FINAL REPORT

TANK GROUT WATER-CONDITIONING TESTS—FISCAL YEAR 2019 STATUS REPORT

Prepared for

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ABSTRACT

Underground steel tanks are used to store liquid waste from processing nuclear materials as part of the defense programs of the U.S. Department of Energy (DOE). At the Savannah River Site (SRS), DOE has implemented a program to remove highly radioactive radionuclides from the underground storage tanks to the maximum extent practical and stabilize the residual waste inside the tanks using a cementitious, chemically reducing grout. The purposes of the grout are to fill and structurally stabilize the tanks, and to provide a hydrologic and chemical barrier limiting the release of radionuclides to the environment. This report describes proactive work conducted to better understand tank grout water conditioning, performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA®) during the latter nine months of fiscal year (FY) 2019 under the project titled "Technical Assistance for the Review of the U.S. Department of Energy's Non-High-Level Waste Determinations." The purpose of the work was to determine the capability of tank grout to condition meteoric water as it percolates through the tank grout matrix and fast flow paths in the waste tanks, such as cracks in the grout, at the interface of grout flow lobes, and through annular gaps at the tank perimeter or around piping, cooling coils, and in-tank equipment, and to understand the impact of residence time on the capability of tank grout to condition percolating water. CNWRA is investigating how interaction between synthetic groundwater (representing meteoric water that may percolate through the tank grout as slow, matrix flow or through cracks or other fast flow paths) and laboratory-scale tank grout specimens or the cementitious materials used to prepare tank grout modifies the chemistry of synthetic groundwater. The work specifically focused on how the grout or cementitious materials would affect the dissolved oxygen (DO) concentrations, pH, and oxidation–reduction potential (Eh) of the synthetic groundwater because these parameters can affect the release of radionuclides from residual waste in grouted tanks.

During early years post-emplacement, waste-stabilizing tank grout generally exists as solid, independent grout flow lobes that collectively fill waste tanks. Over time, the condition of the tank grout is expected to deteriorate, potentially providing more grout surface area for interaction with percolating water. Earlier tests performed at CNWRA were conducted with cubed tank grout to represent the intact condition of grout flow lobes, but in FY 2019, water conditioning tests were performed with pulverized tank grout to represent a later, degraded state of tank grout.

Water-conditioning tests conducted during FY 2019 were performed with (i) pulverized samples of laboratory-prepared grout specimens (see Section 6 of Walter and Dinwiddie, 2019), (ii) individual cementitious material components of SRS Reducing Tank Grout LP#8-016 (i.e., Portland cement, fly ash, and Grade 120 ground granulated blast furnace slag; SRR–CWDA–2013–00026; Walter and Dinwiddie, 2019), and (iii) physical mixtures of the individual cementitious materials that compose the SRS reducing tank grout in mass ratios consistent with the SRS Reducing Tank Grout LP#8-016 formula. Tests conducted during FY 2019 and documented herein are:

1. Pulverized Grade 120 slag tank grout, unstirred
2. Pulverized Grade 120 slag tank grout, stirred
3. Grade 120 slag, stirred (first test)
4. Class F fly ash, stirred
5. Mixture of Portland cement and Grade 120 slag, stirred
6. Portland cement, stirred
7. Grade 120 slag, stirred (second test)

8. Mixture of Portland cement and fly ash, stirred
9. Mixture of Grade 120 slag and fly ash, stirred

A test performed using fresh, pulverized grout resulted in a minimum Eh of −303 mV after 140 days of grout–water interaction, which was lower than the minimum Eh of −258 mV observed during a 130-day test performed with a cubed grout sample (Walter and Dinwiddie, 2019). Although a lower minimum Eh was observed when testing a pulverized sample with a larger surface area-to-volume ratio than the cubed sample, the difference between the two values may not be significant. The larger surface area-to-volume ratio of the pulverized sample did not appear to increase the reaction rate.

A test performed during FY 2019 using fly ash alone resulted in a modest decrease in DO, but did not result in reducing conditions. Other tests performed using Grade 120 slag and slag mixtures resulted in significant concentrations of dissolved, reduced sulfur species in association with strongly reducing conditions. Tests performed using slag alone resulted in the lowest minimum Eh values (−414 to −434 mV) observed to date. Tests performed with physical mixtures of slag/Portland cement and slag/fly ash resulted in minimum Eh values from −313 to −350 mV. The less negative Eh values for mixture tests may be due to chemical interactions occurring between slag and another tank grout component, or to the lower slag-to-water mass ratio of the mixture tests. The tests performed during FY 2019 indicate that slag is the only cementitious material component of tank grout having both a significant effect on DO consumption and on producing strongly reducing conditions in the synthetic groundwater.

With respect to the redox-sensitive metals iron and manganese, ferrous iron (Fe^{+2}) was the only ion detected in tests performed with (i) slag as the sole cementitious material and (ii) unstirred, pulverized grout. However, the total iron, based on inductively coupled plasma (ICP) analyses, was less than the detection limit of 0.1 mg/L, except for the unstirred grout test. Manganese was less than the ICP detection limit of 0.005 mg/L for all tests.

