PNNL-29690, Rev. 0
RPT-DFTP-016, Rev. 0

Testing of an AP-105 Precipitation Simulant

March 2020

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

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

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Abstract

A tank AP-105 chemical simulant was developed and diluted with raw water supplied by Washington River Protection Solutions to evaluate the stability of wastes from the Hanford Site AP Farm with respect to precipitation during typical waste feed staging operations for Direct Feed Low-Activity Waste (DFLAW). The current report provides a high-level summary of the basis for simulant selection, the recommended (and prepared) simulant chemistry, and the observed stability with respect to solids formation upon simulant preparation and subsequent dilution with raw water.

Summary

A chemical simulant targeting the chemistry of Hanford tank AP-105 waste was developed with an emphasis on matching the measured waste content of the following analytes: Al, Ca, Cr, Fe, Na, and Ni. The simulant was initially prepared at a total sodium content of 8.5M and allowed to come to equilibrium. As expected, a combination of both soluble and insoluble solids precipitated from the as-prepared 8.5M Na simulant. These solids were removed by vacuum filtration, and the remaining liquid was diluted with raw water [untreated water intended to be representative of the process water that will be used during full-scale Direct Feed Low-Activity Waste (DFLAW) operations] provided by Washington River Protection Solutions. The addition of raw water was observed to accelerate the precipitation of additional solids from the diluted simulant, with the amount of solids precipitated increasing with increasing time following dilution (and possibly with the amount of water added during dilution). Precipitate formation was first observed 6-8 days following dilution and continued for at least 100 days. Comparison of raw water diluted samples to both undiluted samples and samples diluted with deionized water demonstrated that precipitation was dilution-specific and accelerated by the background chemistry of the raw water. Finally, evaluation of the precipitated solids' chemistry confirmed the presence of the desired target analytes, namely Al, Ca, Cr, Fe, Na, and Ni. As such, the solids precipitated from the simulant appear to match (from an analyte chemistry perspective) actual waste solids thought to be adverse to DFLAW tank feed staging and treatment operations.

Acknowledgments

The authors would like to acknowledge Philip Schonewill and William Dey for their thorough technical and quality reviews of this report. The authors would also like to thank Kris Colosi, Matt Landon, and Jacob Reynolds of Washington River Protection Solutions for their feedback on this report and their assistance in identifying Hanford tank AP-105 chemical data to guide simulant selection.

Acronyms and Abbreviations

ASR	Analytical Service Request
DFLAW	Direct Feed Low-Activity Waste [facility]
DI	deionized (water)
EDS	energy dispersive X-ray spectroscopy
EQL	estimated quantitation limit
FY	fiscal year
ICP	inductively coupled plasma
LAWPS	Low-Activity Waste Pretreatment System
OES	optical emission spectrometry
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
SEM	scanning electron microscope/microscopy
TIC	total inorganic carbon
TOC	total organic carbon
TSCR	Tank Side Cesium Removal
WRPS	Washington River Protection Solutions
WWFTP	WRPS Waste Form Testing Program
XRD	X-ray diffraction

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1.0 Introduction

Dead-end filter testing of nominally solids-free waste supernatant samples from Hanford tanks AP-105 and AP-107 received by Pacific Northwest National Laboratory (PNNL) in fiscal year 2018 (FY18) exhibited unexpected fouling of the dead-end filter membrane (Geeting et al. 2018a,b). Post-test analysis of the filter retentate for the AP-105 sample identified waste solids rich in iron, chromium, and an organic carbon phase presumed to be oxalate. Likewise, post-test evaluations estimated the waste solids contents for the FY18 AP-105 and AP-107 waste samples at approximately 16 ppm and 160 ppm, respectively. Confirmatory tests with a second set of supernatant samples from AP-107 received by PNNL in FY19 did not show evidence of similar fouling (Geeting et al. 2019).

Resolution of the conflicting filtration behaviors observed in FY18 and FY19 testing and, more importantly, determination of the origin of the solids observed in initial AP-105 and AP-107 filter testing are necessary to help manage filter performance and operations during future tank-side filtration and cesium removal of AP Farm supernatant. Comparison of the tank AP-107 history prior to each sampling event identified a likely cause: The first sampling event occurred shortly after the addition of raw water.

For the current study, it is postulated that the addition of raw water led to the precipitation of fine particulates that did not immediately settle and were collected during sampling prior to the first AP-107 filter tests. To confirm this assertion, a bench-scale study was undertaken to evaluate precipitation from an AP tank farm chemical simulant upon dilution with raw water. Although suspected precipitation in tank AP-107 is the primary motivation for this study, an AP-105 simulant was selected for the current study, as waste from tank AP-105 is next-in-line for Tank Side Cesium Removal (TSCR) feed staging and qualification. Thus, an 8.5M Na AP-105 chemical simulant was developed, prepared, and diluted with raw water supplied by Washington River Protection Solutions (WRPS) to evaluate precipitation of solids upon dilution with non-potable reservoir water.

The current report provides a high-level summary of the basis for simulant selection, the recommended (and prepared) simulant chemistry, and observed stability with respect to solids formation upon simulant preparation and subsequent dilution with raw water.

2.0 Quality Assurance

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

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 Simulant Chemical Basis and Make-Up

Development of a simulant to evaluate precipitation of solids from Hanford-like supernatant wastes following dilution with raw water (hereafter referred to as the precipitation simulant) targeted the chemistry of Hanford tank AP-105. While the observations of precipitated solids that motivate the current study derive from tank AP-107 testing, FY19 filter testing reported in Geeting et al. (2019) provided confidence that any solids precipitated by AP-107 waste staging operations in FY18 had settled and were unlikely to impede planned waste treatment filtration in TSCR. Instead, concern that waste feed staging operations with subsequent tanks would yield similar solids precipitation and filtration challenges drove selection of tank AP-105. Since AP-105 is the next tank in line to be staged, its chemistry was used as the basis for guiding simulant development.

As the goal of current testing is to mimic the chemical conditions leading to precipitation under typical waste feed staging and storage conditions, the AP-105 simulant was formulated as a chemical simulant (rather than a simulant whose main purpose was to mimic physical properties like viscosity/density). To this end, simulant development reviewed the available liquid- and solid-phase chemical characterization data for tank AP-105. Based on the findings of this review and feedback from WRPS staff, the two following documents were identified and selected as primary guides for simulant chemistry:

- Report RPP-RPT-43498, Rev. 4, *Derivation of Best-Basis Inventory for Tank 241-AP-105 as of July 1, 2016* (Ferriter 2016)
- Analytical Service Requests (ASRs) 0272 and 0335, as reported in Appendix B of Report RPT-DFTP-006, Rev. 0 (PNNL-27432), *Multi-Cycle Cesium Ion Exchange Testing Using Spherical Resorcinol-Formaldehyde Resin with Diluted Hanford Tank Waste 241-AP-105* (Fiskum et al. 2018)

These two references are primarily concerned with liquid-phase chemistry; however, as staged feeds are nominally considered solids-free, effort was not focused on replicating solid-phase chemistry and physical properties with the general exception that the make-up chemistry of the simulant should contain the insoluble solids phase analytes quantified by Lachut (2016), Buck (2017), and Geeting et al. (2018a,b), namely Fe, Ni, Cr, and Al. Nickel and iron are strongly associated with precipitated solids at the high pH conditions found in tank waste supernatants, and as such, liquid-phase concentrations reported in Ferriter (2016) and Fiskum et al. (2018) fall at or below the analyte quantification limit.

Table 1 summarizes the target analyte contents for the AP-105 simulant formulation and lists the reference used to develop each target. Although the basis for selecting ion concentrations listed in Table 1 is largely attributed to data from Fiskum et al. (2018), the selected ion concentrations compare well with those reported in Ferriter (2016), to the point where a nearly identical target list could be derived solely from Ferriter (2016). The targets listed in Table 1, when combined with the common set of soluble salts and order-of-addition requirements employed in historical low-activity and high-level waste simulant development efforts like Russell et al. (2009, 2017), generate the formal simulant recipe listed in Table 2. Here, the compounds are listed in order of addition. Sodium hydroxide is added as a 50-wt% solution with water. Trim water, which represents the total water content of the simulant less that added by hydrated salts and sodium hydroxide solution addition, is deionized (DI) water.

Table 1. AP-105 simulant ion concentration targets.

Ion	Form/Formula	MW (g mol^{-1})	Target Concentration (M)	Reference
Aluminum	$Al(OH)_4$	95.0	0.769	(a)
Cesium	Cs	132.9	0.0721×10^{-3}	(a)
Nitrite	NO_2	46.0	1.90	(a)
Nitrate	NO_3	62.0	2.51	(a)
Phosphate	PO_4	95.0	0.0147	(a)
Sulfate	SO_4	96.1	0.0257	(a)
Carbon (inorganic)	C	12.0	0.615	(a)
Carbon (organic)	C (speciated below)	12.0	0.297	(a)
as Oxalate	C_2O_4	88.0	3.03×10^{-3}	(a)
as Formate	CHO_2	45.0	0.146	(c)
as Acetate	$C_2H_3O_2$	59.0	0.0728	(c)
Chloride	Cl	35.5	0.170	(a)
Free hydroxide	OH	17.0	1.75	(a)
Potassium	K	39.1	0.141	(a)
Sodium	Na	23.0	8.53	(a)
Boron	B	10.8	6.46×10^{-3}	(a)
Chromium	Cr	52.0	9.71×10^{-3}	(a)
Nickel	Ni	58.7	0.776×10^{-3}	(a)
Iron	Fe	55.8	0.125×10^{-3}	(a)
Calcium	Ca	40.0	2.36×10^{-3}	(a)
Fluoride	F	19.0	0.0130	(b)
Silica	Si	28.1	2.28×10^{-3}	(a)

(a) Fiskum et al. (2018)
(b) Ferriter (2016)
(c) Neither Ferriter (2016) nor Fiskum et al. (2018) provide a basis for organic carbon speciation beyond oxalate ion concentrations. For the current simulant, formate and acetate contributions were selected to provide equal carbon contribution from each ion.

The simulant recipe listed in Table 2 is prepared as follows:

1. The target simulant volume is selected, and the simulant recipe appropriately scaled.
2. The simulant components listed in Table 2 are pre-weighed to a ±1% accuracy.
3. Trim water is added to a vessel of appropriate size, with a small amount held back for rinsing in subsequent steps.
4. The remaining pre-weighed simulant components are added to the vessel, one at a time, in the order listed in Table 2.
5. Remaining trim water not used for rinsing is added to the simulant.
6. The combined salt/trim water mixture is heated to ~65 °C, stirred until all solids have dissolved, and then held for an additional 30 to 60 minutes at temperature.
7. The combined solution is allowed to cool to room temperature overnight and subsequently held for at least 1 week to allow post-batching precipitation of solids.

Table 2. AP-105 simulant recipe at 8.5M Na target. Recipe basis is 1 liter of simulant. Sodium hydroxide is added as a 50-wt% solution in water. Compounds are listed in order of addition (excepting approximately 100 grams of trim water).

