPS has planned both an integrated engineering-scale test facility using prototypic equipment and a full-scale test apparatus for the ion exchange columns. To support these larger-scale facilities, WRPS identified five technical tasks in statements of work (SOWs)[2,3,4] to be performed by Pacific Northwest National Laboratory (PNNL). These tasks are distinct from the larger-scale test facilities and are intended to help achieve the following objectives:

- Provide technical information or data that
  - supports refinements or simplifications of larger-scale test facilities; or
  - provides expected performance of unit operations (guiding larger-scale operation or providing scale-up data).
- Support the safety basis of the planned LAWPS facility, specifically regarding hydrogen management.

The five PNNL technical tasks consist of the following focus areas:

1. Development of LAW waste simulants
2. Small-scale cross-flow filtration (CFF) testing with simulants
3. Gas generation measurements in the presence of spherical resorcinol-formaldehyde (sRF) ion exchange resin
4. Gas retention/release dynamics and fluidization of sRF ion exchange resin
5. General technical support to the larger-scale testing

Tasks 1 and 2 are focused on providing technical information to inform the larger-scale test facilities, whereas the Tasks 3 and 4 support the LAWPS facility safety basis. Task 5 supports the larger-scale testing directly.

This report details work performed to address Task 1, development of LAW waste simulants. The technical approach to simulant development as chemically representative of the waste streams anticipated to be fed to the LAWPS through the 10-year mission for DFLAW is described. Four simulants of varying sodium concentrations were prepared, formulations were modified as needed to achieve target properties, and the final simulant formulations were prepared and characterized. This report presents the final simulant recipes and characterization data for these four simulants.

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[1] Critical Decisions (CDs) are defined in DOE O 413.3B, *Program and Project Management for the Acquisition of Capital Assets*, dated 12/20/2016. The relevant CDs being supported as described in the text of this report are CD-2, Approve Performance Baseline and/or CD-3, Approve Start of Construction/Execution.

[2] Statement of Work, July 29, 2015, Requisition #279909, LAWPS Integrated Support Testing, Rev. 1.

[3] Statement of Work, April 4, 2016, Requisition #279909, LAWPS Integrated Support Testing, Rev. 2.

[4] Statement of Work, August 31, 2016, Requisition #279909, LAWPS Integrated Support Testing, Rev. 3.

2.0 Quality Assurance

This work was conducted with funding from WRPS under contract 36437-187, *“LAWPS Integrated Support Testing,” Low-Activity Waste Pretreatment System (LAWPS) Integrated Testing Project*. The work was conducted as part of PNNL project 67535.

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 QA-NSLW-numbered procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work.

Specific details of this project's approach to assuring quality are contained in the LAWPS Testing Program Quality Assurance Plan (67535-QA-001, Revision 0) and associated implementing procedures. The QA plan describes how the procedures of the WWFTP QA program were used in conducting the 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 proper technical and QA training prior to performing quality-affecting work.

3.0 Selection Basis for Simulant Compositions

The objective of the simulant development task was to develop a series of simulants encompassing a wide range of sodium concentrations (4.0 to 8.0M) that are representative of the LAW expected to be processed in the LAWPS facility. Some or all of these simulant recipes are planned to be used during operation of the larger-scale tests (LAWPS engineering-scale integrated test and full-scale ion exchange column test), and all of the simulants will be tested in the small-scale CFF system (PNNL Task 2). Thus, the simulants presented in this report are key components in lending technical defensibility to the data collected from tests at multiple scales. These simulant formulations include four sodium concentrations: 5.6M Na (nominal), 8.0M Na (high), 4.0M Na, and 6.0M Na. In the SOW (most recent version being Revision 3)[1], WRPS requested that the simulants contain the following key attributes (as a minimum):

- Important chemical species
  - Sodium oxalate
  - Non-radioactive cesium
  - Sodium hydroxide
  - Sodium nitrate
  - Potassium-containing salts
  - Phosphate-containing salts
- Important physical characteristics
  - Solution density – 1.0 to 1.35 g/mL
  - Solution viscosity – 1 to 15 mPa-s (or cP)
  - Undissolved solids concentration – 0 to 3.3 wt%
  - Solids particle size – 0.01 to 210 µm

These properties are based on expected LAW process streams, as outlined in the LAWPS specification document (Servin 2016), and the physical properties are necessarily broad in order to span the range of expected properties that may be processed during LAWPS operations. Note that the current revision (Revision 6) of the specification document (Ansolabehere 2016) contains the same information as Servin 2016 (Revision 4); therefore, reference to values from Servin 2016 in this report is equivalent to referencing the same information found in Ansolabehere 2016. The SOW also provides more specific guidance on target or nominal properties for some of the simulants, as shown in Table 3.1. However, if achieving a physical property value required adding chemically unrepresentative species, priority was given to maintaining the representative chemical compositions over matching physical property targets. The viscosity targets for the 5.6 and 8.0M Na simulants, in particular, were expected to be challenging to achieve without specific additives that were not likely to be in the set of important chemical species.

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[1] Statement of Work, August 31, 2016, Requisition #279909, LAWPS Integrated Support Testing, Rev. 3.

Table 3.1. Target/Nominal Physical Properties for Simulants Established in SOW

Property	5.6M Na Simulant	8.0M Na Simulant	4.0M Na Simulant	6.0M Na Simulant
Density (g/mL)	1.28	1.35	n/a	Upper end of range
Viscosity (mPa-s)	11	15	n/a	Upper end of range
Solid Speciation	Oxalate solids	Self-precipitating solids	n/a	Self-precipitating solids
Solid Concentration (wt%)	0.8	n/a	0.1	n/a
Solid Particle Size (μm)	7.5 [d_{50}]	n/a	Lower end of range	Upper end of range

To this end, the starting basis for the simulant development process was to target the average concentration values of selected chemical species given in Servin 2016, hereafter called the "specification formulation." Since the specification formulation is approximately 5.6M Na, it was used as the basis for the nominal simulant, and the starting point for the other simulants were scaled proportionally with the target sodium concentration. The following sections describe the development of the simulant recipes, including preparation of small test batches with supporting analysis performed.

3.1 Simulant Literature Comparison

To assess the choice of the specification formulation as a basis for simulant compositions, the simulant literature was surveyed. Several different existing LAW simulant compositions with sodium concentrations near the target of the nominal simulant (5.6M) were collected from historical literature on Hanford waste and compared with the average concentrations of chemical species provided in the specification formulation. These historical simulants are not inclusive but were selected to be representative of LAW waste simulants. The majority of these historical simulants had sodium concentrations nearer to 5.0M than 5.6M. The simulants and component concentrations are shown in Table 3.2 along with a reference to the simulant preparation source. The simulants are also compared graphically in Figure 3.1, where the specification formulation is compared to the median values from the historical simulants and the range of concentrations present in those simulants (minimum and maximum). Note that in the data provided in Figure 3.1, all the simulants were scaled to the nominal sodium concentration assuming that each individual chemical species would increase or decrease proportionally with the ratio of the simulant's sodium concentration to the nominal concentration. For most simulants, this is a small adjustment and scaling the concentrations should be a reasonable estimate of constituent concentrations. The largest scale factor was for the DSSF-7 simulant (from 7.0M to 5.6M Na).

Though each of these simulants was used for a different testing program and therefore was designed to meet different criteria, the LAW simulants were fairly similar. They varied in the absolute concentration of some chemical species, but all of them contained the same major constituents as the specification formulation and in similar concentrations. The historical simulants varied most significantly in the range of concentrations for Al, K, and CO_3, but in all cases the specification formulation is within the range and consistent with the median concentrations. Based on this observation, it appeared feasible to begin the simulant development process using the specification formulation (or a formulation appropriately scaled for sodium concentration) and then adjust from that starting point to obtain the desired simulants.

The case for using the specification formulation as the starting point for simulant development is strengthened when the projected feed vector data based on Hanford Tank Waste Operations Simulator (HTWOS) models are examined (see Mills 2016 for more details). The feed vector contains process simulation data of LAW batches, including constituent concentrations of the batches expected to be processed in the LAWPS facility. The feed vector represents the “product” stream from the LAWPS and thus differs from the feed to LAWPS in two significant ways:

1. The Cs concentration is reduced by a large factor (due to being processed through ion exchange columns) and is effectively negligible.
2. All or nearly all of the solid particles are separated out during cross-flow filtration operation in the LAWPS, and are also effectively negligible.

Both of these differences will not meaningfully affect the comparison of the feed vector information to the specification composition, other than negating the usefulness of any comparisons between Cs concentrations. There are 199 batches in total, and they were used to calculate statistical information about the expected concentrations of the same major constituents present in the specification formulation. The maximum, minimum, mean, and median concentrations of the 199 batches were computed; Figure 3.2 compares the median feed vector concentrations with the specification formulation. It was found that the proposed starting simulant composition was either very close to the median feed vector values or within the range of minimum and maximum feed vector concentrations (as indicated by error bars in Figure 3.2) for all constituents. Note that the comparisons with historical LAW simulants and projected feed vectors discussed in this section are strictly based on chemical composition and did not consider comparisons of any other properties that may be important, such as physical properties (density, rheology), solid particles (concentration, particle size, speciation), or filtration/ion exchange processing performance. Since simulants have been used for an array of purposes, the ranges of physical properties and solid particles are more difficult to compare among simulants.

Table 3.2. Previous Simulant Composition Comparisons

Species	Avg for LAWPS(a) (M)	SY-101 Simulant(b) (M)	AN-105 Simulant(c) (M)	AP-101 Actual Diluted Waste(d) (M)	DSSF-7(b) (M)	A-101 Solution(b) (M)	NCAW Stock Solution(b) (M)	AZ-102 Solution(b) (M)	Cold Dissolved Saltcake (S/U Tanks)(e) (M)	Diluted SLAW Simulant(f) (M)
Na	5.61E+00	5.05E+00	5.34E+00	5.00E+00	7.00E+00	5.01E+00	5.92E+00	4.99E+00	5.00E+00	5.00E+00
Al	1.66E-01	4.15E-01	7.36E-01	2.59E-01	7.21E-01	4.23E-01	5.20E-01	4.30E-01	6.40E-02	3.40E-01
K	1.22E-01	3.40E-02	9.50E-02	7.10E-01	9.45E-01	3.70E-02	1.40E-01	1.20E-01	1.24E-02	3.40E-02
Cs	1.04E-04	4.19E-05	6.09E-05	4.51E-05	7.00E-05	---	---	5.00E-04	5.00E-08	---
CO_3	5.23E-01	3.80E-02	1.04E-01	4.46E-01	1.47E-01	6.50E-01	2.40E-01	2.30E-01	4.75E-01	2.30E-01
SO_4	6.61E-02	5.00E-03	4.00E-03	3.73E-02	8.00E-03	1.30E-01	1.80E-01	1.50E-01	9.00E-02	7.10E-02
Cl	9.46E-02	---	1.28E-01	4.09E-02	1.00E-01	5.60E-02	---	---	4.38E-02	4.50E-02
F	6.51E-02	9.20E-02	5.00E-03	2.80E-03	---	2.10E-02	1.07E-01	8.90E-02	3.16E-02	1.24E-01
PO_4	4.32E-02	2.00E-02	3.00E-03	1.24E-02	1.40E-02	2.20E-02	---	2.50E-02	4.92E-02	7.60E-02
C_2O_4	1.27E-02	---	3.00E-03	1.78E-02	---	9.00E-03	---	---	1.18E-02	2.30E-02
NO_2	1.02E+00	1.09E+00	1.21E+00	7.07E-01	1.51E+00	8.30E-01	5.20E-01	4.30E-01	4.24E-01	6.19E-01
NO_3	1.78E+00	1.29E+00	1.33E+00	1.68E+00	3.52E+00	9.20E-01	1.87E+00	1.67E+00	2.51E+00	1.57E+00
OH (free)	1.41E+00	2.11E+00	1.72E+00	1.94E+00	1.75E+00	1.09E+00	2.00E+00	1.68E+00	4.85E-01	---

(a) Servin 2016
(b) Golcar et al. 2000
(c) Burgeson et al. 2004
(d) Russell et al. 2003
(e) Rassat et al. 2003
(f) Crawford et al. 2014.