Samples of Class F fly ash, and Grades 100 and 120 slag underwent energy dispersive X-ray spectroscopy (EDS) elemental analyses to semi-quantitatively determine the percentage of the elemental composition and X-ray diffraction (XRD) analyses to determine mineralogy. Minerals fit to the fly ash spectra included: berlinite, mullite, albite, luogufengite, hematite, aluminohydrocalcite, and wollastonite. Grade 100 slag produced no XRD peaks because it consists of amorphous glassy particles. Minerals fit to the Grade 120 slag spectra included gypsum, calcite, pyrophylite, periclase, and nacrite. Some underfit peaks of Grade 120 slag may be clays; they did not fit minerals in the database. Reduced-sulfur-bearing minerals were not identified in the fly ash and Grade 120 slag samples, although the oxide percentages indicated considerable SO_3.

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PREVIOUS REPORTS IN SERIES

Number	Report Name	Date Issued
14003.01.007.222	Conceptual Design for Small-Scale Grout Monolith Tests	April 2008
14003.01.007.305	Mesoscale Grout Monolith Experiments: Results and Recommendations	May 2009
14003.01.007.445	Intermediate-Scale Grout Monolith and Additional Mesoscale Grout Monolith Experiments: Results and Recommendations—Status Report	September 2010
14003.01.007.121	Bonding and Cracking Behavior and Related Properties of Cementitious Grout in an Intermediate-Scale Grout Monolith	September 2011
14003.01.007.122	Fiscal Year 2012 Meso- and Intermediate-Scale Grout Monolith Test Bed Experiments: Results and Recommendations	August 2012
17860.04.004.510	Feasibility Study of Acoustic Emission Monitoring for Cracking of Waste-Stabilizing Tank Grout and Saltstone—A Progress Report	September 2015
17860.04.004.515	Tank Grout Water Conditioning Tests—Status Report	September 2015
17860.04.004.620	Fiscal Year 2016 Tank Grout Water Conditioning Tests—Status Report	January 2017
23700.04.031.905	Tank Grout Water-Conditioning Tests—Status Report	April 2019

ABREVIATIONS/ACRONYMS

Al	aluminum
Ba	barium
Ca	calcium
Cl	chloride
CNWRA®	Center for Nuclear Waste Regulatory Analyses
DOE	U.S. Department of Energy
DO	dissolved oxygen
EDS	energy dispersive X-ray spectroscopy
Eh	oxidation–reduction potential
Fe	iron
Fe^{+2}	ferrous iron
FY	Fiscal Year
ICP	inductively coupled plasma
K	potassium
Li	lithium
Mg	magnesium
NRC	U.S. Nuclear Regulatory Commission
ORP	oxidation–reduction potential
PA	performance assessment
Si	silicon
SO_4	sulfate
Sr	strontium
SRS	Savannah River Site
sSRS	synthetic Savannah River Site
SwRI®	Southwest Research Institute®
XRD	X-ray diffraction

ACKNOWLEDGMENTS

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The authors gratefully acknowledge energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) technical and interpretation support received from Byron Chapa of Southwest Research Institute's® (SwRI's®) Mechanical Engineering Division, Charity Phillips-Lander of SwRI's Space Science and Engineering Division, and MDI Jade 2010 software access that was provided to Dr. Phillips-Lander by Andrew S. Elwood Madden of the University of Oklahoma. The authors also gratefully acknowledge the technical and editorial reviews of James Prikryl, the programmatic review of Osvaldo Pensado, and the assistance of Arturo Ramos and Lora Neill in preparing this report.

QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: All CNWRA-generated original data contained in this report meet the quality assurance requirements described in the CNWRA Quality Assurance Manual. Sources for other data should be consulted for determining the level of quality for those data. Scientific Notebooks 1289, 1319, 1332 (Dinwiddie and Walter, 2017; Walter and Dinwiddie, 2019a,b) were used to document experimental conditions and in-process entries associated with this work.

ANALYSES AND CODES: Jade version 3.1 and Jade 2010 (Materials Data, Inc., Livermore, California)

REFERENCES:

Dinwiddie, C.L. and G.R. Walter. "Task 2: Tank Grout Water Conditioning Tests, Part 3." Scientific Notebook 1289. San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. 2017.

Walter, G.R. and C.L. Dinwiddie. "Grout DO Reduction Experiments." Scientific Notebook 1319. San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. 2019a.

Walter, G.R. and C.L. Dinwiddie. "Grout Tests." Scientific Notebook 1332. San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. 2019b.

1 INTRODUCTION

Underground steel tanks are used to store liquid waste from processing nuclear materials as part of the defense programs of the U.S. Department of Energy (DOE). At the Savannah River Site (SRS), DOE has implemented a program to remove highly radioactive radionuclides from the underground storage tanks to the maximum extent practical and stabilize the residual waste inside the tanks using a cementitious, chemically reducing tank grout. The purposes of the grout are to fill and structurally stabilize the tanks, and to provide a hydrologic and chemical barrier to limit the release of radionuclides to the environment. This report describes proactive work conducted to better understand tank-grout water conditioning, performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA®) during fiscal year (FY) 2019 under the task order titled "Technical Assistance for the Review of the U.S. Department of Energy's Non-High-Level Waste Determinations." The purpose of the work was to investigate how interaction between synthetic groundwater (representing water that may infiltrate the tank grout as slow, matrix flow or through cracks or other fast flow pathways) and laboratory-scale tank grout specimens or the cementitious materials used to prepare tank grout modifies the chemistry of synthetic groundwater. The work specifically focused on how the grout or cementitious materials would affect the dissolved oxygen (DO) concentrations, pH, and oxidation–reduction potential (Eh) of the synthetic groundwater, because these parameters can affect the release of key radionuclides from the residual waste in grouted tanks.