Compound	Form/Formula	MW (g mol^{-1})	Compound Mass (g)	Concentration (M)
Trim water[(a)]	H_2O	18.0	464.449	-- --
Aluminum nitrate	$Al(NO_3)_3 \cdot 9H_2O$	375.2	288.53	0.769
Nickel nitrate	$Ni(NO_3)_2 \cdot 6H_2O$	290.8	0.226	0.776×10^{-3}
Iron nitrate	$Fe(NO_3)_3 \cdot 9H_2O$	404.0	0.050	0.125×10^{-3}
Cesium nitrate	$CsNO_3$	194.9	0.014	0.0721×10^{-3}
Sodium hydroxide	NaOH (as 50% sol.)	40.0	386.66	4.83
Potassium chromate	K_2CrO_4	194.2	1.89	9.71×10^{-3}
Sodium phosphate	$Na_3PO_4 \cdot 12H_2O$	380.2	5.59	0.0147
Potassium chloride	KCl	74.6	9.09	0.122
Sodium chloride	NaCl	58.5	2.517	0.0430
Calcium chloride	$CaCl_2 \cdot 2H_2O$	146.9	0.346	2.36×10^{-3}
Sodium fluoride	NaF	42.0	0.544	0.0130
Sodium sulfate	Na_2SO_4	142.1	3.65	0.0257
Sodium acetate	$NaC_2H_3O_2$	82.0	5.97	0.0728
Sodium formate	$NaCHO_2$	68.0	9.90	0.146
Sodium oxalate	$Na_2C_2O_4$	134.0	0.41	3.03×10^{-3}
Sodium nitrite	$NaNO_2$	69.0	130.82	1.90
Sodium nitrate	$NaNO_3$	85.0	17.11	0.201
Boric acid	H_3BO_3	61.8	0.40	6.46×10^{-3}
Sodium metasilicate	$Na_2SiO_3 \cdot 9H_2O$	284.1	0.647	2.28×10^{-3}
Sodium carbonate	$Na_2CO_3 \cdot H_2O$	124.0	76.20	0.615
Total	**-- --**	**-- --**	**1405.00**	**-- --**

(a) Trim water is the total water content of the simulant less contributions from hydrated salts and stock solutions (i.e., the 50-wt% hydroxide solution, which already contains water). The bulk of trim water, added as DI water, is added prior to salt addition. A small quantity of water (~100 grams) is held back from the simulant until all salts have been added.

The final prepared simulant has a bulk density of 1.405 kg L^{-1}, and as noted above, it is not immediately stable with respect to solids precipitation. Following preparation, the simulant is vacuum filtered through a 0.45-µm polymer membrane to remove any precipitated solids. As discussed in Section 4.0, Simulant Stability, the as-made and filtered 8.5M Na AP-105 simulant appears stable with respect to further precipitation over the course of at least 6 months when stored under nominal laboratory conditions (approximately 15 to 25 °C and 1 atmosphere).

4.0 Simulant Stability

The as-prepared AP-105 precipitation simulant has an 8.5M Na content that is representative of the actual tank chemistry before feed staging for TSCR operations. For AP tank operations, TSCR feed staging will dilute wastes to approximately 5.6M Na using raw water. As noted in this report's introduction, it is suspected that dilution with raw water leads to precipitation of solids. This section documents testing undertaken to evaluate solids precipitation from the as-prepared 8.5M Na AP-105 simulant to 5.6M Na with raw water supplied by WRPS. Here, simulant stability is considered with respect to the precipitation of solids, with a "stable" simulant showing no precipitation and an "unstable" simulant showing precipitation. As a reference, the as-prepared simulant is also diluted with DI water to isolate the impact, if any, of background ions in the raw water on simulant stability.

The sections below first discuss the chemistry of the water supplied by WRPS for testing. Next, the simulant stability test matrix is described. Finally, the observed precipitation stability is discussed. Given the difficulty in separating the precipitated solids from the solution matrix without altering the chemistry of any solids precipitated or leading to additional precipitation of soluble salts upon drying, observed simulant precipitation behaviors are largely qualitative. Instead, effort was placed on successfully separating the precipitated solids and quantifying the underlying chemistry. The latter is discussed in Section 5.0, Precipitated Solids Chemistry.

4.1 Chemistry of Raw Water Used for Dilution

WRPS provided approximately 4 L of raw water for dilution. The content of key analytes in the water was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES), as well as analyses for total organic carbon (TOC) and total inorganic carbon (TIC).[1] Two approximately 20-mL aliquots (a primary and a replicate) of WRPS-supplied raw water were submitted for analysis.

The ICP-OES results are listed in Table 3 and include only analytes with finite detected content. Note that several analytes reported in Table 3 have concentrations that fall below the estimated quantitation limit (EQL) of the method (which means the results are subject to increased uncertainty relative to the baseline uncertainty of 10% to 15%). For some analytes, namely Tl, B, and Ce, the measured analyte content appears to derive entirely from the diluent used in ICP-OES. Note also that ICP-OES of the two raw water samples could find no detectable trace of Fe, Ni, and Cr. This finding is important, as solids adverse to filtration have been found in actual waste solids and contain Fe, Ni, and Cr (making these analytes a key part of the desired precipitated solids chemistry). The ICP-OES results suggest the most significant analytes present in the supplied water are Ca, Mg, S, Na, Si, K, and Sr. Other trace analytes (such as Al and La) are consistent with groundwater chemistry.

TIC/TOC results for the WRPS-supplied raw water are presented in Table 4 and suggest an organic and inorganic carbon content on the order of ~30 mg L^{-1} (as carbon) and ~25 mg L^{-1} (as carbon), respectively. The results suggest slightly elevated carbon levels in the replicate sample, but the significance of this result cannot be assessed from the limited measurements.

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[1] A brief description of analytical methods is given in Appendix A.

Table 3. Composition of WRPS-supplied raw water as measured by ICP-OES. Only analytes that had detectable contents are listed. Other analytes, notably Fe, Cr, and Ni, were tested for but not detected. Analyte contents below the EQL are italicized and highlighted in red. All concentration units are in micrograms analyte per liter sample (mg L^{-1}). Analytes are listed in order of decreasing concentration.

		Concentration (mg L^{-1})		
Analyte	EQL (mg L^{-1})	Diluent	Primary Sample	Replicate Sample
Ca	0.177	-- --	22.7	22.3
Mg	0.068	-- --	5.42	5.38
S	1.186	-- --	3.85	3.84
Na	0.246	0.12	2.47	2.45
Si	0.237	-- --	1.72	1.73
K	0.240	-- --	0.756	0.778
Sr	0.005	-- --	0.122	0.123
Tl	0.53	0.073	*0.081*	*0.12*
Se	1.595	-- --	*0.19*	-- --
Ba	0.003	-- --	0.0331	0.0321
B	0.067	0.041	*0.03*	*0.02*
Ce	0.069	0.011	*0.01*	*0.017*
Zn	0.043	-- --	*0.013*	*0.012*
Al	0.122	-- --	-- --	*0.022*
La	0.022	-- --	*0.0097*	*0.01*
Cu	0.016	0.0021	*0.0052*	*0.0047*
Li	0.009	-- --	*0.0017*	*0.0011*
Ti	0.004	-- --	*0.0013*	-- --
Mn	0.020	-- --	*0.0003*	*0.0003*

Note: Analyte concentrations below the minimum detection are designated with “-- --”.

Table 4. Total inorganic and organic carbon content of the WRPS-supplied raw water. The primary sample provided for analysis was measured two separate times. All measurements are reported in milligrams carbon per liter sample (mg L^{-1}).

		Sample Content (mg L^{-1})		
Property	EQL (mg L^{-1})	Primary Sample (Meas. 1)	Primary Sample (Meas. 2)	Replicate Sample
TIC	55	23.54	23.77	28.51
TOC	55	24.00	26.16	36.61

4.2 Dilution Test Matrix

This section discusses the test matrix used to study the behavior of the as-made (8.5M Na) simulant with respect to solids precipitation upon dilution with the WRPS-supplied raw water. Dilution targets were roughly bounded by the expected range of process dilutions for AP-105 staging operations, namely dilution to 5.6M Na. The mass of raw water (δm) needed to effect this dilution was estimated by:

$$\delta m = \left(\frac{c_o\,\rho_1}{c_1\,\rho_o} - 1\right) m_o \tag{1}$$

where m_o is the mass of the undiluted simulant; c_o and c_1 are the undiluted and diluted target Na concentrations (assumed to be 8.53M and 5.60M, respectively, for the purpose of calculation)[1]; and ρ_o and ρ_1 are the undiluted and diluted simulant densities (assumed to be 1.387 kg L^{-1} and 1.267 kg L^{-1}, respectively).[2] From these assumed properties, the required mass of diluent (δm) per original mass of simulant (m_o) may be calculated as:

$$\frac{\delta m}{m_o} = \left(\frac{8.53\text{ M}}{5.60\text{ M}}\right)\left(\frac{1.267\text{ kg L}^{-1}}{1.387\text{ kg L}^{-1}}\right) - 1 = 0.391 \tag{2}$$

This means that dilution from 8.5M to 5.6M Na is effected by an addition of approximately 0.40 grams of water for every gram of as-prepared simulant. For simplicity, the test matrix evaluates a dilution range of 0 (i.e., as-made) to 0.4 grams of water per gram of as-made simulant. In practice, simulant dilution testing was implemented as follows:

1. Make 2 L of the simulant formulation listed in Table 2. Hold the simulant at ambient laboratory conditions for 1 week.
2. If solids are present in the as-made simulant after the 1 week of hold time, filter the simulant, collect the solids (termed the “as-made” solids), and collect the filtered liquid. If no solids are present, proceed with the unfiltered liquid. The liquid resulting from this step is termed the “solids-free liquid.”
3. Split the solids-free liquid into 10 × 200-mL aliquots. Process these aliquots as follows:
    a. DI controls: Dilute the five “control” (D) samples with DI water as follows:
        i. D00 – no dilution (control)
        ii. D10 – dilute with 10 grams of DI water per 100 grams of solids-free liquid
        iii. D20 – dilute with 20 grams of DI water per 100 grams of solids-free liquid
        iv. D30 – dilute with 30 grams of DI water per 100 grams of solids-free liquid
        v. D40 – dilute with 40 grams of DI water per 100 grams of solids-free liquid

---

[1] For the purpose of calculating the dilution factor for testing, the more exact representations of the as-made concentration and target dilution concentration, 8.53M and 5.60M, respectively, are assumed. Elsewhere, the approximate 8.5M and 5.6M concentrations are used.

[2] Basis values for density (1.387 kg L^{-1} and 1.267 kg L^{-1} for the 8.5M Na and 5.6M Na simulants, respectively) are taken from Table 3 of the attachment to LTR-72195-007 (letter from Philip Schonewill, PNNL, to Matthew Landon, WRPS, dated January 25, 2019, “Electronic Transmittal of Recommendation for an Updated Nominal Sodium Simulant Based on Tank AP-105 Chemical and Filtration Data,” LTR-72195-007, Pacific Northwest National Laboratory, Richland Washington).

   b. Raw water samples: Dilute the remaining five solids-free samples (R) with the raw water provided by WRPS as follows:
      i. R00 – no dilution (control)
      ii. R10 – dilute with 10 grams of raw water per 100 grams of solids-free liquid
      iii. R20 – dilute with 20 grams of raw water per 100 grams of solids-free liquid
      iv. R30 – dilute with 30 grams of raw water per 100 grams of solids-free liquid
      v. R40 – dilute with 40 grams of raw water per 100 grams of solids-free liquid

4. Hold all (10) D and R samples generated in step 3 at ambient lab temperature for approximately 1 week.
5. If solids are present in any of the 10 samples after the 1-week hold period, filter or centrifuge and collect these solids. Collect the filtered liquid (or any unprocessed solids-free liquids) for continued testing.
6. Continue to hold the 10 filtered/unfiltered liquids at ambient laboratory temperature for at least another 30 days.
7. If solids are present in any of the 10 samples after the 30-day hold period, filter and collect these solids.