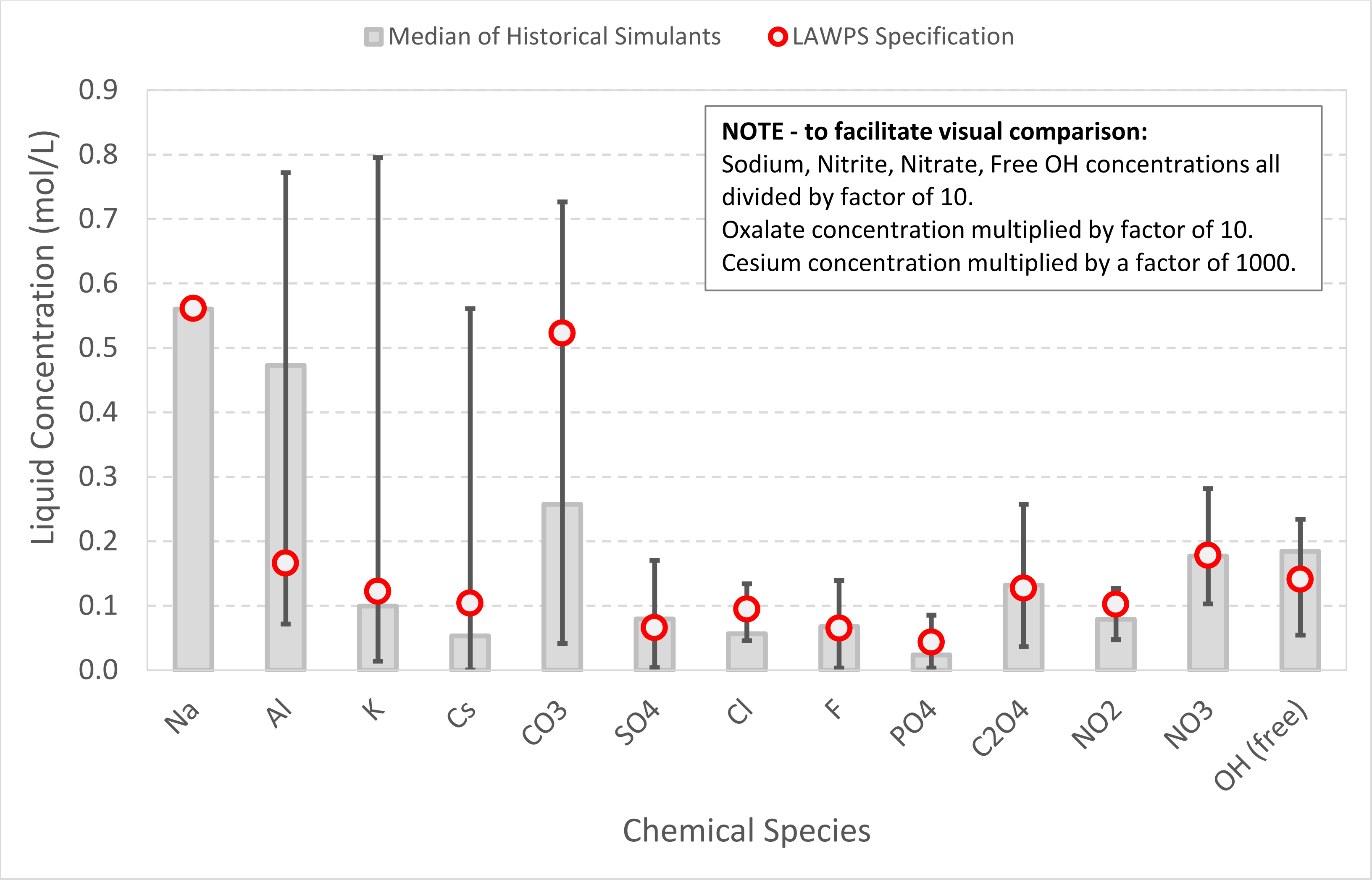

Figure 3.1. Comparison of the LAW Historical Simulants Median Species Concentration (gray bars) with the LAWPS Specification Formulation Species Concentrations (red open circles). With the exception of the sodium concentration (which is scaled), the median values are also shown with the bounds of the range of values, i.e., the minimum and maximum species concentration in the LAW historical simulant data set.

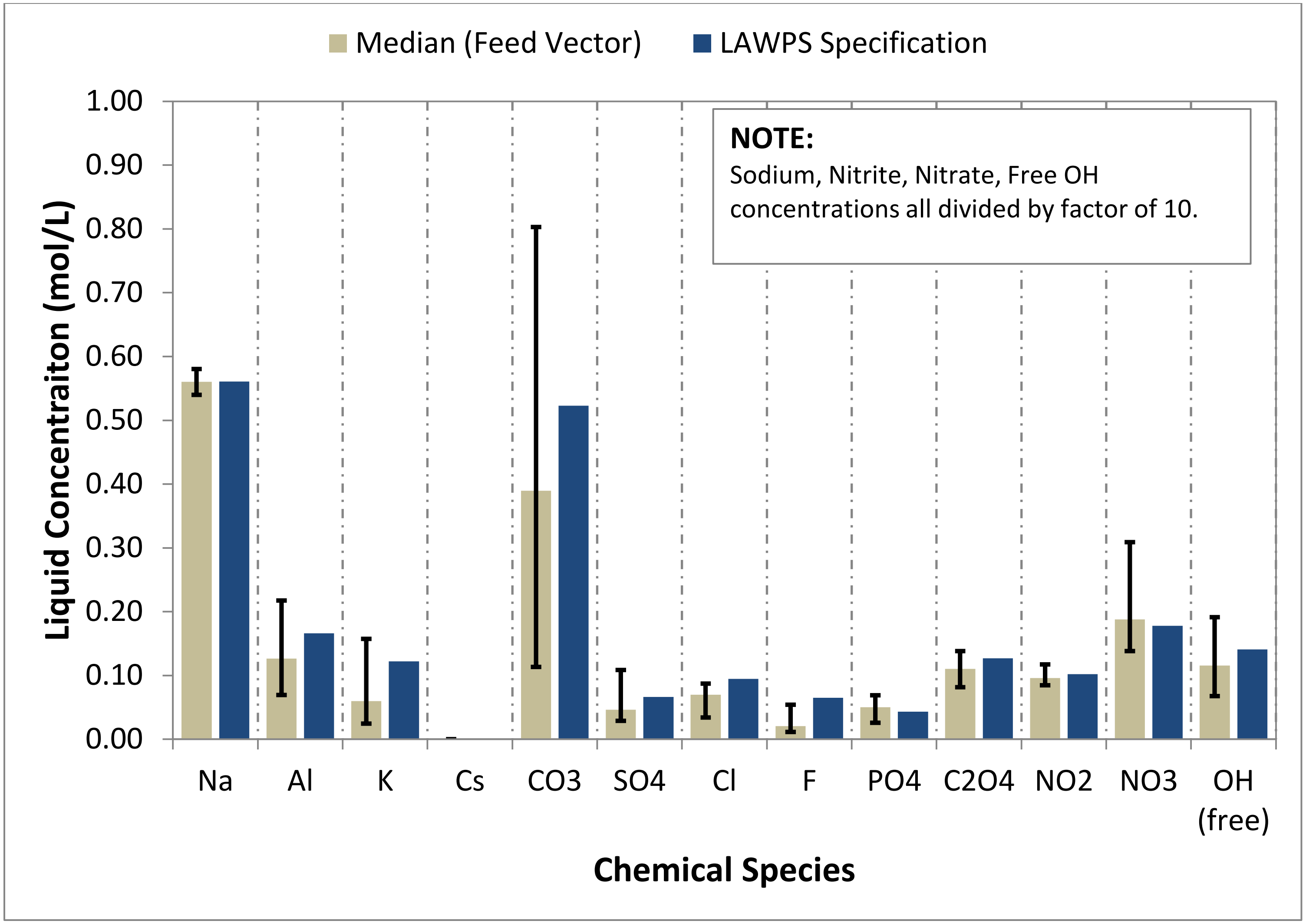

Figure 3.2. LAWPS Specification Formulation Species Comparison with Range of Concentrations Projected for WTP LAW Feed Vectors

3.2 Initial Simulant Compositions

Four simulants containing different amounts of sodium were developed for this work. The initial compositions of supernate (solid components are not included) are shown in Table 3.3 through Table 3.6. The initial composition in Table 3.3 was generated from the average values given in the specification formulation. Table 3.4 through Table 3.6 preserve the constituent ratio from Table 3.3 while scaling the simulant to the specified sodium concentration. Based on the dissolution/precipitation behavior of these compositions and supporting information from other sources (see Section 3.0), the initial simulant compositions were modified as needed to obtain the desired physical and chemical properties. As directed by Revision 1 of the SOW,[1] the target solid phase for the 5.6M Na and 8.0M Na simulants was sodium oxalate. Revision 2 of the SOW[2] (and likewise, Revision 3,[3] which had no impact on the simulant development scope) relaxed the constraint of the solid phase being sodium oxalate for these simulants, and the newly requested 4.0M Na and 6.0M Na simulants had different solid phases in order to meet the required parameters.[4]

There are three notable differences between the Table 3.3 composition and the specification formulation, listed below. When the specification formulation was scaled to create compositions of other sodium concentrations, these differences persisted:

1. The carbonate concentration was reduced by approximately 10% to limit the possibility of undesired carbonate precipitation (or solubility difficulties) during simulant preparation and use.
2. There were no specific organic constituents (other than sodium oxalate) that were planned to be added, i.e., PNNL did not propose to achieve the total organic carbon concentration target in the specification formulation due to the complexity in determining the appropriate speciation that is representative of LAW. This is notable because the organic concentration given in Servin 2016 (0.177 M) is the only component with a concentration greater than 0.1 M that is not included in the simulant.
3. The Cl^- concentration is ~30% higher than the specification formulation value. This was chosen for convenience only, since potassium was added as KCl and the potassium target value was considered to be more important to meet since it affects ion exchange performance.

3.2.1 5.6M Na (Nominal) Simulant

Table 3.3 shows the initial chemical composition for the 5.6M (nominal) Na simulant. The values for the target physical properties were the nominal values from the LAWPS specification document (Servin 2016): 1.28 g/mL for density, 11 mPa-s for the viscosity, solids concentration of 0.8 wt%, and an average solids particle size of ~7.5 µm when the simulant is at 25 °C (to the extent practical).

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[1] Statement of Work, July 29, 2015, Requisition #279909, LAWPS Integrated Support Testing, Rev. 1.

[2] Statement of Work, April 4, 2016, Requisition #279909, LAWPS Integrated Support Testing, Rev. 2.

[3] Statement of Work, August 31, 2016, Requisition #279909, LAWPS Integrated Support Testing, Rev. 3.

[4] Although the sodium oxalate constraint was relaxed as stated, it was still maintained as the target solid component for the 5.6M Na simulant.

Table 3.3. LAWPS 5.6M Na Simulant Initial Liquid Phase Composition

Species	M	Component	FW (g/mole)	g/L
Al	1.66E-01	$Al(NO_3)_3$-$9H_2O$	375.13	62.27
Cs	1.04E-04	$CsNO_3$	194.91	0.02
NO_2	1.02E+00	$NaNO_2$	69.00	70.38
NO_3	1.78E+00	$NaNO_3$	84.99	108.96
PO_4	4.32E-02	Na_3PO_4-$12H_2O$	380.12	16.42
SO_4	6.61E-02	Na_2SO_4	142.04	9.39
CO_3	4.67E-01	Na_2CO_3	105.99	49.50
C_2O_4	1.27E-02	$Na_2C_2O_4$	134.00	1.70
Cl	1.22E-01	KCl	74.55	9.10
K	1.22E-01			
F	6.51E-02	NaF	41.99	2.73
OH free	1.41E+00	NaOH	40.00	82.95
Na	5.60E+00			

3.2.2 8.0M Na (High) Simulant

Table 3.4 shows the initial chemical composition for the 8.0M (high) Na simulant. The values for the target physical properties were the upper values of the physical characteristics listed Section 3.0: a density of approximately 1.35 g/mL and a viscosity of approximately 15 mPa-s. The chemical constituents were maintained in the same ratio as those of the 5.6M Na simulant.

Table 3.4. LAWPS 8.0M Na Simulant Initial Liquid Phase Composition

Species	M	Component	FW (g/mole)	g/L
Al	2.37E-01	$Al(NO_3)_3$-$9H_2O$	375.13	88.80
Cs	1.48E-04	$CsNO_3$	194.91	0.03
NO_2	1.45E+00	$NaNO_2$	69.00	100.36
NO_3	2.54E+00	$NaNO_3$	84.99	155.38
PO_4	6.16E-02	Na_3PO_4-$12H_2O$	380.12	23.42
SO_4	9.43E-02	Na_2SO_4	142.04	13.39
CO_3	6.66E-01	Na_2CO_3	105.99	70.58
C_2O_4	1.81E-02	$Na_2C_2O_4$	134.00	2.43
Cl	1.74E-01	KCl	74.55	12.97
K	1.74E-01			
F	9.28E-02	NaF	41.99	3.90
OH free	2.01E+00	NaOH	40.00	118.29
Na	8.00E+00			

3.2.3 4.0M Na Simulant

The 4.0M Na simulant was intended to represent a more dilute feed that could be processed by the LAWPS. The target for this simulant was a lower concentration of undissolved solids (0.1 wt%) that are also on the lower end of the particle size scale with relevant size distribution at 25 °C. The chemical constituents were maintained in the same ratio as those of the final 5.6M Na simulant composition, and are shown in Table 3.5.

Table 3.5. LAWPS 4.0M Na Simulant Initial Liquid Phase Composition

Species	M	Component	FW (g/mole)	g/L
Al	1.19E-01	$Al(NO_3)_3$-$9H_2O$	375.13	44.48
Cs	7.43E-05	$CsNO_3$	194.91	0.01
NO_2	7.29E-01	$NaNO_2$	69.00	50.27
NO_3	1.27E+00	$NaNO_3$	84.99	77.83
PO_4	3.09E-02	Na_3PO_4-$12H_2O$	380.12	11.73
SO_4	4.72E-02	Na_2SO_4	142.04	6.71
CO_3	3.34E-01	Na_2CO_3	105.99	35.36
C_2O_4	9.07E-03	$Na_2C_2O_4$	134.00	1.22
Cl	8.71E-02	KCl	74.55	6.50
K	8.71E-02			
F	0.00E+00	NaF	41.99	0.00
OH free	1.01E+00	NaOH	40.00	59.25
Na	4.00E+00			

3.2.4 6.0M Na Simulant

The 6.0M Na simulant targeted properties were near the upper values of the physical characteristics listed Section 3.0. The chemical constituents were maintained in the same ratio as those of the 5.6M Na simulant, and are shown in Table 3.6. This simulant was configured to have self-precipitating solids by adding F to the simulant.