For the Eh of water seeping through tank grout to diminish to a value on the order of −500 mV, as projected in some of DOE's performance assessment (PA) modeling (e.g., SRR–CWDA–2010–00128, Revision 1), the DO concentration must be reduced to low levels at which redox couples other than O_2–H_2O control the Eh. Shallow groundwater at the SRS has DO concentrations in the range of 1 to 9 mg/L [1 to 9 ppm] (WSRC–RP–92–450). To attain the low Eh conditions assumed in PA modeling, DO must be removed from infiltrating groundwater by reaction with reductants in the tank grout.

Grout water-conditioning tests conducted during FY 2019 (Table 1-1) consisted of those performed with (i) pulverized samples of laboratory-prepared grout specimens (see Section 6 of Walter and Dinwiddie, 2019); (ii) individual cementitious material components of SRS Reducing Tank Grout LP#8-016 (SRR–CWDA–2013–00026; Walter and Dinwiddie, 2019, Table 1), and (iii) mixtures of cementitious materials in mass ratios that are consistent with the SRS Reducing Tank Grout LP#8-016 formula. The grout components tested were:

- Grade 120 ground granulated blast furnace slag (ASTM C989 Lehigh Cement Company, LLC, Fort Lauderdale, Florida)
- Portland cement (Type I/II, ASTM C150 by Holcim US, Inc., Birmingham, Alabama)
- Class F fly ash (ASTM C618 by SEFA Group, Inc., Lexington, South Carolina).

For simplicity, the Grade 120 ground granulated blast furnace slag will hereafter be referred to as "Grade 120 slag" or "slag." Section 2 of this report describes the methods used to perform the water-conditioning tests and measure DO, pH, and oxidation–reduction potential (ORP), which was converted to Eh in the presentation of test results. Section 3 presents the test results for pulverized grout samples obtained from laboratory-prepared grout specimens. Section 4 presents the test results for individual cementitious grout components, and Section 5 presents of the test results for mixtures of cementitious grout components that were combined in mass ratios consistent with the SRS Reducing Tank Grout formula.

Table 1-1. Chronology of FY 2019 grout water-conditioning tests

Start Date	End Date	Test Material and Conditions*	Reaction Vessel
October 31, 2018	April 18, 2019	Pulverized grout sample contained inside 7 µm mesh bag at rest on the bottom of the reaction vessel (not stirred); this pulverized grout had been previously reacted with sSRS water	2
November 14, 2018	April 18, 2019	Pulverized grout sample contained inside 60 µm mesh bag, suspended by fishing line above a stirring magnet	1
June 20, 2019	July 10, 2019	Grade 120 slag	2
June 21, 2019	July 10, 2019	Class F fly ash	1
July 17, 2019	July 31, 2019	Portland cement/120 Grade slag mixture	1
July 18, 2019	July 31, 2019	Portland cement	2
July 18, 2019	August 23, 2019	Grade 120 slag	3
September 20, 2019	October 7, 2019	Portland cement/Class F fly ash mixture	2
September 20, 2019	October 7, 2019	Grade 120 slag/Class F fly ash mixture	1

*Test materials were typically contained inside a 7-µm nylon mesh filter fabric bag, resting on a Pt-coated Nb screen above a magnetic stirring bar; exceptions are noted above.

2 TEST MEASUREMENT METHODS

All fiscal year (FY) 2019 tests were performed in 4-port, glass reaction vessels, as illustrated in Figure 2-1. Three ports were used for inserting dissolved oxygen (DO), pH, and oxidation–reduction potential (ORP) probes. The probes were inserted through screw caps that were sealed with a rubber O-ring. The fourth port was sealed with a rubber septum stopper that was used to collect water samples. Except for pulverized grout tests, mesh-bagged samples were placed on platinum-coated niobium screens, located above magnetic stirring bars. Each test was performed using synthetic Savannah River Site (sSRS) water (batch prepared March 27, 2017). Methods used to collect water samples are described in Section 3.2.

In the reaction vessels, DO was measured using VisiFerm® D120 optical DO probes by Hamilton® Company (Reno, Nevada), pH was measured using gel-filled double-junction pH probes by Weiss Research, Inc. (Houston, Texas), and ORP was measured using gel-filled double-junction ORP probes by Weiss Research. The pH and ORP probes were connected to pH and ORP mini-controllers (Hanna® Instruments Model 932700, Carrollton, Texas).

Prior to each test, the DO probes were calibrated to 100 percent DO saturation in air above water sparged with air from an aquarium aerator, and to 0 percent DO saturation using a Zero DO standard from Ricca Chemical Company (Arlington, Texas). The pH probes were calibrated using pH 7.00 and 10.00 NIST-traceable pH standards (Fisher Scientific®, Waltham, Massachusetts). The ORP probes were calibrated in standards of known ORP. For the first two tests listed in Table 1-1, the probes were calibrated to +200 mV versus Ag|AgCl ORP standard from Ricca Chemical Company. For tests that began in June 2019, the ORP probes were calibrated to +221 mV in an Orion™ ORP standard and the calibration was checked in Zobell Solution from YSI®, Inc. (Yellow Springs, Ohio) with nominal ORP of +238 mV with respect to Ag|AgCl. ORP measurements were converted to Eh data by adding 200 mV.