Dilution of individual samples with both DI water and WRPS-supplied raw water allows assessment of the role that water chemistry, namely dissolved solids, plays in any observed precipitation. In addition, inclusion of undiluted control samples allows assessment of the role of continued precipitation in the as-made simulant. With respect to the stability of the as-made simulant, precipitation from the as-made, 8.5M Na was expected as it has been observed upon preparation of prior DFLAW-style simulants (see Russell et al. 2017; Daniel et al. 2018). For this reason, the test matrix above includes a step (step 2) to allow the simulant to stabilize and remove initial solids formed during this stabilization period. At the outset of testing, it was unclear if this initial stabilization period of 1 week was long enough to stabilize the as-made simulant, motivating the inclusion of undiluted controls in the test matrix above.

In isolating the chemistry of the solids that result from dilution of the simulant, only solids that form in the undiluted controls after the initial separation effected by step 2 of the text matrix are important. Therefore, the chemistry of any solids formed during stabilization was not tracked. In contrast, solids formed upon dilution with water were evaluated in cases where sufficient solids could be separated from the liquid for analysis. The chemistry of collected solids was characterized using ICP-OES, X-ray diffraction (XRD), and scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS). In addition, the chemistry of the solids-free liquid as-made and maximally diluted simulant (i.e., 0.4 gram per gram simulant) was quantified.

Finally, it should be noted that the as-planned test matrix included provisions for additional testing should dilution with raw water not lead to precipitation. Planned follow-on tests included temperature cycling of the simulant between ambient conditions at 10 and 40 °C and bubbling CO_2 gas through the simulant to saturate carbonate. Ultimately, these tests were not conducted because 1) precipitation was observed upon addition of raw water and 2) the degree of precipitation could be tied strongly to the use of raw water and amount of water added to the simulant.

4.3 Test Observations

The test matrix outlined in the preceding section was executed on a small (2-L) batch of as-made AP-105 simulant. This subsection discusses the key qualitative observations made during testing. To better delineate the observations made during the different steps and dilutions, the discussion is divided into three parts: 1) simulant preparation and precipitation from the as-made 8.5M Na simulant, 2) precipitation of solids from the DI and raw water diluted simulant samples, and 3) a summary of key findings.

Preparation and Handling of the 8.5M Na AP-105 Simulant: A simulant was prepared at 8.5M Na per the recipe provided in Table 2 and allowed to stabilize for a period of 7 days. During this stabilization period, solids were observed to precipitate from the as-made simulant. These solids consisted of two visually distinct phases: a gravimetrically heavier white solid phase and a lighter red solid phase. Figure 1 shows a photo of the as-made precipitated solids; note that the solids pictured correspond to a scaled (12-L) simulant batch and have been concentrated by several settle/decant operations. The 2-L simulant batch was vacuum filtered over a 2-week period to remove these solids and held an additional 5 days before it was split and diluted. No further solids were observed to precipitate from the filtered liquid over the 2-week filter period or during the 5-day wait period.

Figure 1. Photo of solids precipitated from the as-made simulant. The solids shown correspond to those precipitated from a scaled (12-L) batch from which excess supernatant has been settled and decanted. The solids precipitated from the 2-L test batch discussed herein were visually identical.

Dilution of the AP-105 Simulant with DI and Raw Water: The filtered as-made simulant was diluted with 0.1, 0.2, 0.3, and 0.4 grams raw or DI water per gram of as-made simulant (i.e., raw water diluted samples -R10 through -R40 and DI diluted samples -D10 through -D40) and held for 7 days at ambient laboratory conditions. Two undiluted samples (-R00 and -D00) were kept as a control. The samples were monitored for a total of 173 days following dilution, although the frequency of observation was significantly reduced following the first 7-day hold period called for by the test matrix. Table 5 summarizes key events in the sample monitoring history. In all cases, dilution of the simulant with either DI or raw water eventually led to the precipitation of a reddish-hued solid. However, the extent and rate of solids precipitation appear to be greatly accelerated using raw water, leading to precipitation of solids in the 0.3 and 0.4 g g^{-1} dilution levels in the week following dilution. In contrast, precipitation of solids in the samples diluted with DI water only became apparent after 2 months of hold time.

Table 5. Summary of key observations during post-dilution monitoring of the as-made AP-105 simulant with WRPS-supplied raw water and DI water. Raw water dilutions at 0.1, 0.2, 0.3, and 0.4 grams of water per gram of as-made simulant are denoted as -R10, -R20, -R30, and -R40, respectively. DI water dilutions at 0.1, 0.2, 0.3, and 0.4 grams of water per gram of as-made simulant are denoted as -D10, -D20, -D30, and -D40, respectively. Two undiluted controls were kept (-R00 and -D00, respectively).

		Solids Appearance in Sample										
Event	Time Since Dilution (days)	-R00	-R10	-R20	-R30	-R40	-D00	-D10	-D20	-D30	-D40	Notes
As-made simulant diluted	0											No immediate precipitation upon dilution observed.
First solids observed in (-R30/-R40)	6				+	+						Solids are white and easily disturbed by fluid motion.
First solids observed in -R20	8			+	+	+						Solids in -R40 take on reddish hue. Solids from -R30 and -R40 removed for ICP, XRD, and SEM.
End of primary monitoring	30			+								None
Observed additional solids in -R30 and -R40	71			+	++	++						Second-generation -R30 and -R40 solids have reddish hue. Sampled second-generation solids for analysis.
First solids observed in -D40	74			+							+	First-generation -D40 solids have reddish hue. The -D40 solids were sampled on the following day.
Observed solids in all diluted samples	104		+	+	+++	+++		+	+	+	++	Observed third-generation solids in -R30 and -R40 and second-generation -D40 solids. All diluted samples, including DI diluted, now have reddish precipitates.
End of monitoring	173		+	+	+++	+++		+	+	+	++	End of monitoring. All diluted samples still have reddish solids. No precipitates observed in undiluted simulant.

Note: For the “Solids Appearance in Sample” columns, a blank cell indicates no observed solids, a “+” indicates first-generation solids, “++” indicates second-generation solids, and “+++” indicates third-generation solids.

As noted in Table 5, the first solids precipitated from the -R30 and -R40 samples appeared to be white and were easily disturbed by fluid motion. These precipitated solids appeared to take on a reddish hue over time but still appeared fine and easily disturbed by fluid motion. Figure 2 shows photos of the initial white solid precipitate (as best can be captured by digital camera) and the reddish "aged" solids. In contrast, the solids first observed in the -R10 and -R20 samples and in all DI-diluted samples appeared to have the reddish hue; however, after the first week following dilution, the sample observation interval was lengthened considerably (i.e., to the order of once every 30 days), and it is unclear if the initial precipitates that formed after the first week started off white and changed color shortly after (as was observed in the -R30 and -R40 samples). Moreover, from visual observation alone, it is difficult to determine if the reddish hue taken by the solids represents an "aging" of the initial precipitate (through chemical evolution or physical changes like particle growth) or a secondary precipitate that visually obscures the initial precipitate. The former mechanism (i.e., "aging") is assumed for the purpose of discussion herein.

The initial 30-day precipitation behavior observed for the diluted simulants strongly suggests that dilution with WRPS-supplied raw water accelerates precipitation from the simulant relative to DI water. While dilution with raw water accelerates or effects an initial precipitation, dilution generally appears to lead to precipitation across all samples. With respect to the samples diluted with raw water, precipitation occurs well into the 100-day period following dilution, as evidenced by the reappearance of solids in the diluted liquid remaining after removal of first- and second-generation solids for physical characterization. Moreover, this precipitation cannot be entirely linked to the intrinsic chemical or physical nature of the WRPS-supplied water itself, as precipitation is also observed in the sample diluted with DI water. Because precipitation was not observed in either of the undiluted control samples (-D00 and -R00), the as-made chemistry of the simulant can be considered stable and precipitation in the diluted samples can be postulated to occur as a result of 1) the process of dilution itself or 2) interaction between the simulant chemistry and trace environmental contamination (e.g., CO_2 absorbed through the atmosphere).

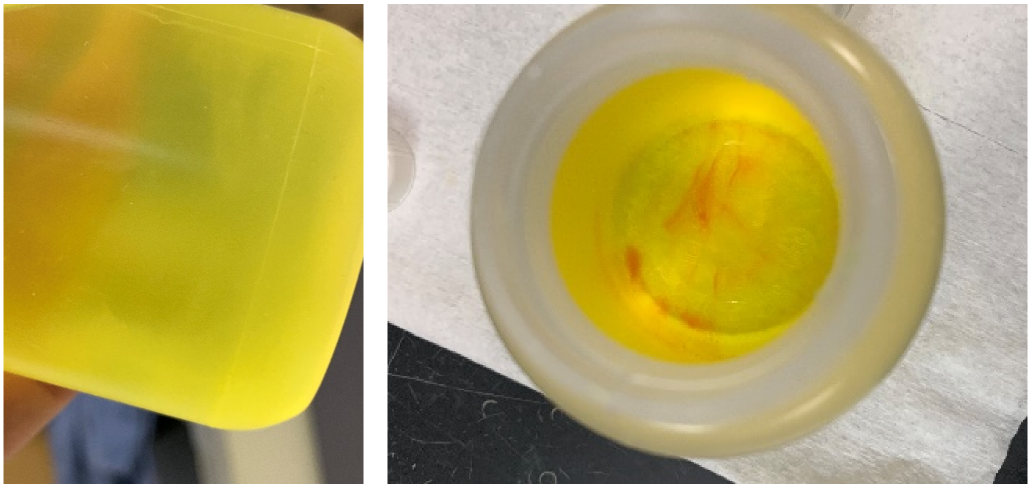
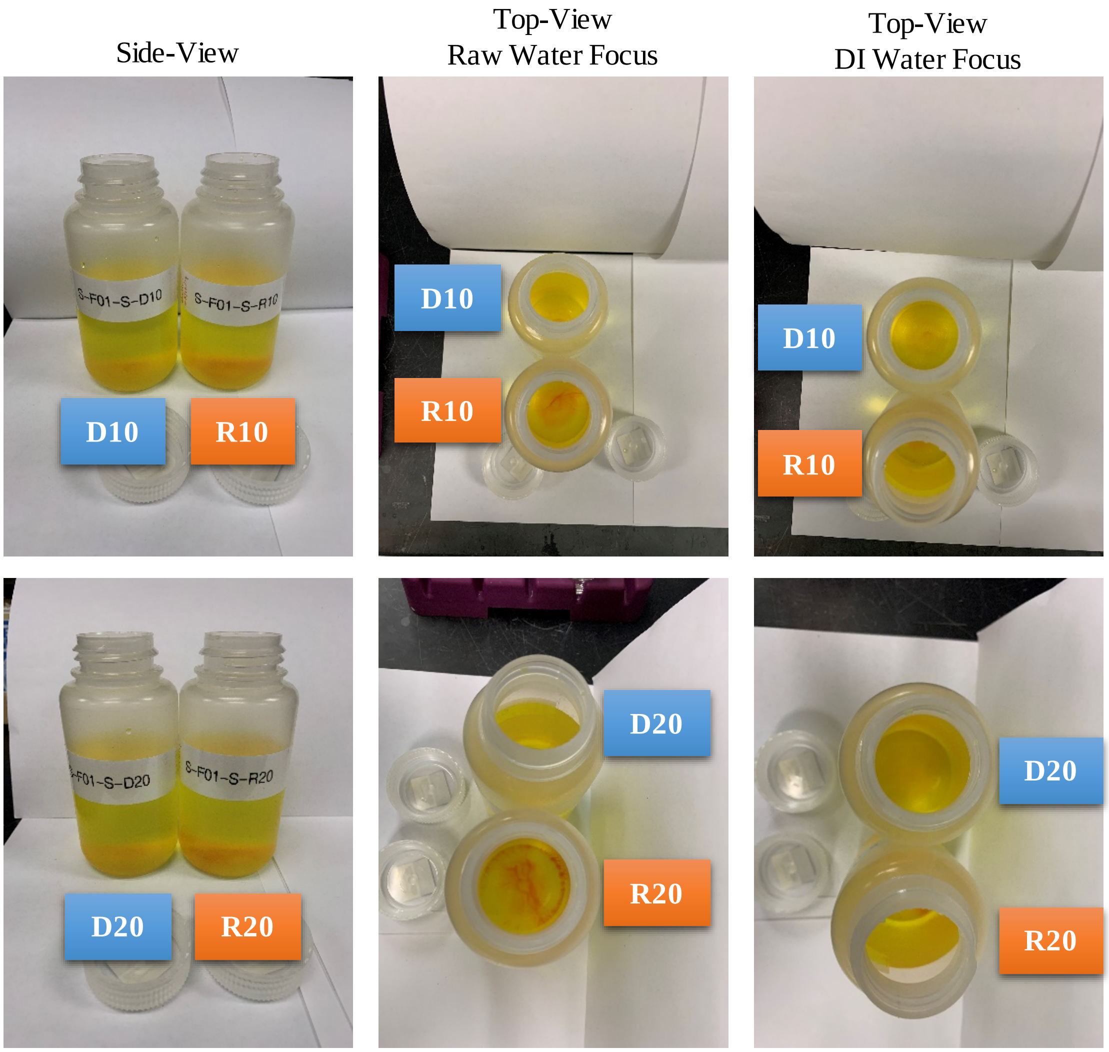