Table 3.6. LAWPS 6.0M Na Simulant Initial Liquid Phase Composition

Species	M	Component	FW (g/mole)	g/L
Al	1.78E-01	$Al(NO_3)_3$-$9H_2O$	375.13	66.72
Cs	1.11E-04	$CsNO_3$	194.91	0.02
NO_2	1.09E+00	$NaNO_2$	69.00	75.40
NO_3	1.91E+00	$NaNO_3$	84.99	116.75
PO_4	4.63E-02	Na_3PO_4-$12H_2O$	380.12	17.59
SO_4	7.08E-02	Na_2SO_4	142.04	10.06
CO_3	5.00E-01	Na_2CO_3	105.99	53.03
C_2O_4	1.36E-02	$Na_2C_2O_4$	134.00	1.82
Cl	1.31E-01	KCl	74.55	9.75
K	1.31E-01			
F	6.98E-02	NaF	41.99	2.93
OH free	1.51E+00	NaOH	40.00	88.88
Na	6.00E+00			

4.0 Simulant Preparation

The starting compositions of the four chemical simulants (described in Section 3.2) were prepared to assess their suitability as simulants. Adjustments were made to address issues related to solubility on an as-needed basis. The adjustments included heating, modification of component masses, or substitution of components.

Each simulant was prepared in a 500-mL volumetric flask at the target concentration. Aluminum nitrate was added first and then sodium hydroxide (50% solution) was added, precipitating aluminum to aluminum trihydroxide. With continued sodium hydroxide addition, the aluminum trihydroxide dissolved into the tetrahydroxide anionic complex. The most-soluble salts ($NaNO_3$, $NaNO_2$, $CsNO_3$, and KCl) were added next, with the least-soluble salts (Na_2SO_4, Na_3PO_4, Na_2CO_3, and $Na_2C_2O_4$) added last so it could be determined during preparation which components were causing solubility issues, if any.

The general approach to simulant preparation was as follows. Deionized water corresponding to about 30% of the final targeted simulant volume was initially added to a tared 500-mL volumetric flask. Each chemical was weighed and added directly, one at a time, to the water with stirring until completely dissolved. More water was added as needed to help maintain the chemicals in solution. After all chemicals were added, water was added to a few mLs below the target amount, and the simulant was heated, if needed, to help all of the chemicals completely dissolve. After cooling to room temperature, the simulant was brought up to the final target volume (500 mL) with more deionized water. The simulants were assessed against the desired chemical and physical properties to determine if the formulation needed to be adjusted. Priority was given to maintaining a representative chemical composition with relatively simple solids that led to a reproducible amount of undissolved solids upon makeup (where applicable) over matching physical properties.

Once the final formulations were obtained, a 500-mL validation batch of each simulant was prepared to perform a suite of characterization measurements. These characterization measurements included chemical analyses for dissolved constituents, total solids, dissolved solids, undissolved solids, particle size distribution, viscosity as a function of temperature, and crystalline solid identification.

Once satisfactory recipes were determined, larger, multi-liter size batches of each of the simulants were prepared for use in the CFF testing (to be described in a future report). Other than the CFF batches, simulant preparation was not conducted at a volume greater than 500 mL; consequently, the scalability of the simulant formulations found in this report cannot be verified. The results of the 500-mL preparations are discussed below for each simulant.

4.1 5.6M Na (Nominal Na) Simulant Results

When the initial (target) simulant (Table 3.3) was prepared in a 500-mL volumetric flask, all chemicals went into solution when heated to ~70 °C for 20 min. However, crystals formed in the supernate while cooling after heating. The solids were filtered using a 0.45-micron filter, rinsed with ethanol three times, and dried in an oven at 85 °C. The dried solids represent 0.4 wt% of the total simulant mass. The solids were analyzed by X-ray diffraction (XRD) and were found to be a mixture of sodium aluminum phosphate and sodium fluorophosphates, as shown in Figure 4.1[1] (For Information Only). Based on this observation, the simulant formulation was altered slightly by eliminating the NaF and increasing the sodium oxalate.

This second simulant preparation remained very clear at 50 °C until the sodium oxalate was added. Once sodium oxalate was added, the solution was heated to ~70 °C for 30 min, and the solution remained very cloudy and never became clear. After cooling, the solids were filtered using a 0.45-micron filter, rinsed with ethanol three times, and dried in an oven at 85 °C. After drying, there were 0.4 wt% solids present. Based on XRD analysis (Figure 4.2, For Information Only) and when the solids appeared, it was assumed that oxalate was above the solubility limit at this level, preventing it from entering the solution. Based on this observation, the formulation was altered again to reduce the sodium oxalate level and increase the NaOH to maintain the Na concentration.

In the third simulant preparation, all chemicals except the sodium oxalate were added and then the simulant was heated to 50 °C. The solution was very clear. Once the simulant was at 50 °C, the sodium oxalate was added, and the solution was heated to 75 °C and held for ~25 min, at which point the solution only had a slight haze left in it. The solution was cooled overnight without any significant solids forming. Based on this observation, 5.04 g of sodium oxalate was added to the solution. Since it was unknown whether any of the 5.04 g of additional oxalate would dissolve, more solids were added than the amount needed (approximately 3.23 g) to bring it to a target of 0.8 wt% undissolved solids. Only a negligible amount of sodium oxalate solids dissolved, so the formulation was adjusted to call for adding the amount of solid sodium oxalate to yield 0.8 wt%. This formulation matched the target properties of density and, upon adding an adjusted amount of sodium oxalate, wt% undissolved solids, so it was chosen as the final composition and is shown in Table 4.1.

Table 4.1. LAWPS Nominal Na (5.6M) Simulant Composition

Simulant Component	Composition (g species/kg liquid)	Composition (g species/L liquid)
$Al(NO_3)_3$-$9H_2O$	49.82	62.27
NaOH (50% solution, w/w)	132.73	165.91
$CsNO_3$	0.016	0.020
KCl	7.28	9.10
Na_2SO_4	7.51	9.39
$NaNO_2$	56.30	70.38
$NaNO_3$	87.17	108.97
Na_3PO_4-$12H_2O$	13.14	16.42
Na_2CO_3-H_2O	46.33	57.91
$Na_2C_2O_4$(a)	1.36	1.70
Water, Deionized	598.35	747.94

(a) Upon makeup of supernate composition listed above, an additional amount of $Na_2C_2O_4$ solids should be added: 8.065 g solid $Na_2C_2O_4$/kg supernate or 10.081 g solid $Na_2C_2O_4$/L supernate.

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[1] The XRD analyses are for information only (FIO) because they were used as a screening tool during simulant development. Only the solids for the final recipe were analyzed with the appropriate QA requirements, i.e. as described in Section 2.0, to be reportable.

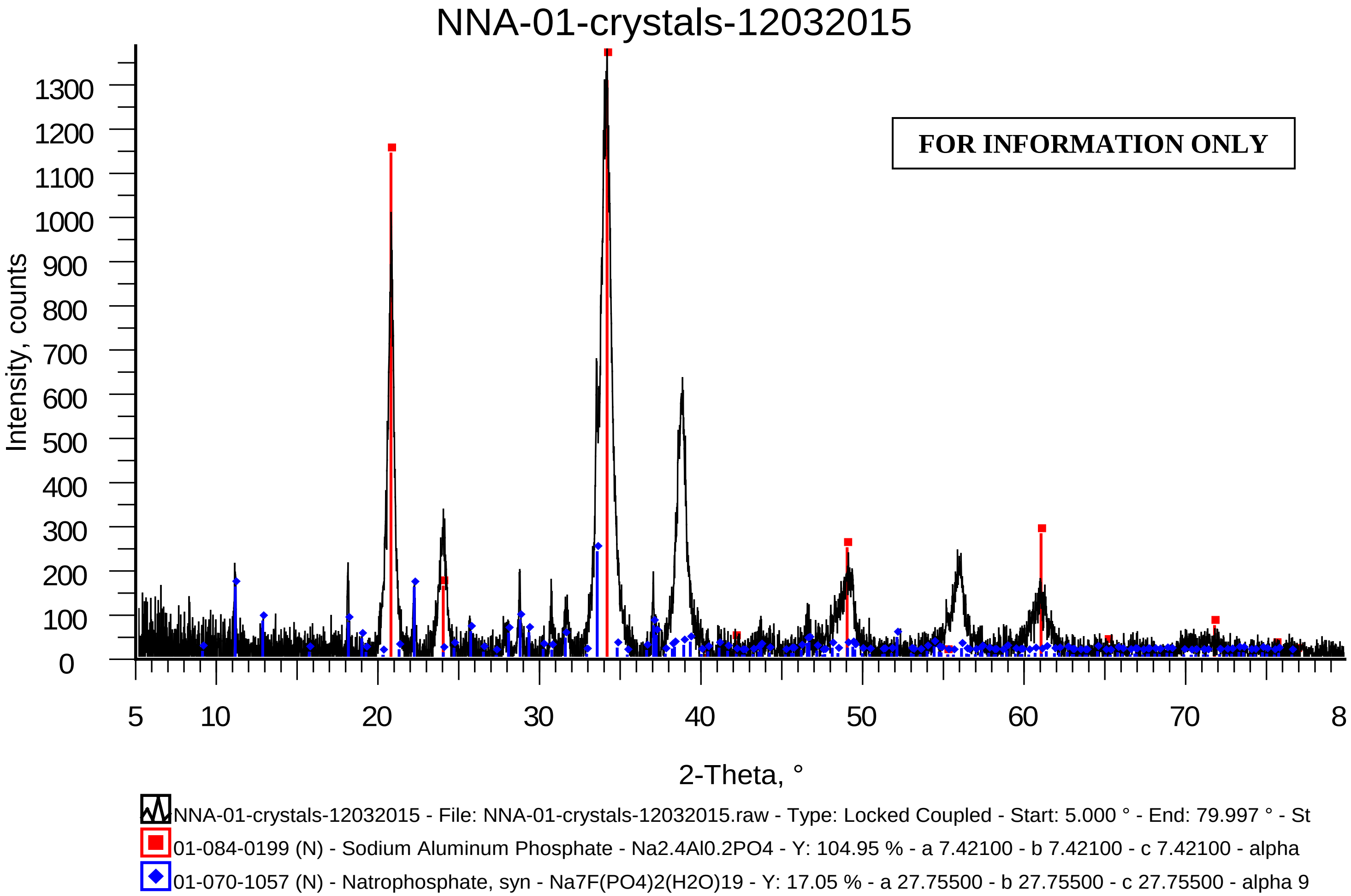
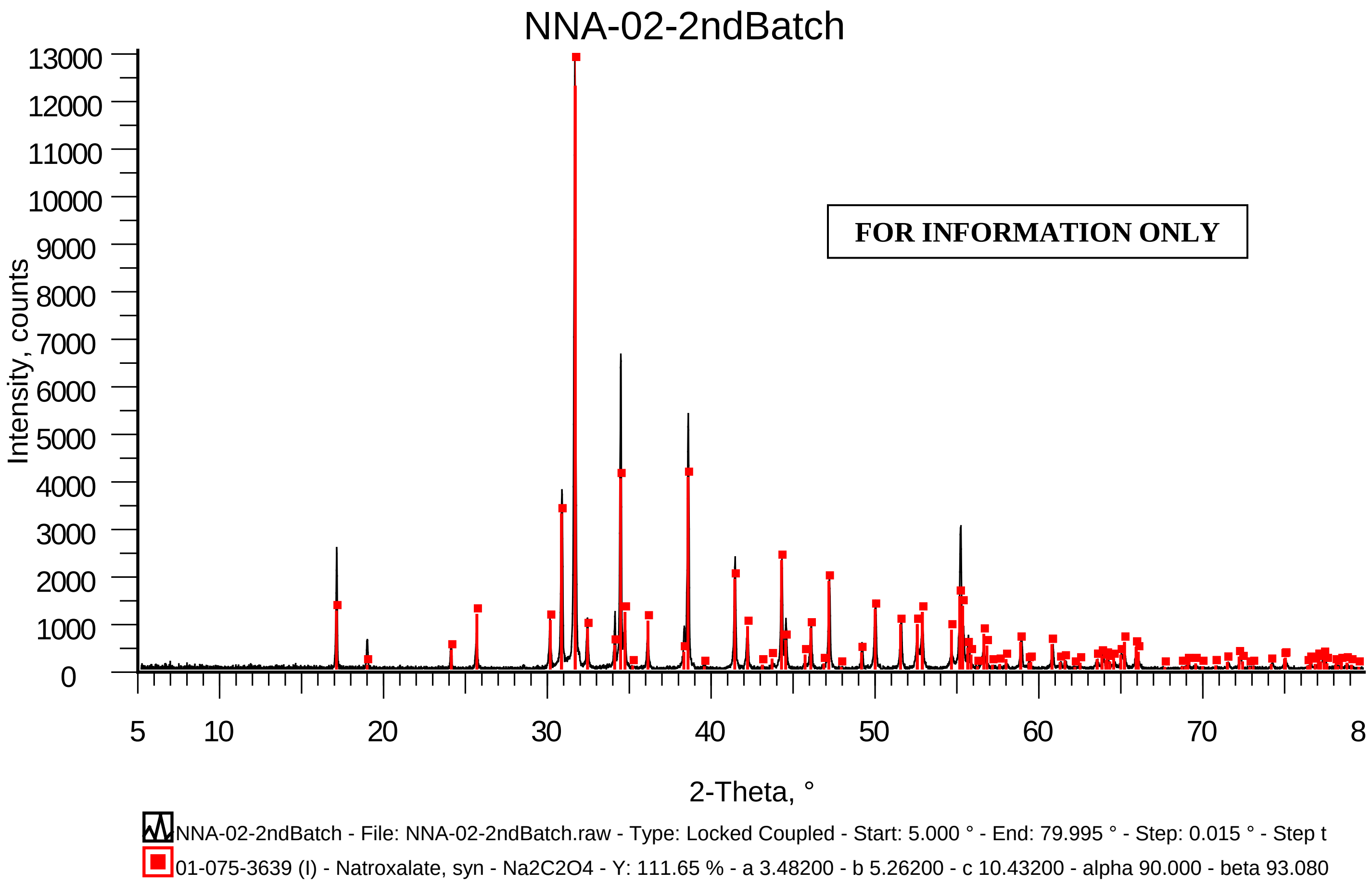