Collected water samples were analyzed by Chemistry and Chemical Engineering Division staff of Southwest Research Institute® for the following parameters:

- Chloride (Cl), EPA SW-846 Method 9056A, Ion Chromatography
- Sulfate (SO_4^{-2}), EPA SW-846 Method 9056A, Ion Chromatography
- Sulfide (S^{-2}), EPA-NERL Method 376.2, Colorimetry
- Sulfite (SO_3^{-2}), EPA SW-846 Method 9056A Mod., Ion Chromatography
- Thiosulfate ($S_2O_3^{-2}$), EPA SW-846 Method 9056A Mod., Ion Chromatography
- Total Sulfides, EPA SW-846 Methods 9030B/9034, Titrimetric Analysis
- Ferrous Iron (Fe^{+2}), Standard Method 3500Fe-B[1]
- Total Metals, EPA SW-846 Method 6010D, Inductively Coupled Plasma (ICP).

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[1] Standard Methods for the Examination of Water and Wastewater, http://standardmethods.org/store/ProductView.cfm?ProductID=497

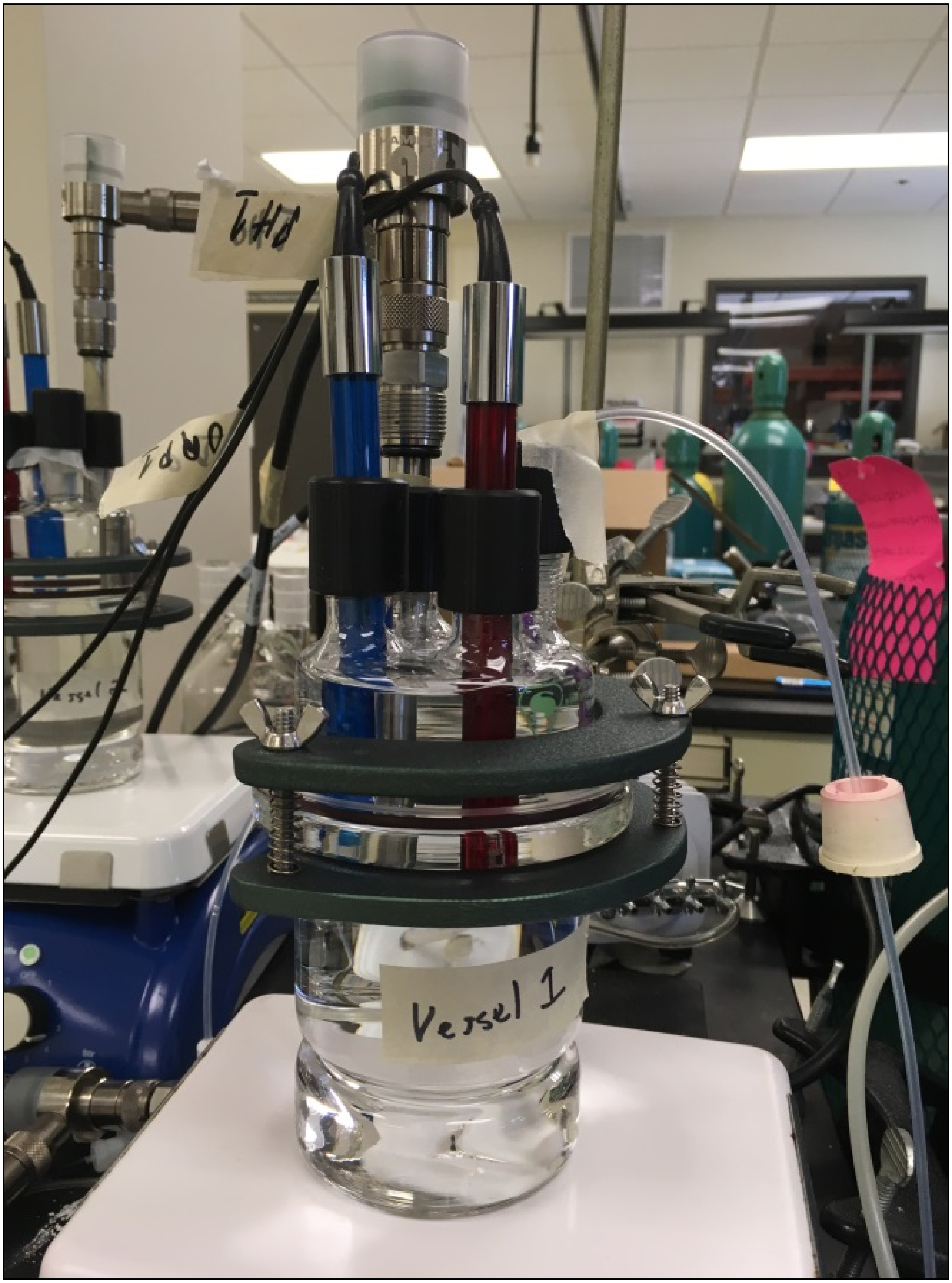

Figure 2-1. 4-port reaction vessel used for grout and cementitious material water-conditioning tests

3 PULVERIZED GROUT TESTS

The pulverized grout tests were performed with samples crushed from a laboratory-prepared Grade 120 grout specimen. The materials and methods used to prepare the grout specimen are described in Section 2 of Walter and Dinwiddie (2019). Two tests were performed using different pulverized grout samples. The grout samples were prepared first by slicing approximately 1-cm-thick disks from a 5-cm-diameter grout specimen, and then by slicing the disks into approximately 1-cm-wide subsamples using a wet diamond saw. Subsamples removed from the interior of the cylinder, minimally affected by exposure to atmospheric oxygen, were then pulverized by a Mini Jaw crusher (Sepor, Inc., Wilmington, California) to form a pulverized grout sample (e.g., Figure 3-1). The first test began on October 31, 2018, and the second test began on November 14, 2018. Interim test results were reported in Section 6 of Walter and Dinwiddie (2019). Both tests were terminated on April 18, 2019, when water samples were collected.