Figure 2. Two photos of solids precipitated in the -R40 sample (i.e., as-made simulant diluted with 0.4 grams of WRPS-supplied water per gram of simulant). The photo on the left shows the initial white, wispy solids as best can be imaged by digital camera. (Note: These solids cannot be easily distinguished from the opacity of the plastic bottle in which the simulant is stored.) The photo on the right shows an example of the -R40 solids after "aging" (here shown at the close of the study, after 173 days).



Side-View

Top-View
Raw Water Focus

Top-View
DI Water Focus

Figure 3. Comparison of -R10 to -D10 (top row) and of -R20 to -D20 (bottom), evidencing greater precipitation in the raw water diluted samples. Images taken at the end of monitoring (i.e., 173 days after dilution). All samples show reddish solids characteristic of the long-term precipitate.

It is important to note that while precipitation was eventually observed in all diluted samples, the total quantity of solids formed appeared to be greatest in the raw water diluted samples. This assertion is based on visual comparison of the -R10 and -D10, and -R20 and -D20, diluted sample sets, in which a greater quantity of aged solids appears in the raw water diluted samples (see Figure 3). This general trend cannot be confirmed in the more highly diluted 0.3 and 0.4 g g^{-1} samples due to periodic collection of solids for analysis.

Finally, note that no attempt was made to quantify the concentration of solids precipitated as a result of dilution level. While general visual observation suggests an increase in the amount of precipitate with increasing dilution level, no hard-quantitative concentration measurements were taken due to the limited quantity of precipitated solids (which impedes gravimetric determination), the difficulty in isolating those solids from their high-dissolved solids suspending phases, and the need to collect and prepare solids for chemical analysis.

Summary of Dilution Matrix Observations: Based on the observations reported collectively in Table 5, Figure 2, and Figure 3, the following general statements can be made about the stability of the AP-105 chemical simulant with respect to dilution with raw process water:

- Dilution of the AP-105 simulant leads to long-term instability with respect to precipitation; for all dilution levels tested that span the 8.5M to 5.6M Na range expected for tank staging operations, precipitation of a fine, easily suspended solid (ranging from white to red in appearance) was observed.
- Use of raw process water greatly accelerates the onset of precipitation and appears to increase the extent of solids precipitated.

As noted earlier in this section, the initial solids precipitated by raw water addition at 0.3 and 0.4 grams water of per gram of as-made simulant appeared to be fine, easily suspended white solids. Later observation of solids in these two raw water dilutions found them to have taken on a reddish hue equal in appearance to solids found as a result of long-term precipitation in both raw and DI-diluted simulant. Whether this change results from chemical/physical aging of the initial solids or later precipitation of a visually dominant red solid phase cannot be readily determined from visual observation alone. Likewise, while currently the results suggest that diluting with raw water accelerates precipitation, visual observation does not provide convincing evidence that the solids precipitated are chemically distinct from those that eventually precipitated from the DI water samples, nor does it provide any insight as to what is the key chemical or material attribute of the raw water that “catalyzes” accelerated and more extensive precipitation.

For these reasons, particularly the latter, samples of the initial solids precipitated from the -R40 (i.e., the 0.4-gram raw water per gram as-made simulant dilution) were collected and characterized using XRD, SEM, and ICP. To differentiate the initially precipitated -R40 solids from those precipitated by DI dilution, the -D40 (i.e., the 0.4-gram DI water per gram as-made simulant dilution) solids were also collected for analysis. However, the quantity of solids collected from this sample was not sufficient to allow both ICP and SEM/XRD analyses. As XRD allows determination of mineral phase, it was decided that the entirety of the -D40 solids should be used for SEM/XRD analyses in lieu of ICP. In the section that follows, the findings of solid chemistry analysis by ICP, SEM, and XRD are discussed.

5.0 Precipitated Solids Chemistry

In the previous section, the test matrix used to evaluate the stability of the AP-105 simulant with respect to precipitation upon dilution and the results of stability testing were discussed. It was shown that solids do precipitate as a result of dilution with water; in addition, the results strongly suggest that dilution with WRPS-supplied raw water accelerates the rate and increases the extent of solids precipitation. While the visual observations discussed in the preceding section suggest a change in the solids with time or a second-stage precipitation, long-term observation of the precipitated solids finds little, if any, visual distinction between the solids formed through raw water dilution and those formed by DI water dilution. Similarly, visual observation alone does not inform on the underlying chemical or physical attributes of the raw water that accelerate the rate and increase the extent of solids precipitation observed. To resolve these issues, samples of the solids precipitated from the maximally diluted raw and DI water samples were submitted for chemical analysis. Enough raw-water precipitated solids were available to allow ICP, XRD, and SEM-EDS analysis. However, limited DI water solids were available for destructive analysis; XRD was selected over ICP in hopes that the mineral phase of the solids could be ascertained and because the XRD stub could be sampled and imaged by SEM-EDS to provide additional information about solids chemistry.

In the subsections that follow, the results of ICP, XRD, and SEM-EDS for the solids precipitated from the raw and DI water diluted samples are discussed. As the suspending phase and diluent chemistries directly inform on the chemistry of solids that can precipitate, analyte contributions from both are also discussed on the pages that follow. Section 5.1 discusses the chemistry of the -R40 solids formed over the 6-to-8-day period following raw water dilution. Section 5.2 discusses the chemistry of the -D40 solids formed approximately 2 months after DI water dilution of the as-made simulant. Finally, concluding remarks about the nature of precipitated solids are given in Section 5.3.

5.1 Characteristics of the -R40 Precipitated Solids

The solids precipitated from the -R40 sample, which is the as-made AP-105 simulant diluted with WRPS-supplied raw water at 0.4 grams water per gram of as-made simulant, were the first to form. While no effort was made to quantify solids as a function of dilution level, the initial -R40 precipitation occurred to a greater extent than in the -R30 sample and contained enough solids to allow collection by centrifuging and separation from the supernatant liquid decant and wash operations. As observed in the original sample, the initial precipitate appeared as white, easily suspended wispy solids (6 days after dilution). When the sample was observed 8 days after dilution, the -R40 solids appeared to have gained a reddish hue, while still being easily suspended. Centrifuge and decant operations yielded a centrifuged solids cake composed of reddish-white solids (see Figure 4). It is possible that these were a mixture of the initially precipitated white solids and second-stage precipitation red solids. However, if there were two distinct phases, their physical properties (namely density and size) were not sufficiently different as to yield gravimetric separation during centrifuging.

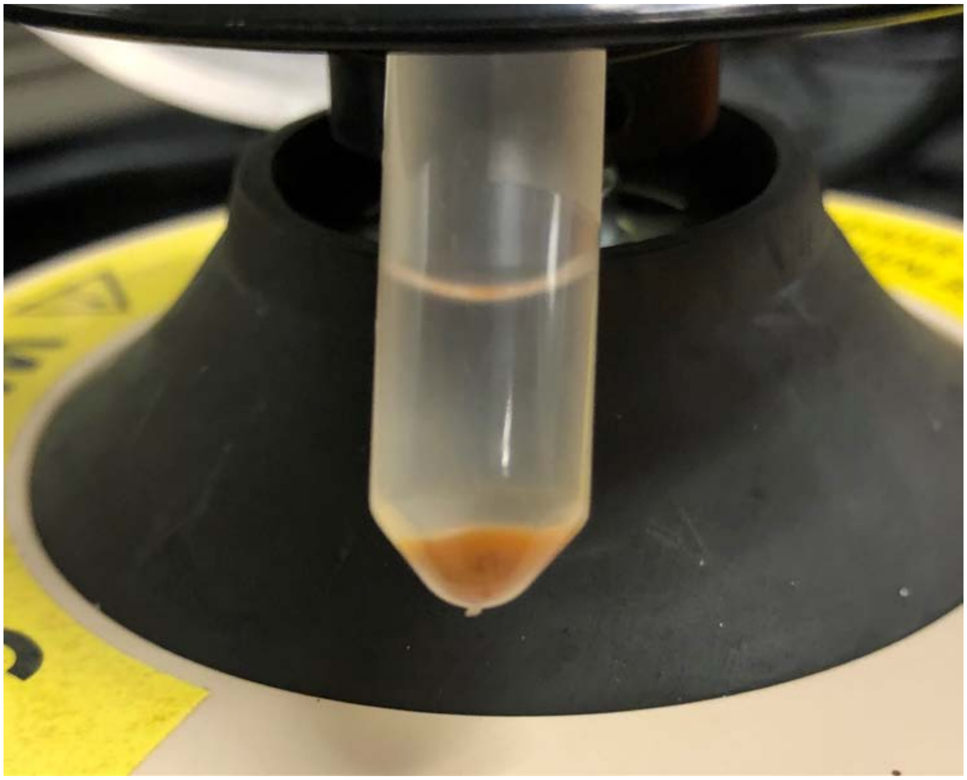


Figure 4. Photo of centrifuged solids (i.e., the reddish-white solids collected at the bottom of a centrifuge vial) precipitated by dilution of the as-made AP-105 simulant with WRPS-supplied raw water. The solids shown here derive from the -R40 dilution (0.4 g g^{-1}). The centrifuge vial shown is approximately 9 mm in diameter. To effect separation and preparation for ICP-OES, XRD, and SEM-EDS, the solids shown have been washed with and suspended in isopropanol.