Figure 4.1. XRD Pattern of Initial Nominal Na Concentration Simulant Solids



FOR INFORMATION ONLY

Figure 4.2. XRD Pattern of Second Nominal Na Concentration Simulant Recipe Solids

4.2 8.0M Na (High Na) Simulant Results

Multiple sample simulant batches were prepared in the laboratory to iterate to the simulant recipe that is provided in this document. Based on the results from the 5.6M Na simulant, fluoride was eliminated and all the remaining component ratios were maintained while increasing the Na from 5.6M to 8.0M.

When the initial simulant was prepared in a 500-mL volumetric flask, all chemicals were added except for oxalate and carbonate. When heated to 45 °C, the solution was clear with few flakes of phosphate present. After oxalate and carbonate were added and the simulant was heated to 60 °C, it remained cloudy and never cleared. Based on this observation, the amounts of oxalate and phosphate added were reduced to the concentrations in the 5.6M Na simulant while maintaining the Na at 8.0M by increasing the sodium hydroxide (50% solution).

The second solution remained very clear at 50 °C until the sodium carbonate was added. Once the sodium carbonate was added, the solution was heated to ~70 °C for 30 min and remained very cloudy and never became clear. Based on this observation, the amount of carbonate was reduced slightly (to 0.65 M) while maintaining the lower concentrations of oxalate and phosphate.

The third simulant behaved very similarly to the second one, with the sodium carbonate still causing additional solids to precipitate. The solids were filtered using a 0.45-micron filter, rinsed with ethanol three times, and dried in an oven at 85 °C. After drying, there were 0.5 wt% solids present. Based on a qualitative XRD analysis (FIO) shown in Figure 4.3, it was found that the solids were a mixture of sodium oxalate, sodium phosphate, and sodium carbonate. Based on this observation, the carbonate was also reduced to the concentration in the 5.6M Na simulant while maintaining the Na at 8.0M by increasing the sodium hydroxide (50% solution) to determine if that improved solubility.

Reducing the carbonate did not seem to improve solubility in the simulant and still resulted in precipitated solids after heating. The solids were filtered using a 0.45-micron filter, rinsed with ethanol three times, and dried in an oven at 85 °C. After drying, there were ~1.0 wt% solids present. Because the solubility did not improve, it was concluded that this composition was above the solubility limit of oxalate, phosphate, and carbonate. Based on this conclusion, it was decided to decrease the amounts of all components to the concentrations in the 5.6M Na simulant except for the sodium nitrate and sodium hydroxide to maintain the Na level at 8.0M.

The phosphate had a difficult time dissolving in this simulant, even with heat and at a lower concentration. Once the oxalate and carbonate were added, the solution became cloudy and never became completely clear, even with heating to 67 °C for 15 min.

Based on these results, it was decided to use the third simulant composition and allow the precipitated solids to form. The solids that were identified in the third composition (Figure 4.3, FIO) are likely to be found in a LAWPS feed and were considered to have reasonable crystal size (a majority of the particles less than 100 μm, based on preliminary measurements) and quantity (~0.5 wt%). As such, no additional solid sodium oxalate was added to the simulant as it was for the 5.6M (nominal) sodium simulant recipe. This formulation appeared to match the target properties (density and wt% undissolved solids) within reason, so it was chosen as the final composition and is shown in Table 4.2.

Table 4.2. LAWPS 8.0M Na (High Na) Simulant Composition

Simulant Component	Composition (g species/kg liquid)	Composition (g species/L liquid)
$Al(NO_3)_3$-$9H_2O$	65.93	89.01
NaOH (50% solution, w/w)	181.61	245.17
$CsNO_3$	0.021	0.029
KCl	9.63	13.00
Na_2SO_4	9.94	13.42
$NaNO_2$	74.51	100.59
$NaNO_3$	115.36	155.74
Na_3PO_4-$12H_2O$	12.16	16.42
Na_2CO_3-H_2O	59.70	80.60
$Na_2C_2O_4$	1.26	1.70
Water, Deionized	469.87	634.32

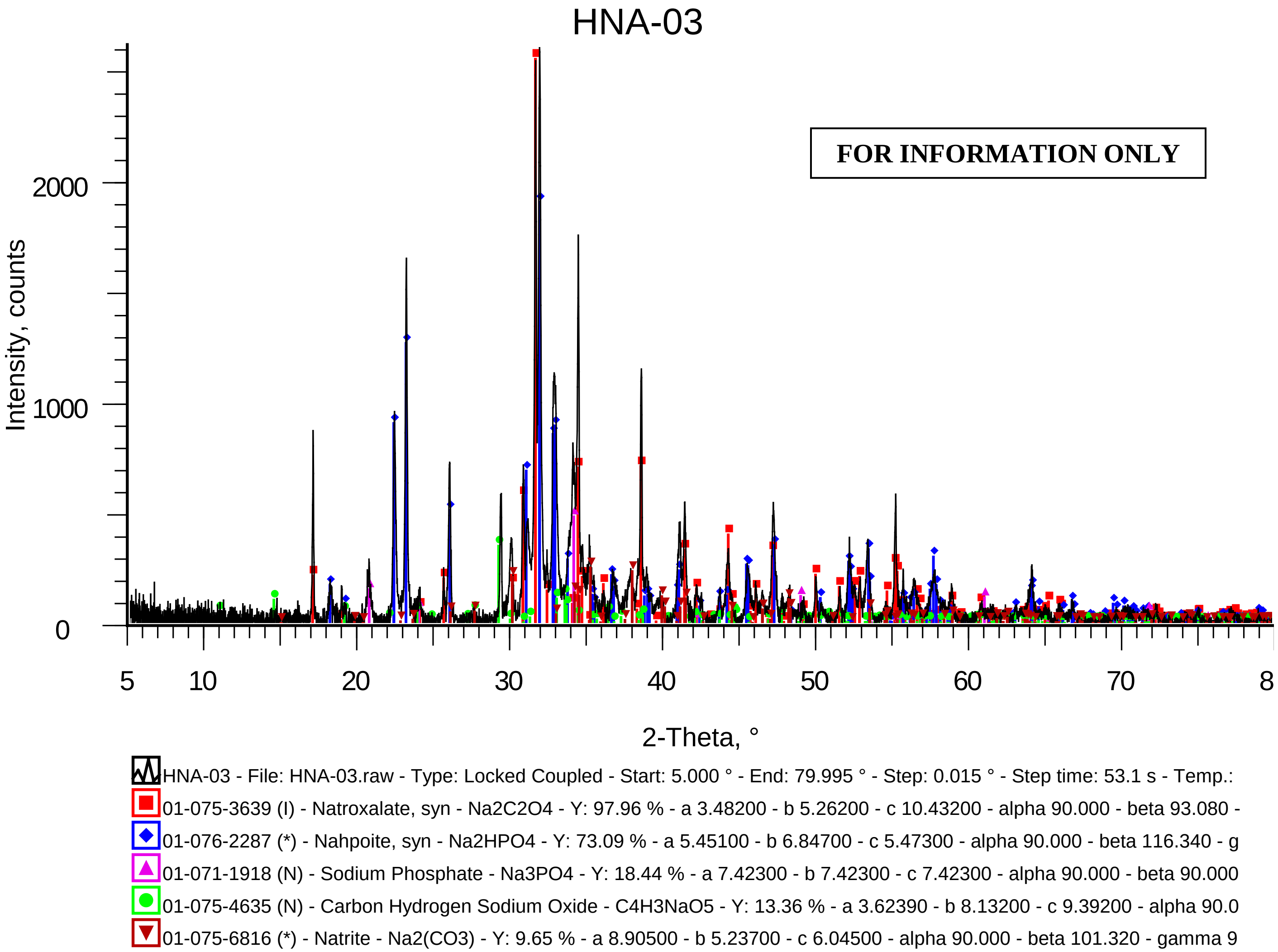


Figure 4.3. Qualitative XRD of Selected High-Na Simulant

4.3 4.0M Na Simulant Results

The initial composition shown in Table 3.5 was prepared in a 500-mL volumetric flask. All of the chemicals dissolved quite easily in the solution and it did not require heating. The sodium carbonate formed a white salt cake before dissolving and took slightly longer to dissolve than the other chemicals but did finally completely dissolve. For this reason, the initial composition was selected as the final composition for this simulant, and is shown in Table 4.3.

The solid component selected was APYRAL AOH 60 boehmite[1] (aluminum oxide hydroxide), which is a relatively fine crystalline powder and resists dissolution in the caustic medium under low-temperature (<50 °C) conditions. The boehmite comprised approximately 0.1 wt% undissolved solids in the slurry. Since the solids content of this simulant is not formed by precipitation, the solids content and physical properties are expected to be repeatable.

Table 4.3. LAWPS 4.0M Na Simulant Composition

Simulant Component	Composition (g species/kg liquid)	Composition (g species/L liquid)
$Al(NO_3)_3$-$9H_2O$	37.51	44.48
NaOH (50% solution, w/w)	99.92	118.51
$CsNO_3$	0.0122	0.0145
KCl	5.48	6.50
Na_2SO_4	5.65	6.71
$NaNO_2$	42.39	50.27
$NaNO_3$	65.63	77.83
Na_3PO_4-$12H_2O$	9.89	11.73
Na_2CO_3	29.81	35.36
$Na_2C_2O_4$	1.02	1.22
Water, Deionized	702.69	833.39

Upon makeup of the supernate composition listed above, an additional amount of APYRAL AOH 60 boehmite solids should be added: 1.00 g solid/kg supernate or 1.19 g solid/L supernate.

4.4 6.0M Na Simulant Results

Multiple sample simulant batches were prepared in the laboratory to iterate to the simulant recipe that is provided in this document. In-situ precipitation was a desirable quality for this simulant. Therefore, fluoride was included based on the precipitation observed in the 5.6M Na simulant; all other component ratios were maintained while increasing the Na from 5.6M to 6.0M.

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[1] As provided by the manufacturer, APYRAL AOH 60 boehmite has a nominal particle size of d_{10} = 0.4 µm, d_{50} = 0.9 µm, and d_{90} = 1.7 µm. See information at the following link: http://www.nabaltec.de/download/produkte/ApyralAOH_20-30-60_Datasheet_DE-EN.PDF.

When the initial simulant was prepared in a 500-mL volumetric flask, the solution appeared cloudy after adding the sodium carbonate. After all the chemicals had been added, there were undissolved solids in the solution. The solution was stirred at room temperature for 2 hours, at which point there were still white powdery solids in the solution. The solution was gradually heated to 73 °C, and the solution was clear after maintaining this temperature for 2 hours. The solution was then allowed to cool to room temperature, at which point there were crystalline solids in the solution. The solids were filtered using a 0.45-micron filter, rinsed with ethanol three times, and dried in an oven at 85 °C. After drying, there were ~0.54 wt% solids present. An XRD analysis (FIO) of the solids was performed and they were found to be a mixture of sodium aluminum phosphate and several forms of sodium fluorophosphates, as seen in Figure 4.4. The particle size distribution was found to be fairly broad based on a preliminary measurement, and there was a preference for particles that, on average, were smaller in size. Based on these results, it was decided to add calcium instead of fluoride to try to make CaC_2O_4 precipitate with a smaller particle size.