The first test addressed by this report, which began on October 31, 2018, used a pulverized grout sample that previously had been reacted with synthetic Savannah River Site (sSRS) water for 30 days during an aborted prior test[1] (Walter and Dinwiddie, 2019). The 107 g sample was placed in a 7-µm nylon mesh filter fabric bag with 2 percent open area (Component Supply Company, Inc., Sparta, Tennessee). The bag was tied shut with Trilene® monofilament fishing line. The test was conducted with the bagged sample resting on the bottom of the reaction vessel, and in the absence of stirring (i.e., it is the "unstirred test"; see Figure 14 of Walter and Dinwiddie, 2019). Initially, the reaction vessel was partially filled with sSRS water and the grout bag was agitated up and down to facilitate removal of entrapped air for a few minutes, then, the reaction vessel was filled with sSRS water. Because this test was primarily performed to develop testing and sampling procedures, the total water mass added to the reaction vessel was not accurately measured but would have been approximately 540 g based on subsequent tests. Two dissolved oxygen (DO) probes, one pH probe, and one oxidation–reduction potential (ORP) probe were inserted into the four necks of the reaction vessel; therefore, each port into the reaction vessel was sealed with a probe. This test continued for 170 days, until April 18, 2019, when a water sample was collected from the reaction vessel. To collect the water sample, the ORP probe was removed from its port and replaced with a one-hole rubber stopper through which the purge and collection syringes were placed.

The second pulverized grout test (the "stirred test") began on November 14, 2018, using a fresh bag of pulverized grout that had not previously been reacted with sSRS water. The 94.1-g sample was placed in a 60-µm nylon mesh filter fabric bag with 49 percent open area (Component Supply Co., Sparta, Tennessee), and the bag was suspended with Berkley® Trilene® monofilament fishing line (Columbia, South Carolina) above a magnetic stirring bar through a port sealed with a rubber septum stopper (see Figure 15 of Walter and Dinwiddie, 2019). The reaction vessel was filled with sSRS water and DO, pH, and ORP probes were inserted into three ports. The fishing line was suspended through the fourth port, which was sealed with a rubber septum stopper. The net water mass in the reaction vessel was 546 g. This test continued for 156 days until April 18, 2019, when a water sample was collected from the reaction vessel in the same manner as previously described.

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[1] The aborted test was terminated after 32 days because the DO remained elevated, possibly because a Parafilm® seal on the fourth neck of the reaction vessel may have been leaking. Alternatively, air may have been entrapped in the grout bag, causing elevated DO levels. See Section 6 of Walter and Dinwiddie (2019) for more information.

Figure 3-1. **Photograph of pulverized reducing tank grout used in pulverized-grout water-conditioning tests**

3.1 DO, pH, and Eh Evolution during Pulverized Grout Tests

DO and Eh measurements for the unstirred and stirred pulverized grout tests are shown in Figures 3-2 and 3-3. Likewise, pH and Eh measurements are shown in Figures 3-4 and 3-5. The stirred pulverized grout test had a greater decrease in DO and Eh than the unstirred test, but the difference could be due to the prior 30-day reaction time that the unstirred, pulverized grout sample underwent when it was previously exposed to sSRS water during the aborted, preliminary test. The unstirred sample was also placed in a bag having a smaller mesh opening than the sample used in the stirred test. The smaller mesh size may have resulted in more air entrainment in the sample. The sudden increase in Eh in the stirred sample shown in Figures 3-3 and 3-5 at approximately 82 days occurred overnight. It was initially suspected to be due to a problem with the Eh probe, which was replaced with a new probe. Subsequent testing of the Eh probe indicated it was working properly, so the reason for the anomalous Eh spike remains unexplained as is the similar, but smaller, spike in Eh that occurred at 99 days into the test.

During the stirred pulverized grout sample test, DO decreased gradually to below the detection limit of the DO probe after approximately 70 days. The final minimum Eh measurement of −299 mV for the stirred grout sample test occurred after 153 days and was similar to Eh values measured during previous tests of cubed grout samples (Walter and Dinwiddie, 2019). The rate of DO consumption was also similar between cubed and pulverized grout water-conditioning tests. These results suggest that the difference in surface area-to-volume ratio between the cubed and pulverized grout tests had little effect on DO consumption and redox behavior; however, these results cannot necessarily be extrapolated to larger grout monoliths. Future work may further test the effect of surface area-to-volume ratio using >1-cm-cubed tank grout samples that are still sufficiently small enough to fit inside the existing reaction vessels.