The chemical speciation of select analytes within the -R40 precipitated solids was evaluated using ICP-OES. Solids precipitated from the -R40 dilution were isolated by centrifuging the diluted suspension, decanting the excess supernatant, and washing and displacing the remaining supernatant with isopropanol. Isopropanol was used to wash the solids in order to minimize dissolution of soluble solids while at the same time displacing dissolved-solids-rich supernatant that could lead to unwanted precipitation upon drying. Note that vacuum filtration, which was the originally planned method of separating precipitated solids from the supernatant, was foregone because of concerns that the quantity of solids precipitated could not be successfully recovered from the filter surface and because of concerns that precipitation of dissolved solids through drying of residual supernatant on the filter would grossly contaminate the target solids.

Table 6. Liquid phase chemistry of the as-made/filtered (8.5M Na) AP-105 simulant (i.e., the as-made simulant after stabilization and solids removal) and the -R40 dilution (after removal of the first-generation solids) as measured by ICP. For reference, the equivalent analyte concentration of the as-made simulant recipe (see Table 2) is included. Estimates of the -R40 analyte contributions that derive from the as-made simulant and from the raw water are provided separately and are based on the ICP results measured for as-made and filtered 8.5M Na simulant and the raw water, respectively. Note: Full precision was maintained in all calculated and extrapolated numbers for reference. Calculated concentrations (i.e., 8.5M as-made recipe calculations) are based on the target recipe. Measured concentrations derive directly from ICP-OES measurements. Extrapolated concentrations are based on measured ICP-OES data but have been corrected for dilution.

	Concentration (µg L^{-1})			Concentration (µg L^{-1})			
Analyte	8.5M As-Made Recipe [Calculated]	Actual Filtered 8.5M Na Simulant [Measured]	Ratio	Estimated R40 Dilution (Simulant) [Extrapolated]	Estimated R40 Dilution (Raw Water) [Extrapolated]	Measured R40 Dilution [Measured]	Ratio
Al	20,748,462	19,000,000	0.916	12,416,830	4	13,000,000	1.047
As	-- --	17,000	(a)	11,110	-- --	12,700	1.143
Ba	-- --	1,100	(a)	719	12	699	0.957
B	69,844	55,600	0.796	36,336	9	39,500	1.087
Ca	94,500	-- --	0	-- --	8,174	-- --	0
Cr	505,039	425,000	0.842	277,745	-- --	295,000	1.062
Cu	-- --	-- --	-- --	-- --	2	-- --	(a)
Fe	6,964	4,410	0.633	2,882	-- --	871	0.302
Li	-- --	-- --	-- --	-- --	1	-- --	(a)
Mg	-- --	-- --	-- --	-- --	1,962	-- --	0
Ni	45,548	-- --	0	-- --	-- --	-- --	-- --
P	455,038	406,000	0.892	265,328	-- --	278,000	1.048
K	5,525,240	4,860,000	0.880	3,176,094	279	3,280,000	1.033
Se	-- --	-- --	-- --	-- --	35	-- --	-- --
Si	64,000	78,500	1.227	51,301	627	54,400	1.048
Na	196,000,000	172,000,000	0.878	112,404,985	894	118,000,000	1.050
Sr	-- --	-- --	-- --	-- --	45	-- --	(a)
S	824,114	759,000	0.921	496,020	1,397	528,000	1.061
Tl	-- --	2,720	(a)	1,778	37	-- --	0
Ti	-- --	-- --	-- --	-- --	0.2	-- --	(a)
Zn	-- --	4,560	(a)	2,980	5	3,140	1.052

(a) Ratio not calculated; analyte in vanishingly small quantity.

Note: Here, original analyte concentrations (and their derivative calculated and extrapolated values) falling below their EQLs are marked as “-- --”.

Table 6 provides the liquid phase concentrations of select analytes for the as-made and -R40 diluted simulants (after solids removal[1]) as measured by ICP-OES. In addition, Table 6 includes the expected as-made analyte concentrations (based on the Table 2 recipe) and estimates of the analyte contributions to the -R40 simulant from both the simulant and the diluent (i.e., the raw water). These results highlight several key differences (and similarities) in expected and measured concentration that provide a basis for the observed precipitation behavior upon as-made simulant dilution. For the as-made simulant, these differences are as follows:

- Except for silicon, the measured concentrations of all analytes in the filtered, as-made simulant fall below those expected (calculated) from the recipe (with the difference generally being greater than the 10-15% error typical of ICP methods). This difference is not surprising given the observed solids precipitation immediately following simulant preparation and suggests that the proposed recipe is generally oversaturated in most soluble salts; however, the relative decrease in measured analyte content seems large relative to the final mass of solids filtered from the as-made simulant (~2.5 grams) The increase in the silicon concentration suggests contamination of the simulant by the glassware used to prepare the recipe or the vials used to prepare samples for ICP-OES.
- The as-made simulant is particularly deficient in iron and does not evidence any of the expected calcium or nickel. The lower-than-expected iron content, when considered with the reddish appearance of the as-made solids (see Figure 1), suggests partial, but not complete, precipitation of iron oxide in the as-made solids. As such, iron is expected to carry over to the diluted simulant. The complete lack of calcium and nickel suggests that neither is soluble in the simulant supernatant (or alternately, that their detection is limited by other analytes). On this basis, no calcium or nickel content is expected in the diluted samples, save for the contribution that derives from the raw water itself. With respect to the latter, the raw water contains calcium but not nickel.
- The as-made simulant appears to be contaminated by barium, arsenic, thallium, and zinc. While it is possible that these contaminants derive either from cross-contamination during ICP measurement or trace contaminants in the stock chemicals used to prepare the simulant, their exact origin is unknown.

With respect to the -R40 simulant dilution, the key observations derived from Table 6 ICP data are as follows:

- In general, the content of the -R40 solids-free supernatant matches that estimated from extrapolations of the liquid phase ICP measurements of the as-made/filtered 8.5M Na simulant. Indeed, the difference in analyte contents for all but a few key analytes falls within the 10-15% error typical of ICP-OES. While this may suggest that most analytes (and their associated soluble salts and/or mineral phases) are stable in the diluted simulant, the large concentrations of several analytes (such as sodium) allow for modest precipitation without effecting measurable change in the analyte content determined by ICP.
- The -R40 dilution evidences no calcium, magnesium, or thallium. The first two analytes are expected to derive largely from the raw water addition, whereas thallium should largely derive from the as-made simulant (where it is considered a contaminant). From this observation, it can be postulated that any solids precipitated from the diluted simulant should contain any of these three analytes: calcium, magnesium, and thallium.
- The -R40 dilution is deficient in iron. This, along with the observation of fine red precipitates during visual inspection of the -R40 solids, suggests that iron oxide/hydroxide (and associated mineral phases) is a likely precipitate. Moreover, that iron persists in the solids-free -R40 supernatant after precipitation of first-generation solids suggests that additional precipitation of second- and third-

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[1] Here, the -R40 liquid analyzed corresponds to that after removal of the first-generation solids 8 days after simulant dilution. The -R40 liquid was not analyzed after removal of second-generation solids.

generation reddish solids in the -R30 and -R40 simulants and in all other dilutions could be iron oxide/hydroxide solids.

Based on liquid phase ICP measurements alone, precipitates derived from simulant dilution are expected to contain iron, calcium, and magnesium. In addition, major simulant components including sodium, potassium, and aluminum are also likely to be found in or along with the precipitated solids, either because they are slightly unstable in the simulant (and precipitate to an extent that cannot be quantified by ICP) or because of cross-contamination of the solids by dried supernatant (despite best efforts to limit such contamination during the solids centrifuging and washing process used to isolate solids for analysis).

Table 7 shows the ICP-derived chemical composition of the first-generation solids collected from the -R40 diluted sample 8 days after dilution. Major analytes include aluminum, calcium, iron, magnesium, and sodium. All observed components are expected based on liquid phase ICP data. Comparison of the analyte content of the -R40 precipitate relative to that expected in the dilute simulant suggests the following:

- ICP indicates that the precipitate contains other trace analytes (As, Bi, Li, Mn, Sr, Sn, and Zr, all at contents at or below 6 µg L^{-1}). However, concentrations for these analytes fall near or below the EQL for these species (such that their actual content is subject to increased uncertainty). [1]
- The relative contents of iron, calcium, and magnesium in the precipitate (roughly 30%, 55%, and 60%, respectively) represent a significant fraction of the available inventory for precipitation. This observation is consistent with the observed deficiencies in expected calcium, magnesium, and iron content in the -R40 liquid phase.
- Nickel is present in the precipitated solids in relatively small amounts (12 µg L^{-1}) but could derive from the original content added to the as-made simulant. While the Ni content is small, it still exceeds the EQL by nearly a factor of 10. Similar statements can be made for chromium-bearing solids, with Cr present at 99 µg L^{-1} (nearly 300 times its EQL).
- The aluminum and sodium content of the -R40 solids is small relative to the content available in the -R40 liquid (i.e., both precipitated fractions represent less than 0.05% of available content). As such, it is not clear if this content derives from precipitation during the 8-day hold period or from contamination of the solids by dried permeate.

Thus, ICP analysis of the -R40 solids largely confirms the expectations of the precipitate chemistry derived from liquid phase ICP, namely that the precipitates should contain iron (based on the partial decrease in iron content after dilution). In addition, solid phase chemistry appears to suggest Ca- and Ni-bearing precipitates (despite Ca and Ni not appearing in the as-made and filtered liquid phase chemistry after stabilization). Finally, the solids appear to contain Na-, Al-, Cr-, and Mg-bearing phases. Inclusion of the first three analytes is not surprising given their high concentrations in the as-made simulant and diluted suspending phases. Magnesium, which is not part of the as-made simulant recipe, appears to derive from the water used to dilute the simulant.

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[1] Presentation of analytes in both Table 6 and Table 7 uses a single set of common species. The decision to include trace analytes is based on detection of a given analyte in any liquid phase measurement (be it the as-made/filtered simulant, diluted simulant, or raw water diluent). For this reason, some solid phase analytes observed in ICP do not appear in Table 7. The concentrations of these species that were observed but are not tabulated here fell below 5 µg L^{-1}.

Table 7. ICP measured chemical speciation of the first-generation solids collected from the -R40 simulant dilution 8 days after addition of WRPS-supplied raw water. The ICP results have been corrected from a dry precipitated solids mass basis (µg analyte per gram dry solid) to a diluted simulant volume basis (i.e., µg analyte per liter diluted simulant). Included for reference is the estimated analyte content available for precipitation in the -R40 simulant (derived from the as-made simulant and the raw water diluent); these values are the same as those reported in Table 6.

	Concentration (ug L^{-1})			
Analyte	Measured R40 Solids	Available R40 Inventory from As-Made Simulant	Available R40 Inventory from Raw Water	Precipitate Relative to Total Analyte Inventory (%)(a)
Al	5,046	12,416,830	4	0.04
As	6	11,110	-- --	0.05
Ba	3	719	12	0.4
B	13	36,336	9	0.04
Ca	4,668	-- --	8,174	57
Cr	99	277,745	-- --	0.04
Cu	8	-- --	2	>100
Fe	843	2,882	-- --	29
Li	4	-- --	1	>100
Mg	1,081	-- --	1,961.8	55
Ni	12	-- --	-- --	(b)
P	103	265,328	-- --	0.04
K	119	3,176,094	279	0.004
Se	-- --	-- --	35	(c)
Si	43	51,301	627	0.08
Na	9,840	112,404,985	894	0.009
Sr	2	-- --	45	5
S	167	496,020	1,397	0.03
Tl	-- --	1,778	37	(c)
Ti	2	-- --	0.2	>100
Zn	8	2,980	5	0.3

(a) Several species (Cu, Li, and Ti) show measured solids content that grossly exceed available inventories. For these analytes, relative precipitate amounts are marked with “>100” [Li content falls at ~90% EQL; Cu and Ti are near 10% EQL]. Measured analyte concentrations (and the extrapolated R40 values) falling below their EQLs are marked as “-- --“.