Calcium was added as calcium nitrate and the sodium nitrate and sodium hydroxide were adjusted to maintain the sodium level at 6.0M in the second simulant. The second simulant solution became cloudy after the sodium phosphate was added and didn't clear again, even with heating of the solution. Based on when the cloudiness appeared and what had been added, it appeared that the solids were calcium phosphate. The solids were filtered using a 0.45-micron filter, rinsed with ethanol three times, and dried in an oven at 85 °C. After drying, there were ~0.21 wt% solids present. An XRD analysis (FIO) of the solids was performed and they were found to be a mixture of sodium oxalate, calcium phosphate, calcium hydroxide, and calcium carbonate, as shown in Figure 4.5. However, a qualitative particle size analysis of these solids indicated the particles were considerably larger than those in the initial simulant without calcium.

Based on the smaller average particle size of the simulant without Ca, it was decided to use the initial simulant composition as the final composition, as shown in Table 4.4. Note that either of the simulants would have been reasonable selections, but for consistency with the other simulants (which did not include Ca) the composition without Ca was preferred.

Table 4.4. LAWPS 6.0M Na Simulant Composition

Simulant Component	Composition (g species/kg liquid)	Composition (g species/L liquid)
NaOH (50% solution, w/w)	138.91	177.80
$Al(NO_3)_3$-$9H_2O$	52.17	66.78
$NaNO_2$	58.77	75.22
$NaNO_3$	91.39	116.97
Na_2CO_3	41.41	53.01
Na_3PO_4-$12H_2O$	13.75	17.60
Na_2SO_4	7.86	10.06
KCl	7.63	9.77
NaF	2.29	2.93
$Na_2C_2O_4$	1.42	1.82
$CsNO_3$	0.0169	0.0216
Water, Deionized	584.38	748.01

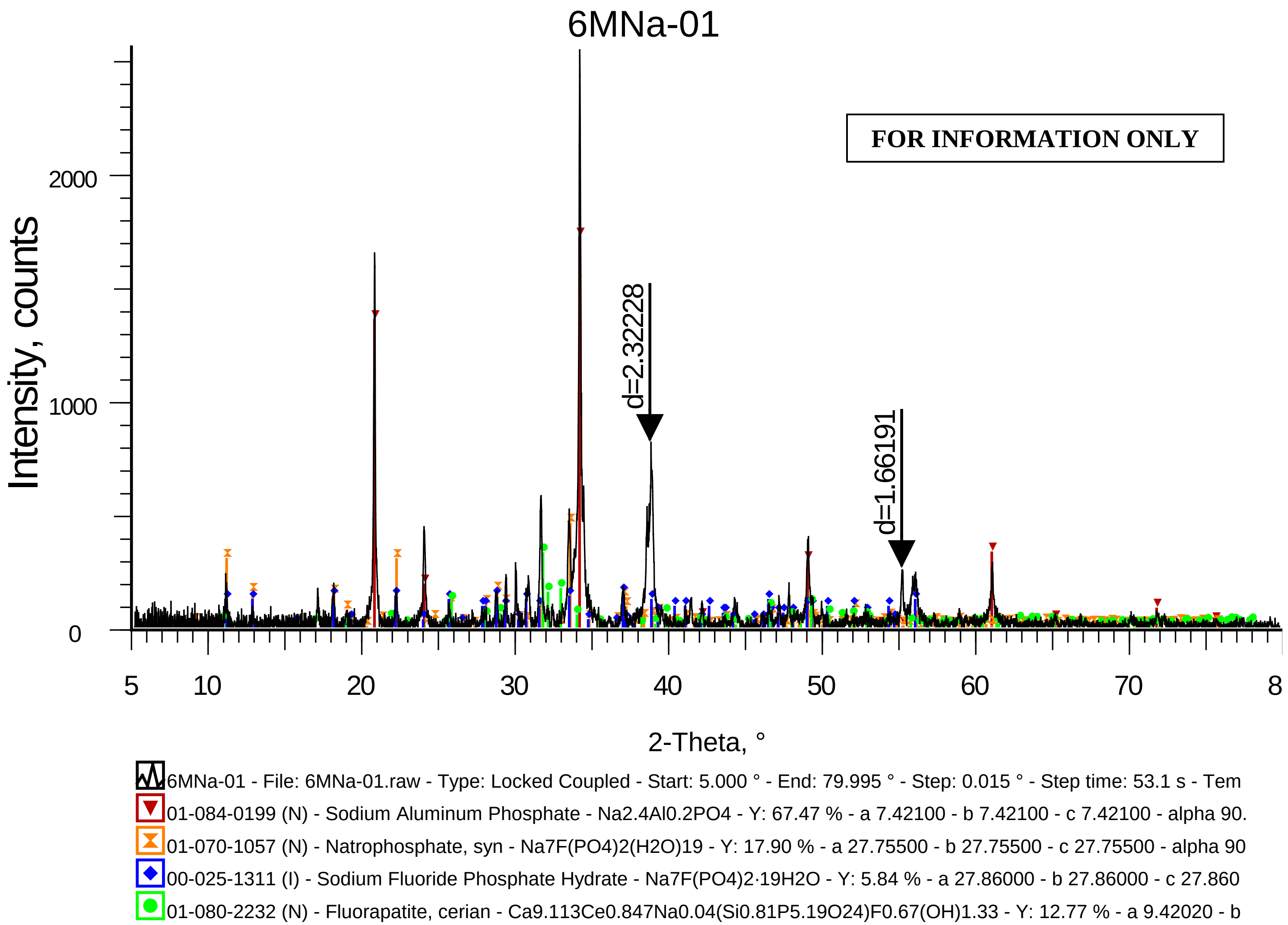

Figure 4.4. Qualitative XRD of Initial 6.0M Na Simulant

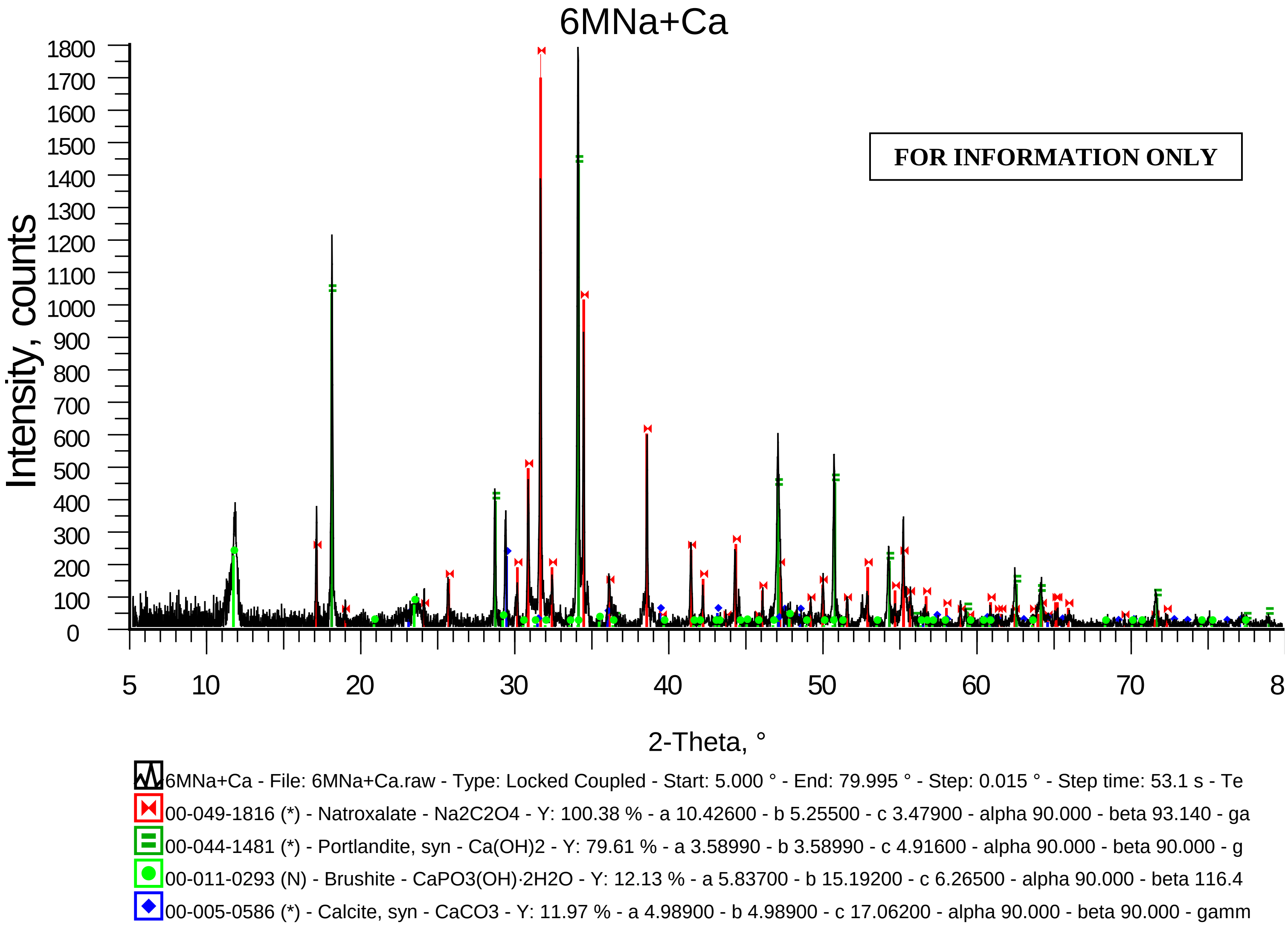

Figure 4.5. Qualitative XRD of Second 6.0M Na Simulant

4.5 Simulant Development Uncertainty

The final simulant compositions (interchangeably referred to as recipes) described in the preceding subsections were individually documented in a series of letters to WRPS (Russell and Schonewill 2016a, 2016b, 2016c, 2017). The short reports attached to those letters describe applicable assumptions or uncertainties of the recipes that were provided in advance of the simulant development work being completed. Some of these uncertainties have been assessed, i.e., a full suite of characterization of the simulants has been performed and is reported in this document. However, others are still applicable, and they are briefly summarized here for reference:

- The simulant preparation was performed with reagent-grade chemicals and deionized water. Simulant batches prepared with chemicals of other grades and process/city water may have differences in solution chemistry or stability that cannot be predicted from the PNNL work.
- The simulant preparation was performed at a scale that is small relative to its use in the larger-scale test facilities (500 mL vs. > 1000 gallons). Chemical constituents were added with a high level of precision in a 500-mL batch that is likely unachievable at larger scale. In order to avoid precipitating undesired solids due to imprecision in large-scale constituent addition, it is recommended that target masses for constituents be treated as one-sided, i.e., for a target mass of x kg of a species, treat the target as x +0/-y, where y is the uncertainty of the large-scale measuring equipment and any additional uncertainties. This approach specifically aims to avoid adding too much of a component and obtaining unexpected insoluble solids in the simulant; instead, it errs on the side of potentially adding slightly less than the target.
- After preparation, the simulants were stored at approximately ambient temperature (20 ± 5 °C). The stability of the simulant formulation outside of these temperature bounds was not studied and is not known.
- Multiple batches of the same simulant recipe were not prepared at the same time, so the batch-to-batch variability has not been studied. Though the simulants, as constructed, provide some feedback on any anomalies during the preparation process due to unexpected precipitation and/or failure to dissolve chemical species, the probability of a particular batch to deviate from expectation is unknown.
- Following their preparation, the simulants were not analyzed for the effects (if any) of time/aging on the chemical stability of the simulant. There was some visual evidence that some additional “long-time” chemistry may have been occurring, as indicated by slight color changes (from predominantly white to orange/brown) in the simulant solids over time. The impact of this visual observation has not been quantified.

It is difficult to estimate the impacts of the listed uncertainties on simulant properties and/or simulant performance without conducting additional testing or analysis. It is recommended that when any of the simulants described in this report are produced at much larger scales (and possibly retained using different storage conditions), they be characterized to verify that the appropriate chemical and physical properties were obtained.

5.0 Simulant Analytical Results

A validation batch of each final simulant was sampled and characterized. Simulant characterization involved measurement of dissolved solids concentration, X-ray diffraction analysis, wt% total and undissolved solids, rheology, density, and particle size analysis.

5.1 Dissolved Solids Concentration

Chemical compositions were measured using several different methods to determine the concentrations of each of the constituents present in the simulants. The cations (Al, Na, and K) were measured using inductively coupled plasma-optical emission spectroscopy. The anions (NO_2, NO_3, PO_4, SO_4, and Cl) were measured using ion chromatography. The fluoride concentration was not measured in the supernate due to the combination of two factors: (1) it was only present in one of the four simulants (6.0M Na), and (2) it was assumed that the majority of it in the 6.0M Na simulant would be precipitated. The total OH was measured by acid titration and potentiometric determination with a pH electrode, and the total organic carbon (TOC), i.e., C_2O_4, was determined from the difference of total carbon (TC) and total inorganic carbon (TIC) measurements using hot persulfate wet oxidation and coulometric measurement of the evolved CO_2. These results are shown in Table 5.1. The results were then compared with the target (i.e., as-prepared) concentrations and these are shown in Table 5.2.