3.2 Chemistry of Conditioned Water Collected from Pulverized Grout Tests

Water samples were collected from the two reaction vessels containing reacted, pulverized Grade 120 grout on April 17, 2019, before the tests were terminated. The stirred test lasted 156 days, and the maximum pH and minimum Eh of the grout-conditioned solution in Reaction Vessel 1 were 11.5 and −300 mV, respectively, with DO below detection limits. The unstirred test lasted 170 days, and the maximum pH and minimum Eh of the grout-conditioned solution in Reaction Vessel 2 were 11.38 and +175 mV, respectively, with DO approximately 30 percent of saturation.

The water samples were collected from the reaction vessels by inserting two syringe needles through a rubber septum stopper that was used to seal one of the four ports. Compressed, ultra-pure nitrogen gas was introduced through one needle to displace water from the reaction vessel through the other needle that was connected with polyethylene tubing to a 1-liter, Tedlar® gas sampling bag (SKC, Inc., Eighty Four, Pennsylvania). Some spillage occurred during water collection from Reaction Vessel 2, which resulted in a small sample volume that required dilution for metals analysis. The water sample from Reaction Vessel 1 was collected without spillage. An unreacted sSRS water sample was also collected from the carboy that stored the sSRS water, which was the source of the water used for the grout water-conditioning tests.

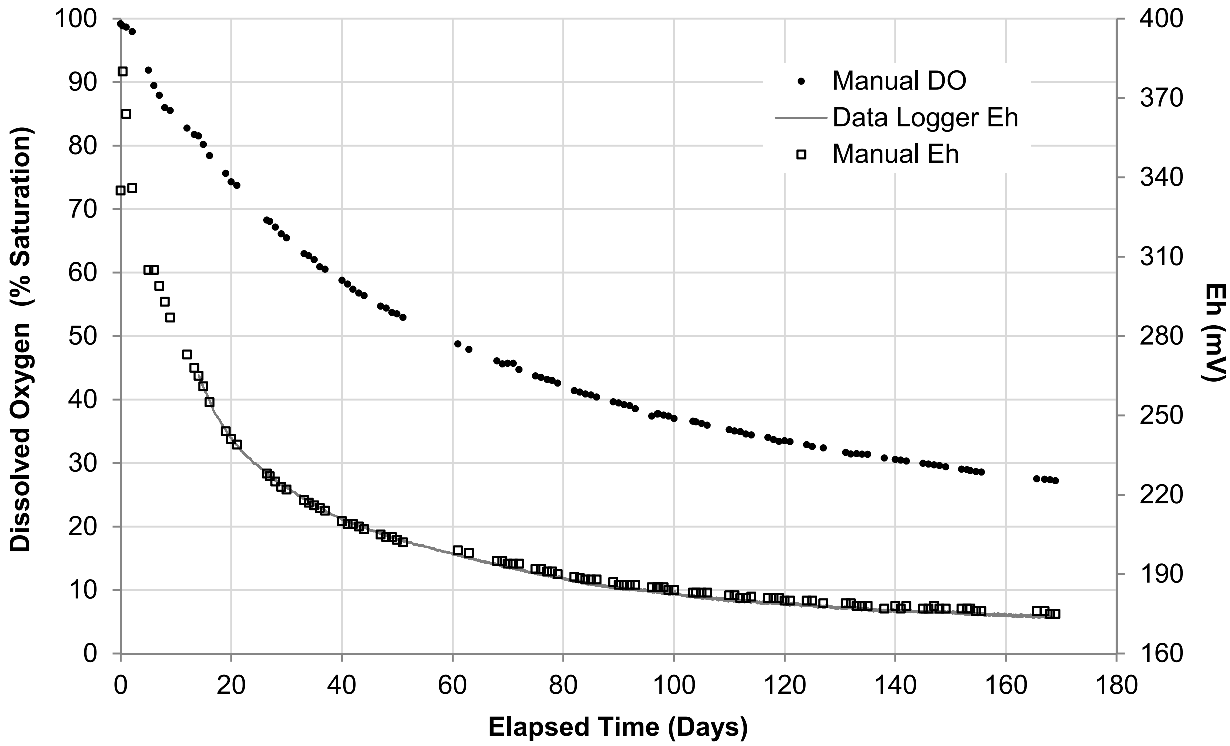

Figure 3-2. **DO and Eh measured during test of previously reacted, pulverized grout sample (i.e., unstirred test)**