(b) Nickel solids measured in -R40 precipitate and included in as-made formulation, but not detected in either the as-made and filtered 8.5M Na supernatant or the diluted -R40 supernatant accompanying the precipitated solids.

(c) Analyte detected in raw water or as-made simulant but not detected in -R40 solids.

SEM-EDS analysis of the -R40 solids yielded both chemical and morphological information. Figure 5 shows a representative SEM image of the solids. In general, it shows many visually distinguishable particles that are relatively large (25-50 µm) and rounded. Closer examination found fine needle-like particles (with the long linear dimension on the order of 10 to 20 µm and short linear dimension less than 2 µm). The image also suggests fine, plate-like ~1-µm particles; however, these are generally found on the surface of larger particles and it is not clear if they are permanently fused to these larger agglomerates or can be re-dispersed as primary fine particulate.

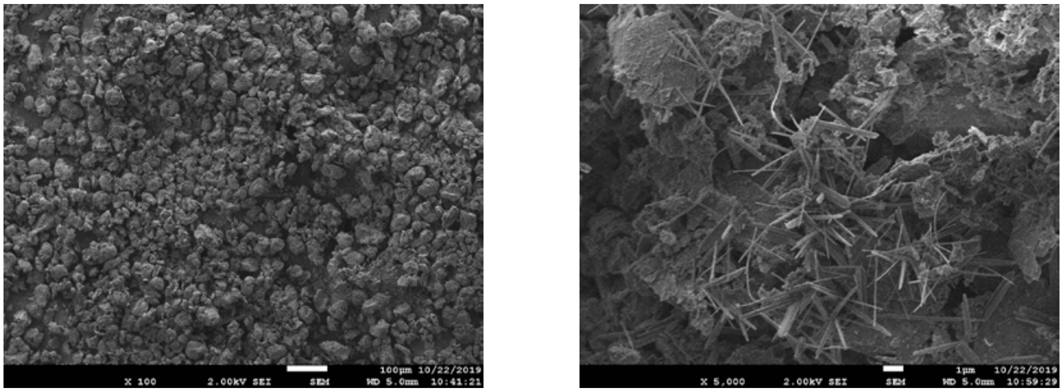

Figure 5. SEM image of the -R40 solids. In general, the solids are populated by relatively (25-50 µm) rounded particles interspersed with larger block particles (left image). Closer examination finds fine dendritic structures in the small grain areas between the larger rounded particles along with plate-like particles (that exist on the surface of larger agglomerates). Result is “For Information Only” (see note in Appendix A).

Figure 6 and Figure 7 show two EDS scans of the -R40 solids. The first, Figure 6, is focused on a particle representative of the large rounded particles that make up the bulk of those that are visually observable. EDS suggests these particles are composed primarily of Na, Al, and Ca (and oxygen). The EDS also suggests trace Mg, P, S, K, Fe, and Si (which is not surprising given the results of ICP analysis). Examination of the EDS scan shows localized P-, S-, and Fe-rich phases. EDS scattering of other particle morphologies found slight differences in EDS-inferred composition. The blocky log-like particle shown in Figure 7 is decreased in Mg, Ca, P, and Fe and elevated in C, Al, K, and Si compared to rounded particulates that make up the general particle population. EDS analysis of the fine needle-like particles shown in Figure 5 finds them rich in Na and O but unresolvable in terms of the other EDS analytes considered (i.e., those listed in Figure 6 and Figure 7).

Apart from localized hot spots of iron, phosphorous, and sulfur phases (which could suggest iron oxide and phosphate and sulfate salt precipitates), EDS suggests that key solid phase analytes (Na, Al, Ca) are distributed throughout the precipitated phase. The degree of analyte commingling is difficult to interpret but could suggest that the rounded and log-like 20- to 30-µm solids are fused agglomerates of smaller, two-to-three component oxide/salt precipitates (with agglomeration driven by the drying process used to prepare the SEM-EDS solid sample stub). Likewise, it could suggest a prevalent mineral phase(s) that incorporates many of the analytes, such as an aluminosilicate.

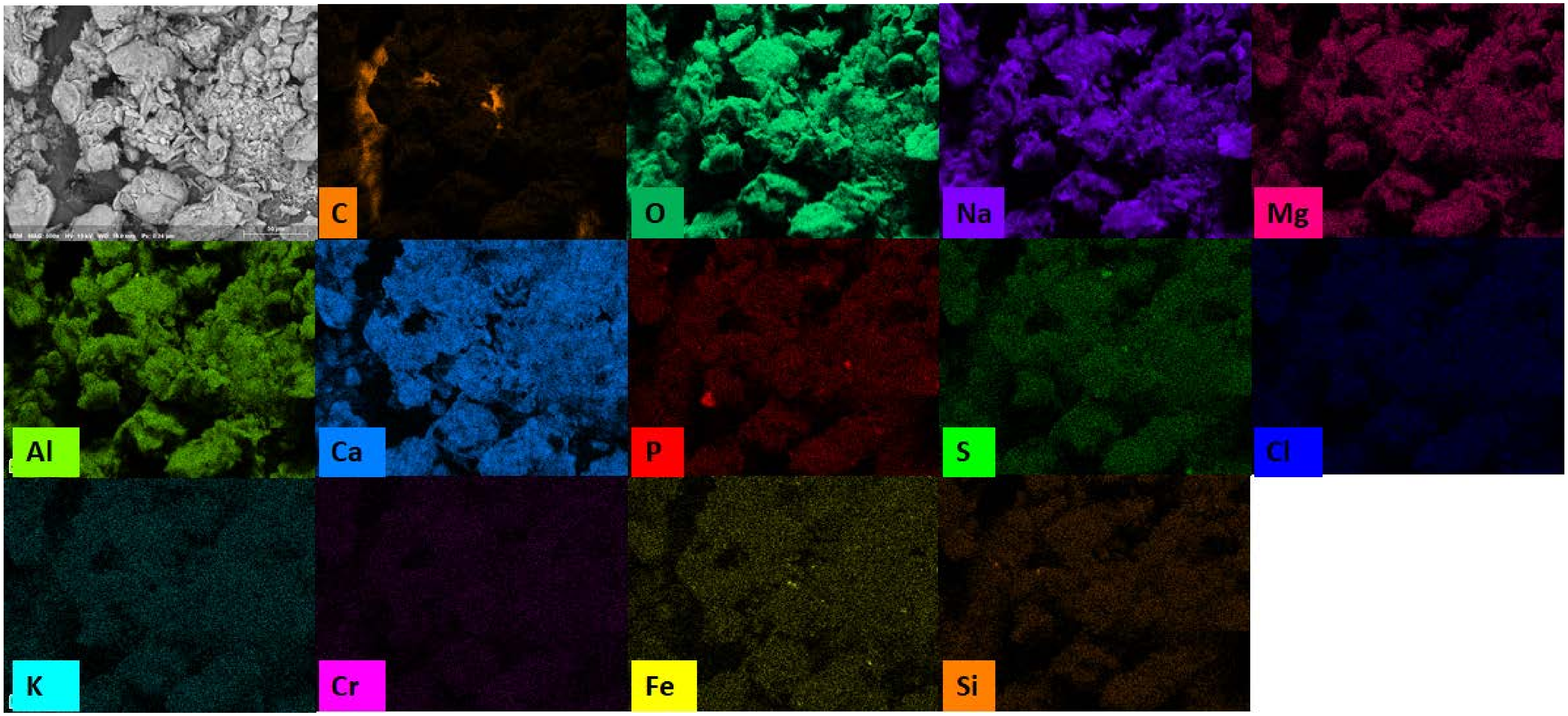

Figure 6. SEM-EDS image of the -R40 solids. Here, backscatter response for select analytes is not normalized and therefore only loosely represents actual analyte content. Carbon tape is used on the stub, and the carbon response shown above derives solely from the tape background. Normalization finds that Na, Al, and Ca are the major solid phase species. The remaining analytes showing response above (Mg, P, S, K, Fe, and Si) are present in relatively small amounts (with occasional “hot” spots for P, S, and Fe). Result is “For Information Only” (see note in Appendix A).

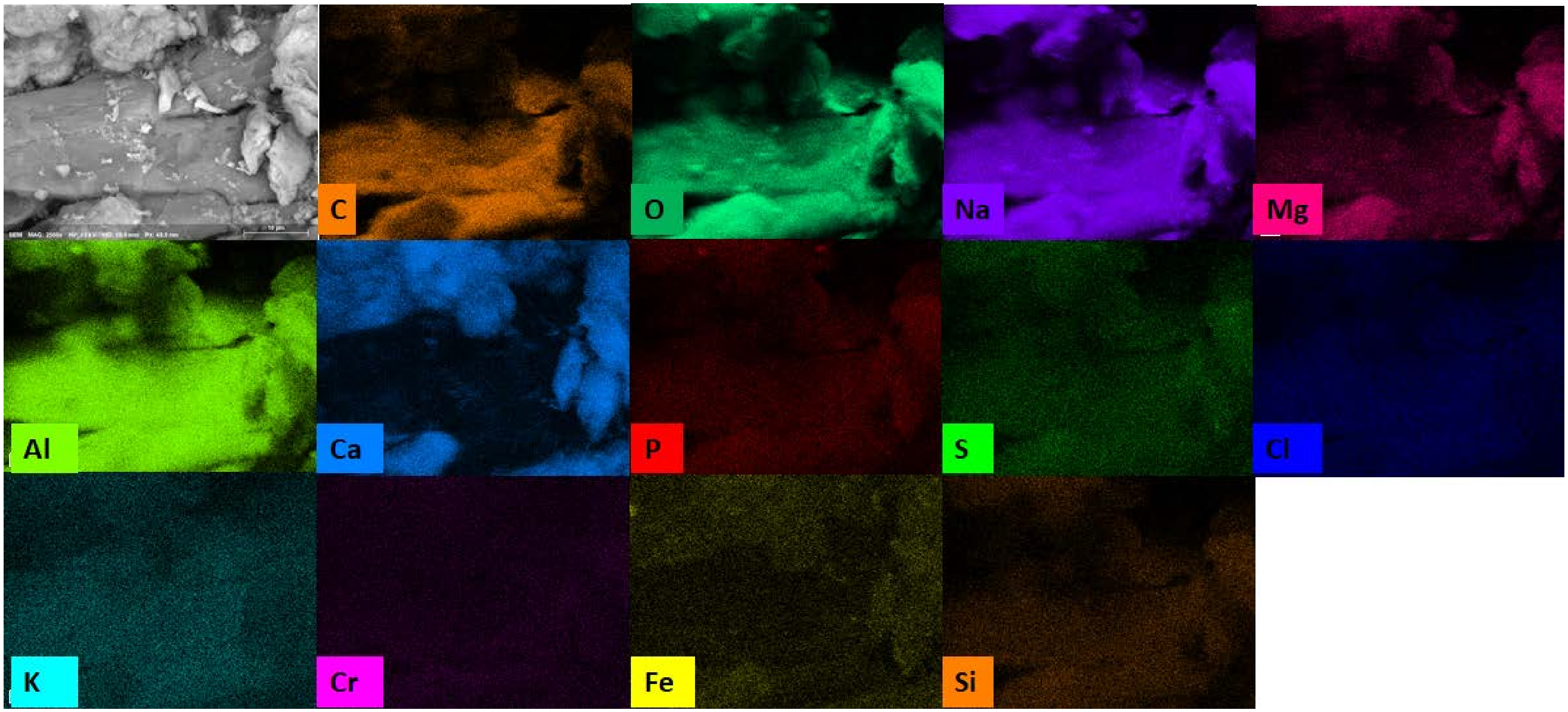

Figure 7. SEM-EDS image of the -R40 solids focused on a carbon-rich, blocky, log-like particle. As before, the backscatter response for select analytes is not normalized and therefore only loosely represents actual analyte content. Carbon is associated with the particulate in the image rather than the carbon tape used for analysis. EDS suggests the log-like particle is decreased in Mg, Ca, P, and Fe and elevated in C, Al, K, and Si compared to rounded features that make up the general particle population. Result is “For Information Only” (see note in Appendix A).