Table 5.1. Simulant Concentration Analytical Results

Species (mg/L)	5.6M Na (Nominal)	8.0M Na (High)	4.0M Na	6.0M Na
Al	4,600	6,420	3,260	4,720
Cs	14.9	20.3	9.71	15.4
NO_2	52,300	75,000	38,200	59,500
NO_3	111,000	164,000	81,200	124,000
PO_4	4,000	2,940	2,650	1,410
SO_4	5,740	7,920	3,280	6,240
CO_3	31,200	38,700	22,300	33,100
C_2O_4	<MDL	1,190	150	<MDL
Cl	4,470	6,490	3,290	4,780
K	4,970	6,960	3,480	5,110
F	NM	NM	NM	NM
OH (total)	35,100	50,200	24,500	35,500
Na	131,000	179,000	92,200	132,000

NM = not measured

MDL = method detection limit, 43 mg carbon/L

Table 5.2. Simulant Concentration Comparison

Species (mg/L)	5.6M Na (Nominal)			8.0M Na (High)			4.0M Na			6.0M Na		
	Target	Measured [(a)]	% Diff	Target	Measured [(a)]	% Diff	Target	Measured [(a)]	% Diff	Target	Measured [(a)]	% Diff
Al	4,480	4,600	2.7	6,400	6,420	0.31	3,200	3,260	1.9	4,800	4,720	-1.7
Cs	13.6	14.9	9.3	19.8	20.3	2.7	9.89	9.71	-1.8	14.7	15.4	4.6
NO_2	46,900	52,300	12	67,100	75,000	12	33,500	38,200	14	50,100	59,500	19
NO_3	110,000	111,000	0.91	158,000	164,000	3.8	78,800	81,200	3.0	118,000	124,000	5.1
PO_4	4,100	4,000	-2.4	4,100	2,940	-28	2,930	2,650	-9.6	4,400	1,410	-68
SO_4	6,350	5,740	-9.6	9,070	7,920	-13	4,540	3,280	-28	6,800	6,240	-8.2
CO_3	28,000	31,200	11	39,000	38,700	-0.77	20,000	22,300	12	30,000	33,100	10
C_2O_4	1,120	<MDL	--	1,120	1,190	6.3	801	150	-81	1,200	<MDL	--
Cl	4,330	4,470	3.2	6,180	6,490	5.0	3,090	3,290	6.5	4,650	4,780	2.8
K	4,770	4,970	4.2	6,820	6,960	2.1	3,410	3,480	2.1	5,120	5,110	-0.20
F	0	NM	--	0	NM	--	0	NM	--	1,330	NM	--
OH (total)	35,300	35,100	-0.57	52,100	50,200	-3.6	25,200	24,500	-2.8	37,800	35,500	-6.1
Na	129,000	131,000	1.6	184,000	179,000	-2.7	91,900	92,200	0.33	139,000	132,000	-5.0

(a) Measurement uncertainties for reported analytical measurements are ±15%

NM = not measured

MDL = method detection limit, 43 mg carbon/L

Overall, the agreement (as shown by the percent difference in Table 5.2) between the measured and target concentrations was within ~10% for most species. This falls within the reported uncertainties for the analytical techniques. The two notable exceptions were phosphate and oxalate.

Phosphate was measured to be much lower in the 6.0M Na and 8.0M Na simulants because it was a participant in forming precipitated solids and thus was present at a much lower level in the liquid phase. When it did not precipitate (4.0M Na and 5.6M Na simulants) the analytical measurements were within 10% of the target.

Accurate measurement of the oxalate concentration was complicated by the method used. The TC was measured, but this includes all carbon sources in the solution, e.g., carbonate and oxalate. The TIC (carbonate) was then measured, with the TOC (oxalate) determined by difference. In these simulants, the carbonate concentration was much larger than the oxalate concentration, and in three of the samples, the measured TIC (carbonate) and TC were similar in magnitude (or the carbonate concentration exceeded the TC); by difference, then, the oxalate concentration was determined to be unexpectedly small. In the one case (8.0M Na simulant) where the measured carbonate concentration was very close to the target, the oxalate concentration was also in agreement. Thus, the low oxalate concentrations reported in Table 5.2 were considered to be artifacts of the analytical method in the presence of a relatively high abundance of carbonate.

Note that the analytical titration method for hydroxide measures the total hydroxide (as provided in Table 5.1 and Table 5.2). The total hydroxide in these simulants include both the free hydroxide in solution and the hydroxide bound to aluminum as $Al(OH)_4^-$. For these simulants, the free hydroxide can be calculated from the total by difference (total hydroxide molarity minus four times the aluminum molarity). The total hydroxide values reported in Table 5.2 were constructed using the reverse of the same process.

5.2 X-ray Diffraction Analysis

The solids of the 6.0M Na and 8.0M Na validation simulant preparations were characterized using XRD to determine what was present and how much was present. Dried and powdered solids samples were prepared using 5 wt% CaF_2 as an internal standard phase with approximately 1 g of sample. The solids sample and CaF_2 were ground and thoroughly blended together. The powdered samples were loaded into XRD sample holders and scanned at a 0.015° 2θ step size, 0.6 sec dwell time, from 5° to 75° 2θ scan range. XRD spectra were analyzed with Jade® 6.0 Software (MDI, Inc., Livermore, CA) for phase identification. Full-pattern Rietveld refinement using RIQAS® 4 (MDI, Inc., Livermore, CA) was performed to quantify the fraction of each phase.

In the 8.0M Na simulant, it was found that the solids were ~40% sodium oxalate and ~30% of a type of sodium phosphate. There were also ~10% sodium carbonate and ~2% sodium nitrate present with the remaining solids unidentified. The sodium nitrate was most likely due to unwashed matrix solution on the solids. The XRD scan is shown in Figure 5.1. The loss of oxalate and phosphate from solution was confirmed by the analytical results showing that the phosphate measured in the supernate was ~30% lower than what was added to the simulant (see Table 5.2).

The 6.0M Na simulant had ~40% sodium aluminum phosphate and ~17% sodium fluorophosphates present. Sodium fluoride (~12.5%) and sodium oxalate (~6.2%) were also present with the remaining solids unidentified. The XRD scan is shown in Figure 5.2. The loss of phosphate from solution was confirmed by the analytical results showing that the phosphate measured in the supernate was 68% lower than what was added to the simulant (see Table 5.2).

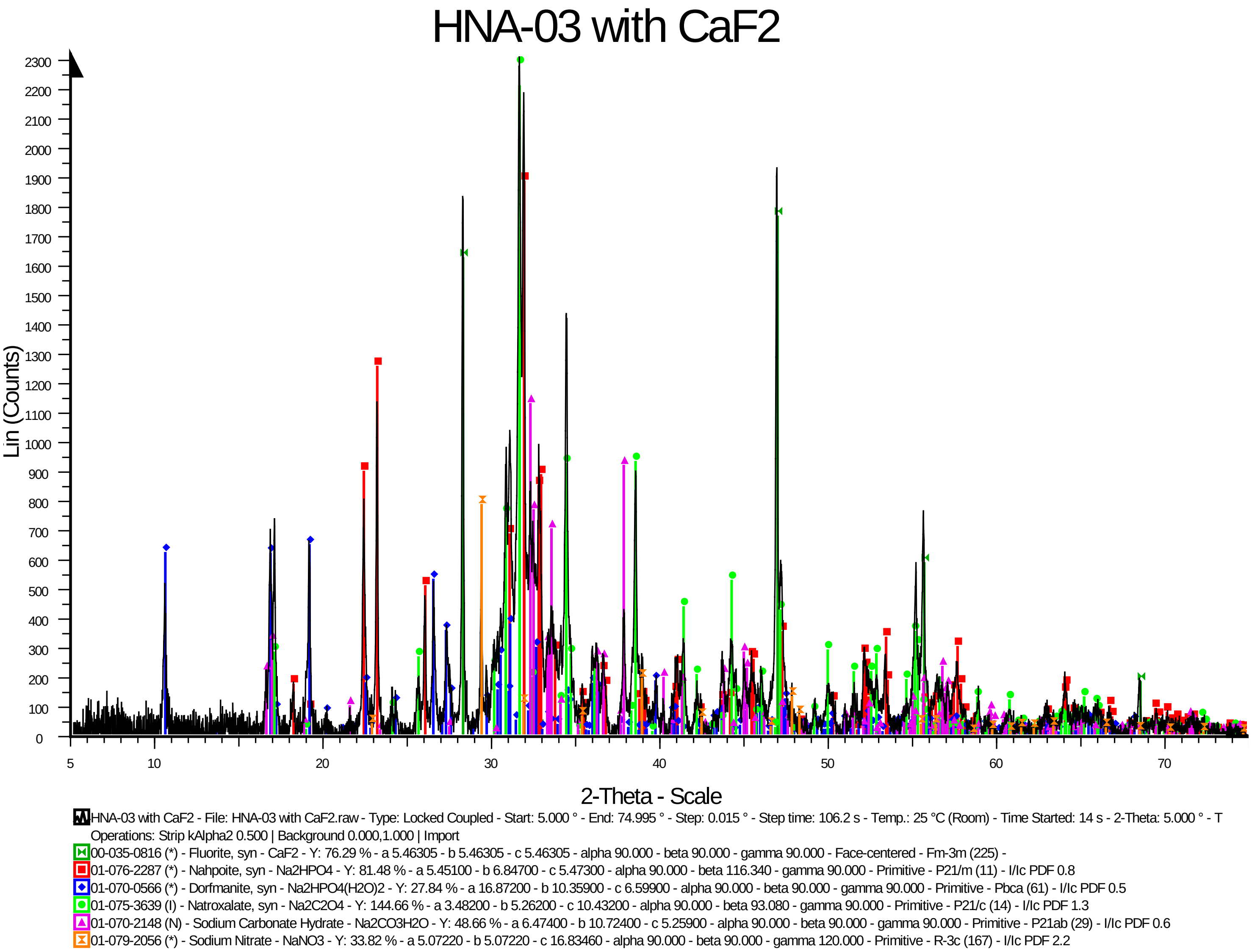

Figure 5.1. XRD of 8.0M Na Simulant Self-Precipitating Solids

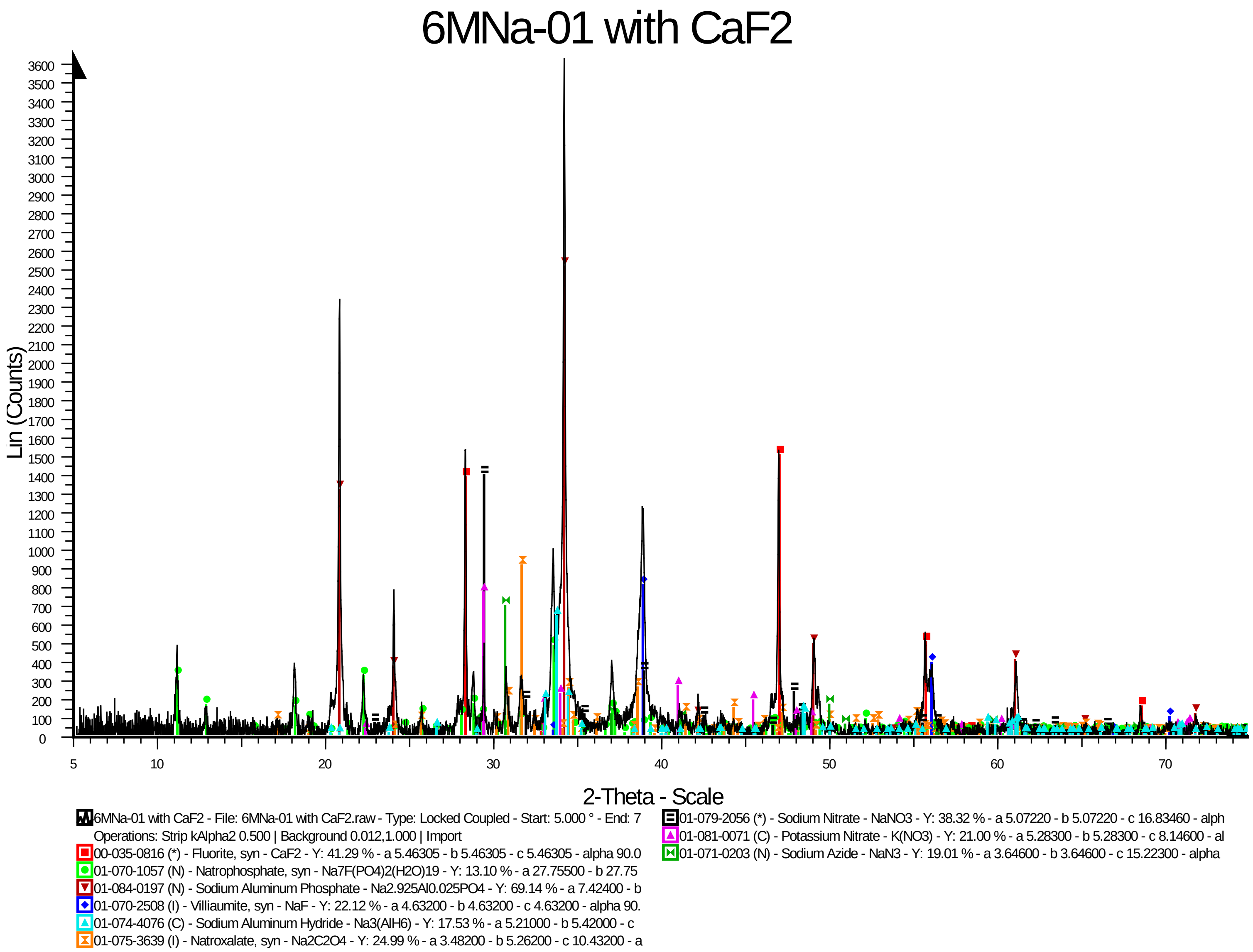

Figure 5.2. XRD of 6.0M Na Simulant Self-Precipitating Solids

5.3 Weight Percent Solids

Analysis of the validation batch simulant solids concentration included determination of the total solids content of the slurry (which includes both dissolved and undissolved solids), and supernate dissolved solids. The wt% undissolved solids is a calculated value. These analyses employed an HR83 halogen moisture analyzer from Mettler Toledo.