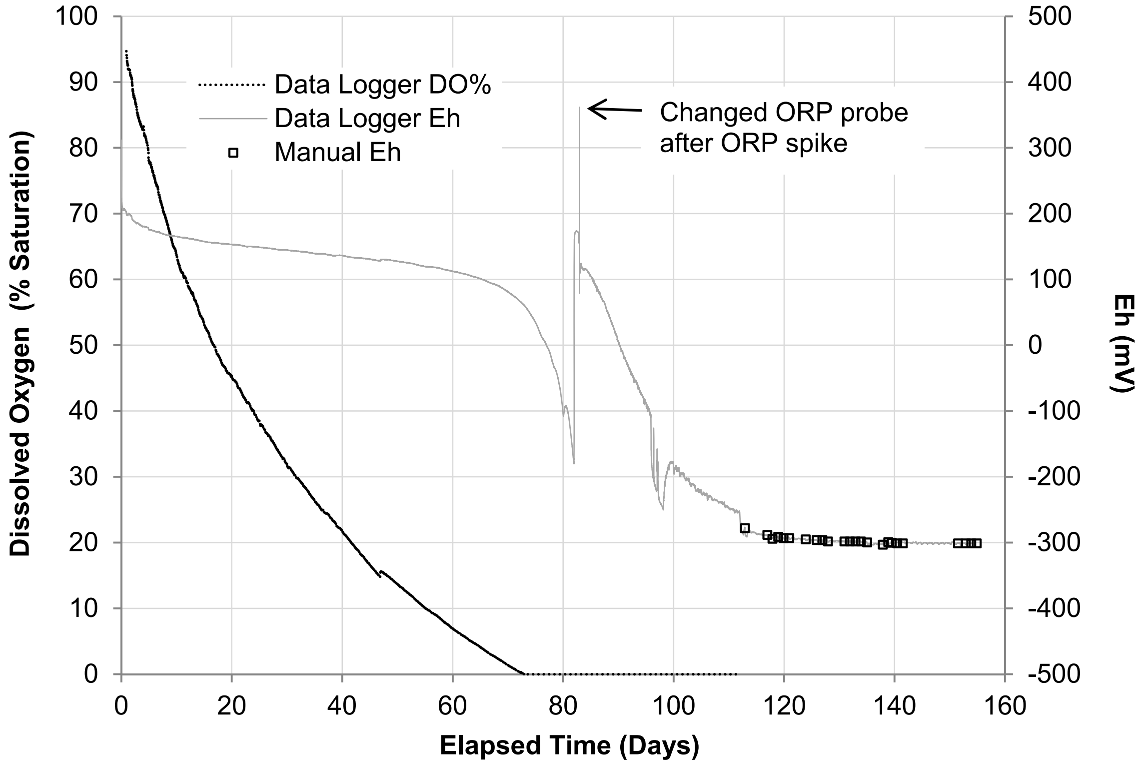

Figure 3-3. **DO and Eh measured during test of fresh, pulverized grout sample (i.e., stirred test)**

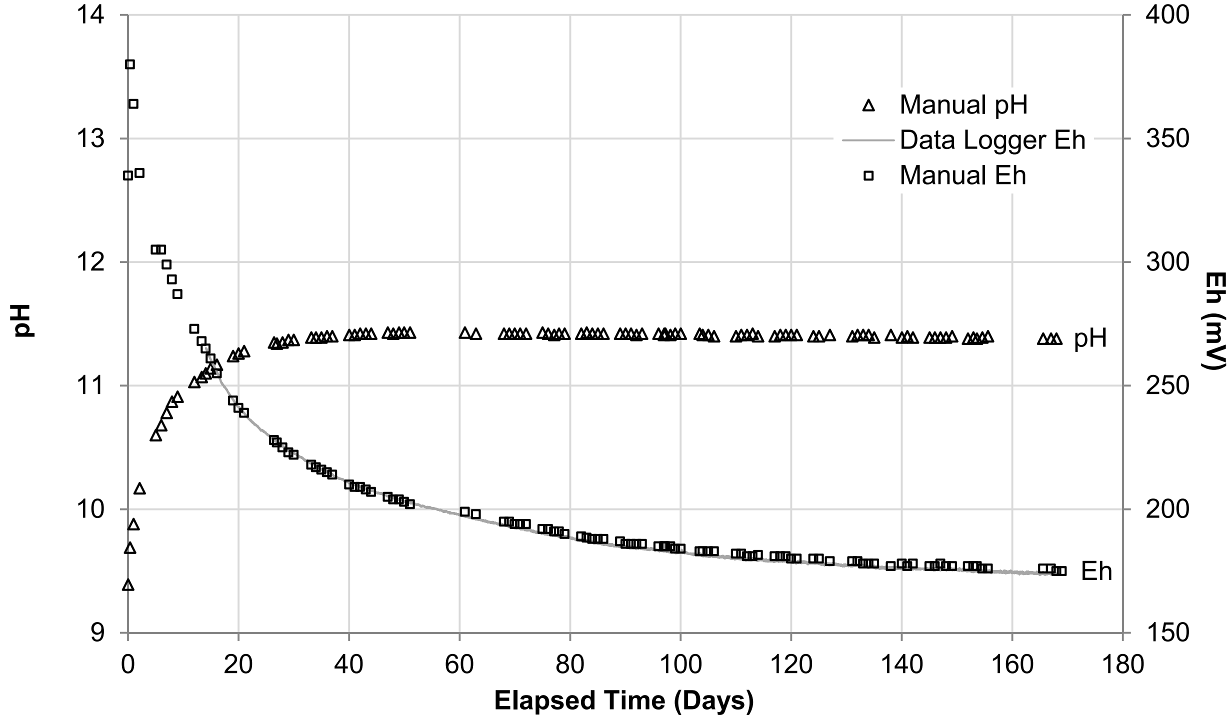

Figure 3-4. pH and Eh measured during test of previously reacted, pulverized grout sample (i.e., unstirred test)