XRD analysis was executed in hopes of providing direct identification of the mineral phase speciation of the -R40 precipitates. Table 8 lists the key XRD scan peaks identified for the precipitates along with the mineral phase(s) suggested by the XRD software.

Table 8. XRD results for analysis of the -R40 precipitated solids. Only peaks with corrected intensities above ~500 counts are reported. Results are "For Information Only" (see note in Appendix A).

Peak Angle [Range] (2θ) (degrees)	Corrected Peak Intensity (counts)	Suggested Phase(s)
6 to 7	11,500	Aluminosilicate (various Na-, Al-, Mg-, and Cr-bearing silicate variants). No single mineral phase matches.
11 to 12	6,000	Iron carbonate hydroxide [$Fe_6(OH)_{12}(CO_3)$]
17	800	Thermonatrite [$Na_2CO_3 \cdot H_2O$]
23 to 24	1,300	Iron carbonate hydroxide [$Fe_6(OH)_{12}(CO_3)$]
29 to 30	3,000	Sodium nitrate ($NaNO_3$)
32 to 33	700	Thermonatrite [$Na_2CO_3 \cdot H_2O$]
38	1,000	Iron carbonate hydroxide [$Fe_6(OH)_{12}(CO_3)$] – shifted Thermonatrite [$Na_2CO_3 \cdot H_2O$]

5.2 Chemistry of the -D40 Solids

The -D40 solids were first observed 74 days after dilution of the AP-105 simulant with DI water. These solids had a reddish appearance that, given the chemistry associated with similarly red solids precipitated by raw water dilution, is likely iron oxide, iron hydroxide, or some analogue thereof. Attempts to assess the chemistry of the -D40 solids were made by centrifuging and washing the available solids. Sampling operations were performed 75 days after dilution and did not yield enough solids to run ICP, SEM-EDS, and XRD. The limited inventory was submitted to XRD and SEM-EDS in hopes of identifying the particle morphology, chemistry, and mineral phase. The results of SEM-EDS analysis and XRD are discussed below and on the pages that follow.

Figure 8, Figure 9, and Figure 10 shows select SEM images and EDS maps for the first-generation -D40 solids. The observed particle morphologies generally match those observed in the -R40 solids and include needle-like, log-like, and rounded particles. In general, the sizes associated with the observed morphologies in the -D40 solids are comparable to those in the -R40 solids, namely 25-50 µm for the rounded and log-like particles and 2 µm (short axis) by 10-20 µm (long axis) for the needle-like particles. Relative to the -R40, the concentration of particles on the -D40 stub is greatly reduced (owing to the limited quantity of solids available for analysis). For this reason, the carbon tape on the imaging stub (colored in orange) is visible in all EDS maps (making resolution of carbon-bearing minerals impossible). As with the -R40 solids, minor species (Fe, Si, P) are greatly overshadowed by the Na, Al, and Ca content of the solids. The EDS maps show Na as dominant, but also evidence individual particles rich in Al and Ca. By far, the EDS suggests that the nature of the -D40 solids is like that observed in the -R40 solids. It is presumed that the DI water used to make the -D40 dilution was largely free of soluble calcium; as such, the presence of calcium in the EDS maps could derive from the original simulant make-up itself.

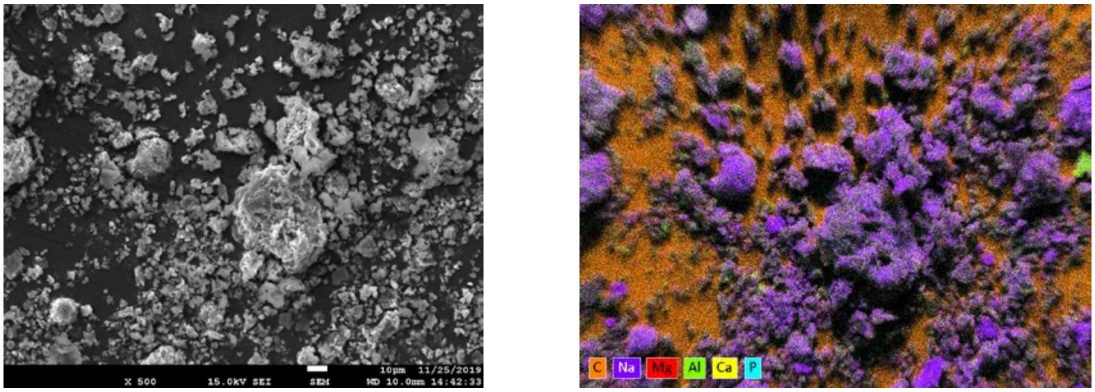

Figure 8. SEM images showing a 20-30 µm rounded and 5-10 µm flake-like particles from the first-generation -D40 solids first observed 74 days after dilution of the as-made simulant with DI water. The left image shows the solids morphology, the right shows the EDS composition map for key analytes. Iron backscatter is minimal and is not included.

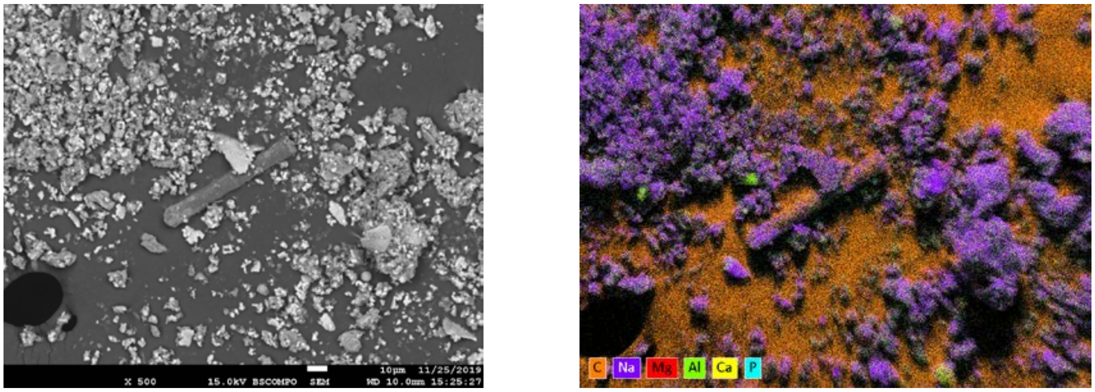

Figure 9. Additional SEM images showing log-like, rounded, and flake-like first-generation -D40 solids. The left image shows the solids morphology, the right shows the EDS composition map for key analytes. Iron backscatter is minimal and is not included.

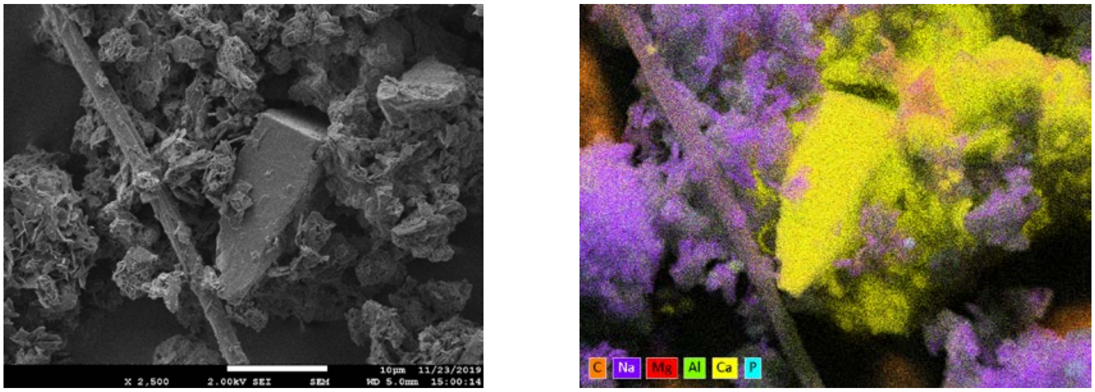

Figure 10. Magnified SEM image of needle-like, log-like, and rounded particles in the first-generation -D40 solids. The left image shows the solids morphology, the right shows the EDS composition map for key analytes. Iron backscatter is minimal and is not included.

XRD of the -D40 solids was attempted; however, analysis of the stub prepared did not return a coherent diffraction pattern, suggesting that the solids are either amorphous or that there were insufficient solids for analysis. Precipitation of amorphous solids is consistent with solid phase chemistries observed in other chemically representative low-activity waste simulants (see Daniel et. al 2018); here, a chemical simulant containing iron oxide solids precipitated by addition of sodium hydroxide to a solution containing iron nitrate (much like iron solids precipitated from the as-made simulant in the current report) was found to be amorphous (i.e., nanocrystalline). On the other hand, given the size and crystallinity of select -D40 solids imaged by SEM (see Figure 8, Figure 9, and Figure 10), the more likely explanation is that the quantity of first generation -D40 solids recovered from the simulant was insufficient for XRD analysis. As such, it is difficult to make conclusive statements regarding the chemical nature of the -D40 solids other than that they are visually and chemically (by EDS) similar to the -R40 solids imaged and discussed in the preceding section.

5.3 Summary of -R40 and -D40 Precipitate Chemistry Findings

The preceding sections have discussed the postulated stability and chemistry of the -R40 and -D40 solids in detail and made inferences based on ICP-OES, XRD, and SEM-EDS results. The purpose of this subsection is to summarize these findings. First, with respect to liquid stability of the simulant components, ICP data suggest that calcium solids are immediately unstable in the simulant. This inference, based on the fact that calcium solids are absent from the as-made simulant and filtered simulant (to which $CaCl_2$ is added and seemingly precipitates out during as-made simulant stabilization), suggests that any calcium added by raw process water addition (which is calcium-rich) should precipitate in the diluted simulant during DFLAW-typical operations. ICP data suggest that the iron added to the simulant is partially stable. Precipitation of red solids, presumed to be iron-bearing, is observed during the as-made simulant stabilization period and is accompanied by a partial, but not complete, reduction of iron concentration in solution. Evaluation of the diluted -R40 simulant liquid after precipitation and solids removal finds yet another partial reduction in iron. This, when considered with the re-appearance of reddish solids after several precipitated solids collection/removal cycles, suggests slow precipitation by iron over the period of observation in the current studies (173 days).