Total weight percent solids, x_T, is defined as the mass of dried solids per initial wet mass of sample before drying. Total solids were determined by drying an aliquot of simulant slurry in the HR83 moisture analyzer. Supernate dissolved solids, x_{DS}, are defined as the mass fraction of solids dissolved in a supernate sample. This was determined by drying an aliquot of supernate in the HR83 moisture analyzer. Supernate samples were obtained by first centrifuging a sub-aliquot of slurry to settle the slurry solids and then carefully decanting the supernate off the centrifuged solids. Undissolved solids concentration, x_{UDS}, is defined as the mass fraction of undissolved solids in a slurry sample. It was calculated from values of x_T and x_{DS} using the following formula:

$$x_{UDS} = \frac{x_T - x_{DS}}{1 - x_{DS}} \tag{5.1}$$

All solids content analyses performed in the HR83 moisture analyzer involved heating the sample to 95 °C for 30 min to drive off bulk moisture without boiling. Then, the sample was heated to 105 °C to drive off the remaining moisture until the sample reached a weight stability criterion in the analyzer user interface settings. Weight percent solids were then determined by dividing the dried solids weight by the initial sample mass.

Undissolved solids concentration was specified as 0 to 3.3 wt% in the specification formulation. All of the simulant undissolved solids concentrations measured within this range and were approximately at or below 1 wt%, as shown in Table 5.3. The 4.0M and 5.6M Na simulants also matched closely to the expected undissolved solids calculated from the mass of solids that was added (0.11 wt% and 0.51 wt%, respectively). The 6.0M and 8.0M Na simulants were self-precipitating and therefore cannot be readily compared.

Table 5.3. Simulant Measured Undissolved Solids

	4.0M Na	5.6M Na (Nominal)	6.0M Na	8.0M Na (High)
Wt% Total Solids	22.7	30.1	31.3	39.1
Wt% Dissolved Solids	22.6	29.8	30.6	38.9
Wt% Undissolved Solids	0.14	0.45	1.1	0.24

5.4 Rheology Measurement

Aliquots of simulant were taken to measure the viscosity of the supernate. The supernate viscosity was measured using a Haake RS600 rheometer (now sold by Thermo Fischer Scientific, Waltham, MA 02454 USA). A Z41 concentric cylinder measuring system was employed for testing. Rheometer control and data acquisition were accomplished using the RheoWin Pro Job Manager Software, Version 4.41.0019.

Flow curve measurements (i.e., material stress response versus applied shear rate) were performed at temperatures of 20, 25, and 45 °C for each simulant sample. Each flow curve was measured over an 11-min period. During the first 5 min, the shear rate was gradually increased from 0 to 1000 s^{-1}. Next, the shear rate was held constant at 1000 $s\text{-}^{1}$ for 60 sec, and finally the shear rate was gradually reduced back to zero (1000-0 $s\text{-}^{1}$) over 5 min. During this time, the resisting torque and rotational rate were continuously monitored and recorded. After measurement, the recorded flow curve data were analyzed using a Newtonian fit. The fit range was reduced to the linear portion of the flow curve and is given in Table 5.4 along with the viscosity data.

It was found that the viscosities ranged from 2.38 mPa-s for the 4.0M Na simulant to 6.25 mPa-s for the 8.0M Na simulant at 25 °C as shown in Table 5.4. The viscosity increased with increasing salt concentrations and decreased with increasing temperature as expected (temperature dependence is shown in Figure 5.3). These values all fall within the specification viscosity limits of 1 to 15 mPa-s. However, in general the viscosities are lower than targeted values at 25 °C (where applicable, see Table 3.1). This was anticipated due to the absence of species that typically increase viscosity in waste: for example, organic compounds or colloidal solids (e.g., aluminum, silica). These species were not included either due to the complexity in appropriate specification (organic compounds) or difficulty in obtaining/synthesizing the necessary particle size range (colloidal solids). Where viscosity data are available (see Russell et al. 2003), the nominal simulant viscosity at 25 °C compares favorably with AP-101 simulant and actual waste (3.4 mPa-s and 3.5 mPa-s, respectively).

Table 5.4. Simulant Measured Rheology

	4.0M Na	5.6M Na (Nominal)	6.0M Na	8.0M Na (High)
Viscosity at 20 °C (mPa-s)	2.64[(a)]	3.82	4.09	7.33
Viscosity at 25 °C (mPa-s)	2.38[(b)]	3.41	3.70	6.25
Viscosity at 45 °C (mPa-s)	1.97[(c)]	2.20[(b)]	2.29[(b)]	3.81

If not specified, the linear fit range used was 20-500 s^{-1}. Otherwise, the linear ranges used were:
(a) Fit range of 20-400 s^{-1}
(b) Fit range of 20-350 s^{-1}
(c) Fit range of 20-250 s^{-1}

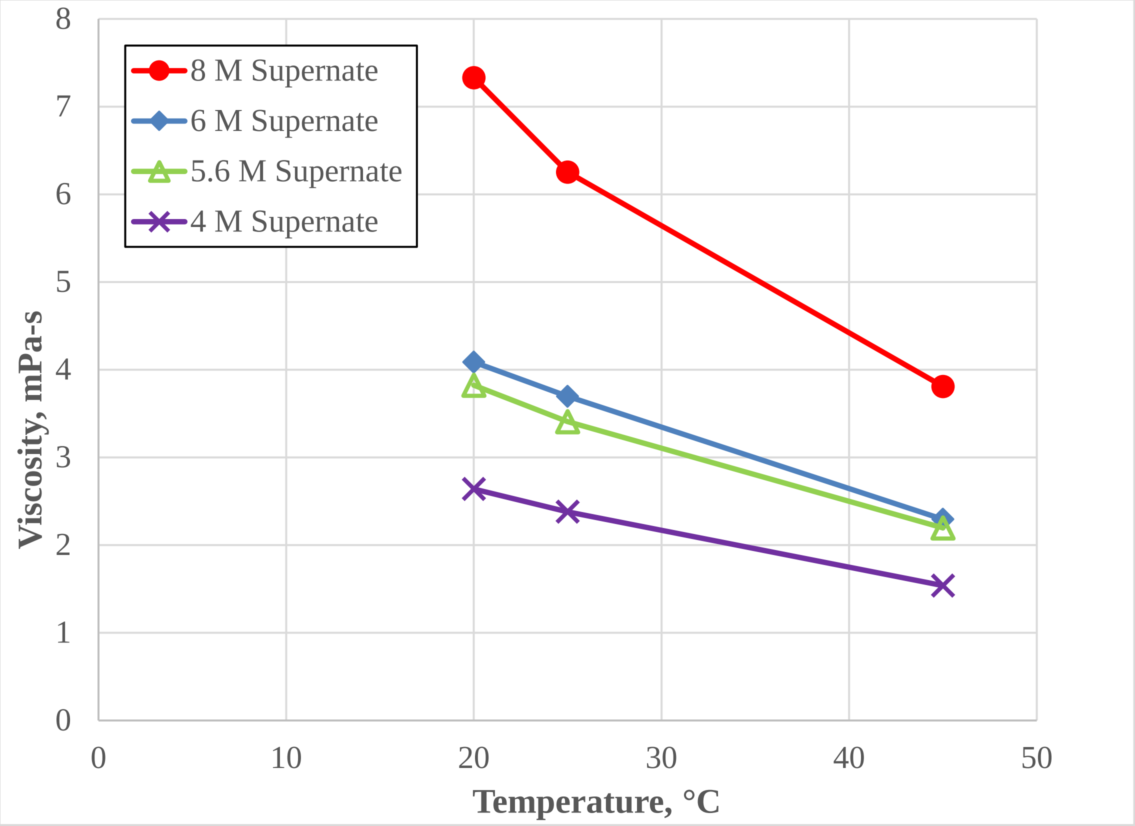

Figure 5.3. Viscosity of Simulants vs Temperature

5.5 Simulant Density Measurements

Simulant density measurements were made using the 500-mL volumetric flask in which the simulant was prepared. Each flask was pre-weighed, and the simulant volume was brought to the marked level at the end of simulant preparation. The total mass of the filled volumetric flask was weighed using a three-place analytical balance. Next, the mass of simulant in the volumetric flask was determined by the difference of the total filled mass and the volumetric flask tare. Density was then determined by dividing fluid mass by the standardized volumetric flask volume (500 mL). The amount of undissolved solids present was insignificant and did not affect the density measurement outside standard error.

Densities specified for the simulants were listed as from 1.0 to 1.35 g/mL, which represents the full specification range. All of the simulant measured densities were within this range and are shown in Table 5.5. The 8.0M Na simulant was at the high end of the range and the 4.0M Na (the least dense of the four simulants) was at about the mid-range.

Table 5.5. Simulant Measured Densities

	4.0M Na	5.6M Na (Nominal)	6.0M Na	8.0M Na (High)
Density (g/mL)	1.19	1.26	1.27	1.34
Target Density (g/mL)	n/a	1.28	n/a	1.35

5.6 Particle Size Analysis

Particle size was characterized using a Mastersizer 2000 (Malvern Instruments, Inc., Southborough, MA 01772 USA) with a Hydro 2000 µP wet dispersion accessory. The Mastersizer has a nominal size measurement range of 0.02 to 2000 µm. The actual range is dependent on the accessory used as well as the properties of the solids being analyzed. Table 5.6 summarizes instrument information for the analyzer/accessory and the measurement parameters used.

Table 5.6. Summary of Malvern Mastersizer 2000 Instrument Information and Measurement Parameters

Analyzer	Mastersizer 2000
Measurement Principle	Laser diffraction (Mie Scattering)
Analyzer Accessory	Hydro µP
Measurement Range	0.02-600 µm nominal
Type	Flow cell system with continuously variable and independent pump and ultrasound
Pump Speed/Stirrer Range	0 to 2000 rpm (variable), used 2000 rpm
Ultrasound Power	0 to 20 W (variable), used 50% power
Software Version/date	5.6/1998-2009
Particle RI/Absorption	1.48/1 (6.0, 5.6, and 8.0M simulant) 1.78/0.01 (4.0 M Simulant)

Particle size distributions were measured pre sonication, at 50% applied sonication, and post sonication. The d_{10}, d_{50}, and d_{90} results for each simulant are listed in Table 5.7, with the particle size distribution curves shown in Figure 5.4 through Figure 5.7. These results show there was significant de-agglomeration observed in the 4.0M Na simulant and slight de-agglomeration in the 8.0M Na and 5.6M Na simulants.

Evaluation of the raw data obtained for the 6.0M Na simulant showed indications of dissolution with the sonication and post sonication curves, and a combination of de-agglomeration and dissolution for the pre sonication data. The particle obscuration, a property that is dependent on both material type and concentration, decreased for both the red (larger particles) and blue (small particles) light scattering, which suggests the number of particles observed for both red and blue light was decreasing. The observed dissolution could be attributed to changes in temperature as the sample is being measured. A temperature increase of 3 to 4 °C is typical of the µP dispersion cell used for these measurements. The particular species that dissolved, or if these species re-precipitated over time, was not determined.

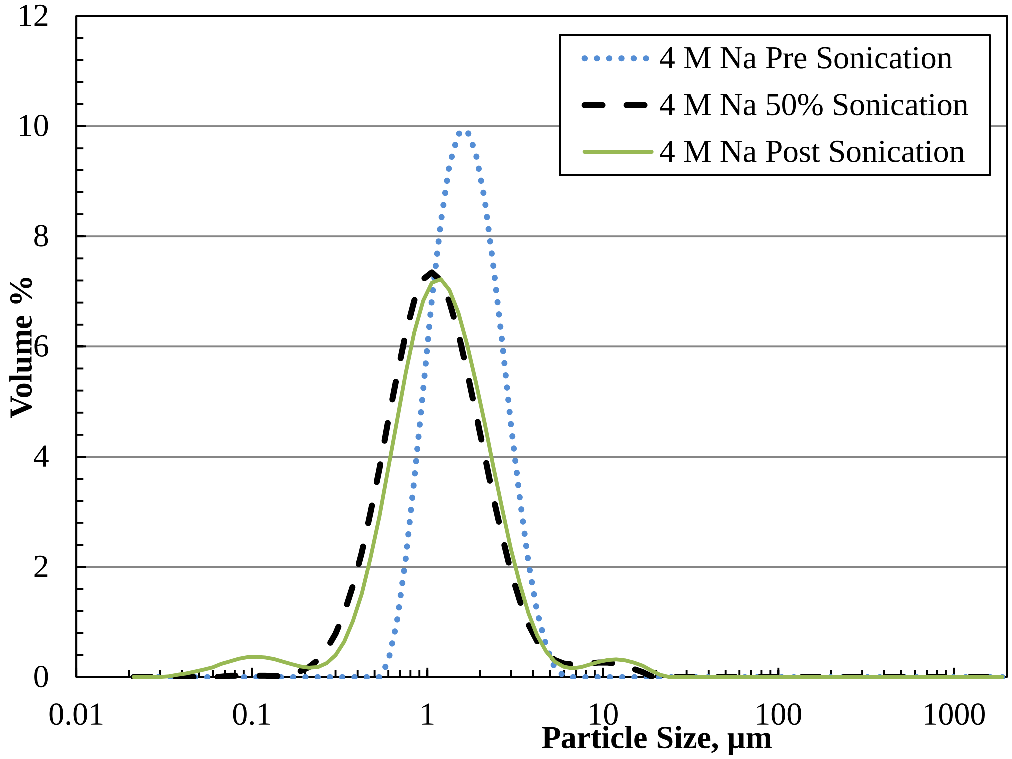

Figure 5.4. 4.0M Na Simulant Particle Size Distribution (primarily boehmite solids).

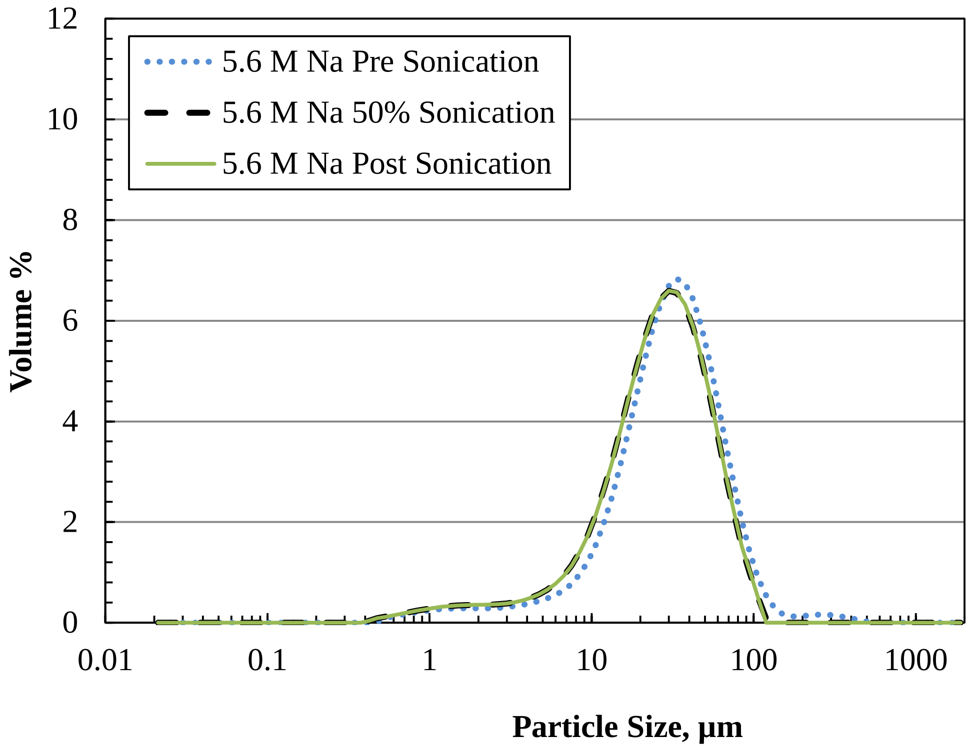

Figure 5.5. 5.6M Na Simulant Particle Size Distribution (primarily sodium oxalate solids).

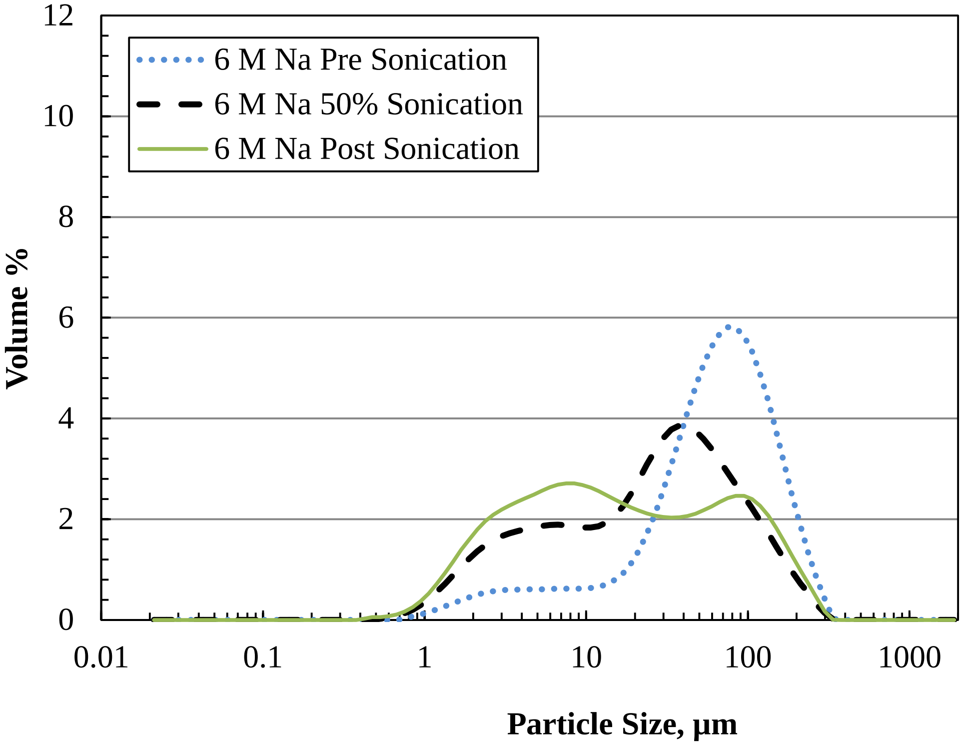

Figure 5.6. 6.0M Na Simulant Particle Size Distribution (self-precipitated solids).

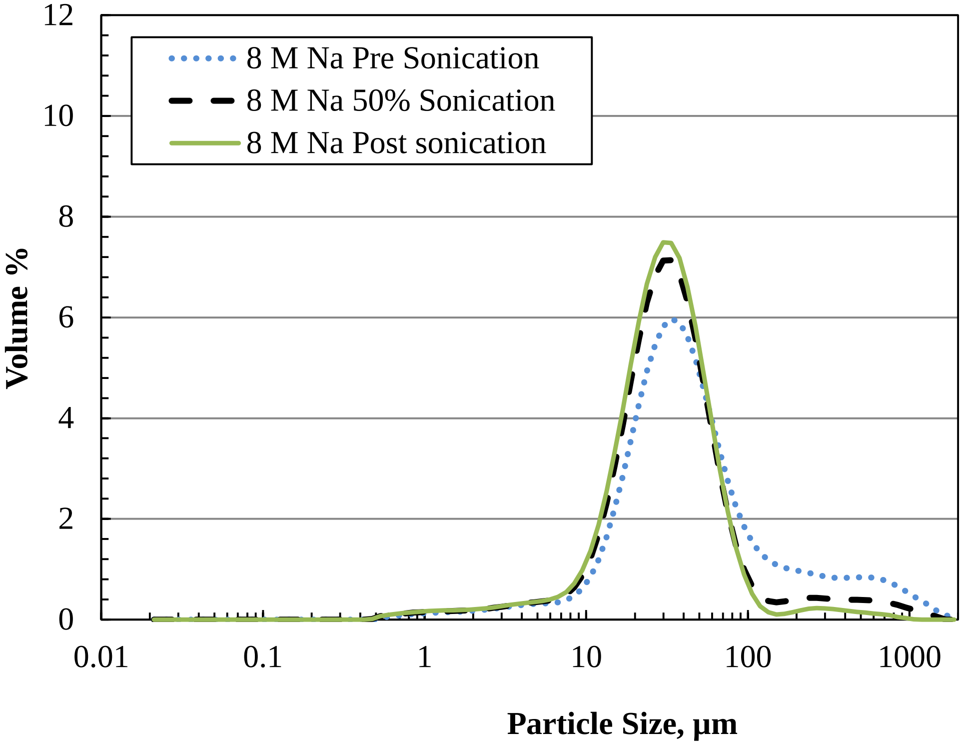

Figure 5.7. 8.0M Na Simulant Particle Size Distribution (self-precipitated solids).

Table 5.7. Simulant Particle Size Distribution Results

Particle Size Percentiles	4.0M Na	5.6M Na (Nominal)	6.0M Na	8.0M Na (High)
Pre Sonication d_{10}	0.959	10.0	9.43	14.6
Pre Sonication d_{50}	1.65	30.9	64.8	39.5
Pre Sonication d_{90}	2.95	69.3	159	283
50% Sonication d_{10}	0.499	7.84	2.82	12.7
50% Sonication d_{50}	1.10	26.8	26.7	31.8
50% Sonication d_{90}	2.56	59.7	107	84.6
Post Sonication d_{10}	0.506	7.85	2.35	12.1
Post Sonication d_{50}	1.18	26.9	15.1	30.2
Post Sonication d_{90}	2.74	59.8	120	65.2

6.0 Summary

The objective of the work described in this report was to develop four simulants that are representative of the waste chemistry expected to be fed to the LAWPS and cover (as much as practical) the waste property range for feed streams to the LAWPS. These simulant recipes have been (and will be) used to support the LAWPS engineering-scale integrated test, full-scale ion exchange column test, and the CFF testing. The simulant recipes include four sodium concentrations: 5.6M Na (nominal Na), 4.0M Na, 6.0M Na, and 8.0M Na (high Na). At each Na concentration, a simulant was developed from a simplified number of constituents containing only the major species, exclusive of NH_3 and substituting oxalate for the total organic carbon. As such, the impact of the presence of trace constituents (and organic compounds other than sodium oxalate) on simulant properties, stability, and performance is not addressed by the simulants described in this report.

Several formulation iterations of each simulant were prepared by adjusting species concentrations while maintaining the Na concentration, primarily in an effort to control precipitated solids formation and obtain simulants that could be reproduced for other testing conducted at larger scales. Once an acceptable recipe was established, it was sampled and analyzed for composition, viscosity, particle-size distribution, weight percent solids, and density to confirm that the properties were within the desired range. All of the simulants described in this report fall within the physical property target ranges specified for processing in LAWPS; however, they do not span the entire range of specified physical properties. Simulants that are bounding with respect to a particular physical property – for example, viscosity – may be formulated, but with a high probability that the simulant is less chemically similar to LAW. These simulants also were not developed to have a particular performance in LAWPS unit operations; however, the recipes provided in this report could serve as a starting point for chemically representative performance-based simulants.

Table 6.1 shows the final simulant target concentrations for the major constituents in the four LAWPS simulants that were developed. Also summarized in the table are selected physical properties of each simulant. The target concentrations are the expected liquid phase concentration of each constituent assuming complete dissolution during preparation. Some of the simulants, the 6.0 and 8.0M Na simulants in particular, may differ slightly from these values upon makeup due to the formation of precipitated solids.

Table 6.1. Final Target Liquid Concentrations of LAWPS Simulants with Selected Measured Physical Properties.

Simulant Constituent	5.6M Na (Nominal Na)	8.0M Na (High Na)	4.0M Na	6.0M Na
	Concentration (mol/L)			
Al	1.66×10^{-1}	2.37×10^{-1}	1.19×10^{-1}	1.78×10^{-1}
Cs	1.04×10^{-4}	1.49×10^{-4}	7.43×10^{-5}	1.11×10^{-4}
NO_2	1.02×10^{0}	1.46×10^{0}	7.29×10^{-1}	1.09×10^{0}
NO_3	1.78×10^{0}	2.54×10^{0}	1.27×10^{0}	1.91×10^{0}
PO_4	4.32×10^{-2}	4.32×10^{-2}	3.09×10^{-2}	4.63×10^{-2}
SO_4	6.61×10^{-2}	9.45×10^{-2}	4.72×10^{-2}	7.08×10^{-2}
CO_3	4.67×10^{-1}	6.50×10^{-1}	3.34×10^{-1}	5.00×10^{-1}
C_2O_4	1.27×10^{-2}	1.27×10^{-2}	9.07×10^{-3}	1.36×10^{-2}
Cl	1.22×10^{-1}	1.74×10^{-1}	8.71×10^{-2}	1.31×10^{-1}
K	1.22×10^{-1}	1.74×10^{-1}	8.71×10^{-2}	1.31×10^{-1}
F	N/A	N/A	N/A	6.98×10^{-2}
Free OH	1.41×10^{0}	2.12×10^{0}	1.01×10^{0}	1.51×10^{0}
Na	5.60×10^{0}	8.00×10^{0}	4.00×10^{0}	6.00×10^{0}
Density (g/mL)	1.26	1.34	1.19	1.27
Viscosity at 25 °C (mPa-s)	3.41	6.25	2.38	3.70
Wt% UDS	0.45	0.24	0.14	1.1
UDS component	$Na_2C_2O_4$	Precipitated[(a)]	AlO(OH)	Precipitated[(b)]

(a) Precipitates were determined to be sodium oxalate, a type of sodium phosphate, and sodium carbonate.

(b) Precipitates were determined to be sodium aluminum phosphate, sodium fluorophosphates, sodium fluoride, and sodium oxalate.

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