With respect to the -R40 solids, the results of XRD, ICP, and SEM-EDS analyses suggest that the precipitates contain a mixture of primarily Na-, Al-, and Ca-bearing solids. The results suggest the presence of Fe-, Mg-, S-, and P-bearing phases as well, albeit to a lesser extent. XRD analysis indicates Na-bearing sodium nitrate and sodium carbonate salts; this is not surprising given the sodium salt content and speciation in the as-made, 8.5M Na simulant. However, it is unclear if the contribution from these salts derives from insoluble $NaNO_3$ and Na_2CO_3 in the diluted supernatant or cross-contamination of the solids by dried supernatant. In addition, XRD suggests the presence of aluminosilicates that may incorporate Na, Al, Ca, and Mg (along with less-abundant analytes like Cr). However, no single aluminosilicate phase provides an exact match to the measured XRD pattern (i.e., the expected companion peaks for “best-fit” aluminosilicates are not found in the measured XRD patterns). XRD also suggests the presence iron carbonate hydroxide [$Fe_6(OH)_{12}(CO_3)$]. Finally, analysis of the solids precipitated from the -D40 dilution (i.e., dilution of the as-made simulant with DI water) finds solids that are visually and chemically (by XRD) like those precipitated by raw water addition. However, the quantity of solids collected from the DI water dilution was insufficient to effect the ICP-OES and XRD analyses needed to confirm similarity between -D40 and -R40 solids. That said, if verified, the similarity would suggest that raw water only serves to accelerate the precipitation mechanisms underlying precipitation that accompanies simulant dilution (rather than producing solids unique to raw water addition).

6.0 Conclusions

An AP-105 chemical simulant was developed based on measurements of actual waste chemistry reported in Ferriter (2016) and Fiskum et al. (2018), with an emphasis on matching the measured waste content of Al, Ca, Cr, Fe, Na, and Ni. These analytes have been observed to occur in precipitated AP-105 solids adverse to filtration operations typical of the Low-Activity Waste Pretreatment System (LAWPS) (see Buck 2017; Geeting et al. 2018a,b, 2019). A 2-L batch of the AP-105 simulant was prepared at a total sodium content of 8.5M and allowed to come to equilibrium. As expected, a combination of both soluble and insoluble solids precipitated from the as-made simulant. These solids were removed by vacuum filtration and the remaining liquid diluted with raw process water provided by WRPS. As a control reference, simulant was also diluted with DI water and two undiluted controls were kept. Observation of the raw process and DI water diluted simulants (along with the controls) over a 173-day period following dilution found the following:

- In all cases, dilution of the simulant led to precipitation of fine, easily dispersed solids within an approximately 100-day period (while the undiluted controls remained solids-free over the entire duration of observation).
- Dilution with raw process water greatly accelerated the rate and increased the extent of precipitation relative to dilution with DI water. Samples diluted with raw water first exhibited solids approximately 6-8 days after dilution, whereas DI-diluted simulant solids were first observed approximately 75 days after first dilution. In all cases, raw water diluted samples had substantially more solids than their DI-diluted counterparts.
- The rate (and possibly extent) of precipitation appears to be impacted by the degree of dilution. As-made simulant diluted with 40 grams of water per 100 grams of as-made simulant (which effects a decrease from 8.5M to 5.6M Na) was the first to show solids relative to the lower 10, 20, and 30 gram per gram dilution levels using the same water.

Solids precipitated by dilution with either DI or raw water appeared red (after aging) and visually similar to the fine iron oxide precipitates commonly used in previous PNNL LAWPS simulant testing (e.g., see the iron oxide solids used in Daniel et al. 2018). However, when concentrated by centrifuging in smaller sampling vials, the reddish solids appeared to be mixed with equally fine white-to-yellow solids. Chemical analysis of both the as-made and diluted simulant liquid phase and of the solid precipitates found the solids to be rich in Na-, Al-, and Ca-bearing solids, with trace Fe- and P-bearing solids. The solid phase minerals suggested by XRD were sodium nitrate, sodium carbonate,[1] and iron hydroxide carbonate. In addition, there was a significant XRD peak that was generally associated with aluminosilicates composed of some variant of Na, Al, Ca, K, Mg, and Cr; however, no single aluminosilicate mineral was an exact match for this peak when the remainder of the XRD pattern was considered. Indeed, of all the solids targeted by the chemistry above, only Ni, included in the simulant formulation at levels 10 times that of Fe, was not largely present in the precipitate.[2]

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[1] Quantification of carbon was limited to SEM-EDS; use of carbon tape on the SEM stub made resolution of carbon-bearing solids difficult. However, carbon-bearing solids were observed in at least one location imaged during SEM analysis, and as such, the appearance of sodium carbonate solids in the postulated XRD mineral list is not surprising.

[2] This is not to say that Ni was absent, but rather the amount of Ni in the precipitate (12 µg L^{-1}) was less than anticipated based on its make-up concentration (roughly 45,000 µg L^{-1}). For comparison, iron was detected at ~850 µg L^{-1} in the solids (with a make-up concentration of 7,000 µg L^{-1}).

Given that the precipitate chemistry includes analytes found in the as-made simulant, it is unclear what intrinsic physical or chemistry attribute of the WRPS-supplied raw process water causes and accelerates precipitation. Analysis of the raw water chemistry finds calcium as the most prevalent cation (followed by magnesium, sulfur, and sodium). These analytes, coupled with the similarly high content of TIC/TOC in the raw water, could play a role in accelerating precipitation from the as-made simulant relative to DI water dilution.

Note that calcium is not detected in the as-made liquid following simulant stabilization despite being present in quantifiable concentrations in the simulant recipe, suggesting that it largely precipitates out during the simulant stabilization period (~1 week). If calcium delivered to the simulant through raw water dilution were equally unstable, it could explain the relatively rapid formation of solids 6-8 days following raw water addition. It could also be speculated that the remaining (long-term) precipitation is associated with iron precipitation from the simulant, as a partial decrease in the iron content of the as-made simulant liquid collected immediately before dilution with water and in the diluted simulant liquid (associated with raw water dilution). Slow precipitation of iron falls in line with the re-appearance of red solids after first-generation solids have aged and in the second- and third-generation precipitates that formed in samples whose solids were removed for analysis. This argument is undercut by the calcium-bearing phases in precipitates formed by DI water addition; however, presence of calcium solids in the DI diluted sample solids could just as likely be attributed to carry-over of calcium (in concentrations below the ICP quantitation limit) from the as-made simulant.

Regardless of the mechanism, the test results strongly suggest that raw water will increase the rate and extent of solids precipitation from Hanford AP tank wastes during typical DFLAW dilution operations associated with feed tank staging. The solids precipitated in the current testing contain known solid chemistries, namely iron-bearing mineral phases and fine aluminosilicates, that are adverse to sustained filter performance (see Daniel et al. 2018). Additional testing is recommended to confirm that the precipitation behavior is repeatable and to quantify the fouling proclivity of the raw water precipitates during DFLAW prototypic filter operations. Furthermore, as current testing observed continued precipitation over at least 100 days of the simulant observation period, there is a need to understand how long precipitation will continue to better understand the required settling time to avoid feeding the finest suspended solids in AP Farm staging tanks to downstream filter operations. To this end, the following additional tests are proposed:

- Prepare a scaled batch of simulant, dilute, and monitor for a 6-month period to determine the rate and extent of precipitation. Here, the batch should be split into several smaller sub-batches to allow removal of solids at 1-month intervals from specific batches, with the intent of observing whether the solids reappear in batches from which solids have already been collected.
- Using the sub-batches split in the effort outlined in the preceding bullet, evaluate at 1-month intervals the fouling proclivity of solids formed using LAWPS prototypic filter operations.

As a final note, it is important to recognize that evaluation of the solids' chemistry confirms the presence of the desired target analytes, namely Al, Ca, Cr, Fe, Na, and Ni, in the precipitate formed by dilution. Notably, all target analytes, save Ni, were present in significant (i.e., readily quantifiable) concentrations. The motivating concern for the current study was the unexpected presence of solids bearing Al, Ca, Cr, Fe, Na, and Ni that were adverse to sustained dead-end filter performance using actual waste from tank AP-107. And as discussed in the introduction to this report, it was postulated that dilution of the AP-107 waste from 8.5M to 5.6M Na conducted as part of waste staging operations drove precipitation of the unexpected solids. Relative to the motivating factors discussed above, two observations made herein are important: 1) dilution of DFLAW-style simulants leads to the precipitation of solids, and 2) these precipitated solids contain key analytes that match those associated with adverse filter performance in bench-scale DFLAW evaluations of actual waste from AP-107. Taken together, these observations appear to confirm the postulated source of solids in the AP-105/AP-107 actual waste samples observed during FY18 by Geeting et al. (2018a,b), namely, that dilution by raw water led to precipitation of fine solids that did not immediately settle and that were collected in the samples provided to PNNL for analysis. This conclusion is not definitive, as the current results are limited to a single test and simulant and should be (at a minimum) replicated to confirm reproducibility with a second, independent batch of simulant. Indeed, final attribution of the source/cause of unexpected solids precipitation in AP-105 and AP-107 waste samples to dilution with raw water cannot be made until dilution-induced precipitation is demonstrated with an actual waste sample. To this end, it is recommended that a sample of AP-105 or AP-107 waste be diluted with raw water (with nominally the same ion content as tested in the current report) to determine its stability with respect to precipitation over the course of several months following dilution.

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Appendix A – Analytical Methods

Chemical analysis of the AP-105 simulant liquids and solids derived from the testing reported in the current report comprised inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray diffraction (XRD), and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS). This appendix provides a high-level summary of the instruments and methods used to support these three characterization techniques.

ICP-OES: Samples were submitted for chemical characterization by ICP-OES to the Subsurface Science & Technology Group's Sample Analysis Service Center at Pacific Northwest National Laboratory's Environmental Sciences Laboratory. All samples were submitted as Batch # 4153 under Laboratory Information Management System Work Order # 1911001. To facilitate analysis, samples were diluted with 2-wt% nitric acid at dilution factors of 10, 100, and 10,000 and analyzed on a Perkin Elmer Optima 8300 DV ICP-OES.

XRD: Solid mineral phase identification was accomplished through using a Bruker D8 Advance diffractometer (Bruker AXS Inc., Madison, WI) with Cu Kα X-rays and a LynxEye® position-sensitive detector with a collection window of 3° 2θ. Scan parameters were 5-75° 2θ with a step of 0.015° 2θ and a 0.6-s dwell at each step. Bruker AXS DIFFRACplus EVA software (Version 14.0.0.0) was used to identify crystalline phases from the measured XRD patterns. XRD analyses were not performed in accordance with the requirements of the quality assurance (QA) program described in Section 2.0, and as such should be considered unqualified and "For Information Only." As employed in the current report, XRD analysis was used only to provide insight into the possible mineral phases (and their constituent analytes) precipitated by dilution with raw and DI water.

SEM-EDS: Solid phase morphology and chemistry were evaluated using SEM-EDS. Here, a JEOL 7001F field emission gun SEM was used to collect all images and EDS maps. SEM conditions of 2-kV accelerating voltage, probe current 5, aperture 4, and 5-mm working distance were used to capture secondary electrons for micrograph collection. EDS was performed using a short-working-distance backscatter electron detector, and SEM conditions of 15-kV accelerating voltage, probe current 13, aperture 4, and 10-mm working distance. Spectra were collected with a Bruker X-Flash|60 EDS detector and Esprit 2.1 software for analysis. SEM-EDS analyses were not performed in accordance with the requirements of the QA program described in Section 2.0, and as such should be considered unqualified and "For Information Only."

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