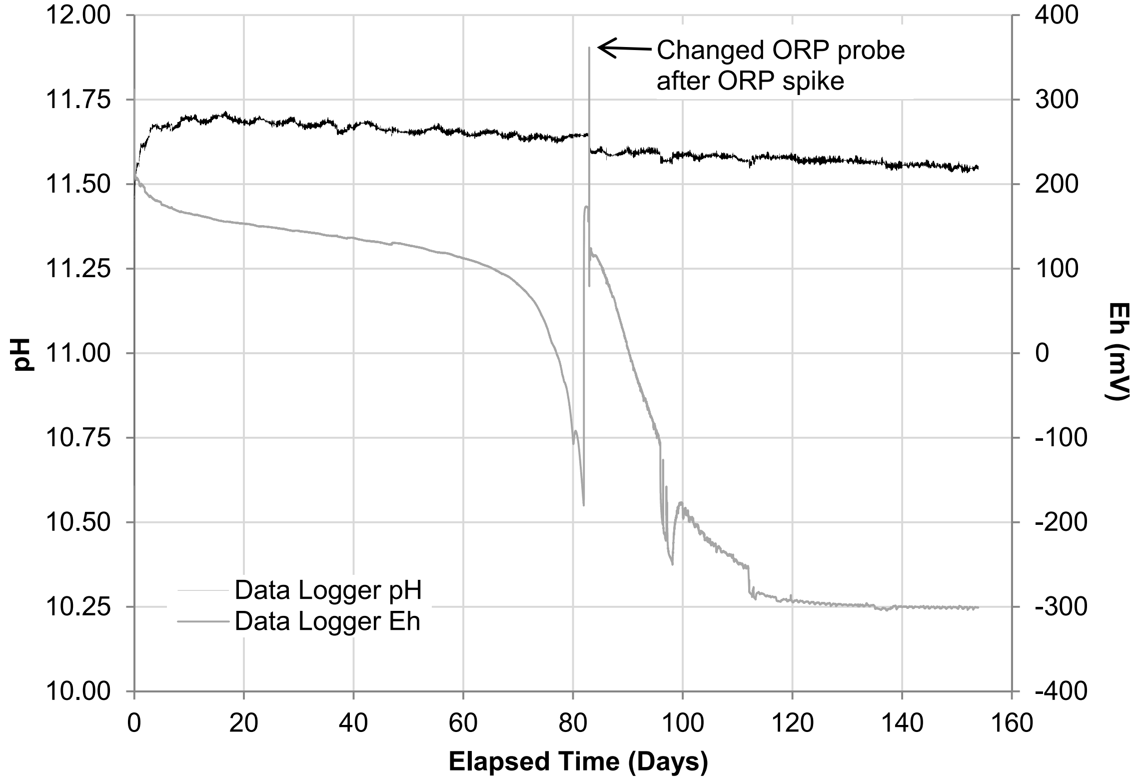

Figure 3-5. pH and Eh measured during test of fresh, pulverized grout sample (i.e., stirred test)

Results of the major ion analyses for the two grout-conditioned water samples and the sSRS water sample are shown in Figure 3-6. The analytical results demonstrate significant increases in all major ions except magnesium (Mg) after reaction of the sSRS water with the grout samples. The increase in calcium (Ca) was expected due to the Ca content of the Portland cement component of the grout. Likewise, the increase in potassium (K) could be due to either alkali sulfates or potassium silicate minerals (such as feldspars) in the aggregate (e.g., Leemann and Lothenbach, 2008). The increase in chloride (Cl) was unexpected and was not repeated in subsequent tests of individual and mixed grout components. The increase in sulfate (SO_4) was likely due to alkali sulfates in the Portland cement or to oxidation reactions with metal sulfides in the slag.

Trace metals detected in the two grout-conditioned water samples are shown in Figure 3-7. No trace metals were detected in the sSRS water sample. The only trace metals detected in the grout-conditioned water samples at greater than 1 mg/L concentrations were aluminum (Al), silicon (Si), and strontium (Sr). The increase in Al and Si were expected due to aluminosilicate reactions between the grout constituents. The increase in Sr could be due to its presence in the carbonate rocks that were used to manufacture the Portland cement, although it was detected at relatively low concentrations in samples from the individual component tests (Section 4).

The results of the analyses of sulfur species that could play a role in the redox chemistry of the grout–water reactions are shown in Figure 3-8 for the two grout-conditioned water samples. No reduced sulfur species were detected in the sSRS water sample. In Figure 3-8, the sum of the species equals the sum of the sulfur components within rounding error. The water sample collected from Reaction Vessel 1 contained more total sulfur and a higher concentration of the reduced sulfur species thiosulfate than did the water sample from Reaction Vessel 2, although the Vessel 1 sample also had a higher sulfate (i.e., oxidized sulfur) concentration. The elevated reduced sulfur concentration of the Reaction Vessel 1 water sample caused it to have a lower Eh (−300 mV) and lower DO saturation than did the Reaction Vessel 2 water sample. The dissolved, reduced sulfur in Vessel 1 must have been sourced through dissolution of solids containing reduced sulfur. The Reaction Vessel 2 water sample may not have contained reduced sulfur species because its grout had previously reacted during an aborted 30-day water-conditioning test. Only trace levels of other reduced sulfur species (sulfide and sulfite) were detected in the samples. Pabalan et al. (2009) assumed that thiosulfate controls Eh but acknowledged the need for additional studies to confirm Eh control and to determine the poising capacity of the slag(s) used in the tank grout formulation(s) for tank closure.

The water sample from Reaction Vessel 2 was the only one having detectable iron (Fe), with total iron of 0.17 mg/L and ferrous iron of 0.034 mg/L. Based on the absence of dissolved, reduced iron in results for individual grout components described in Section 4, dissolved iron does not appear to play a role in controlling Eh.

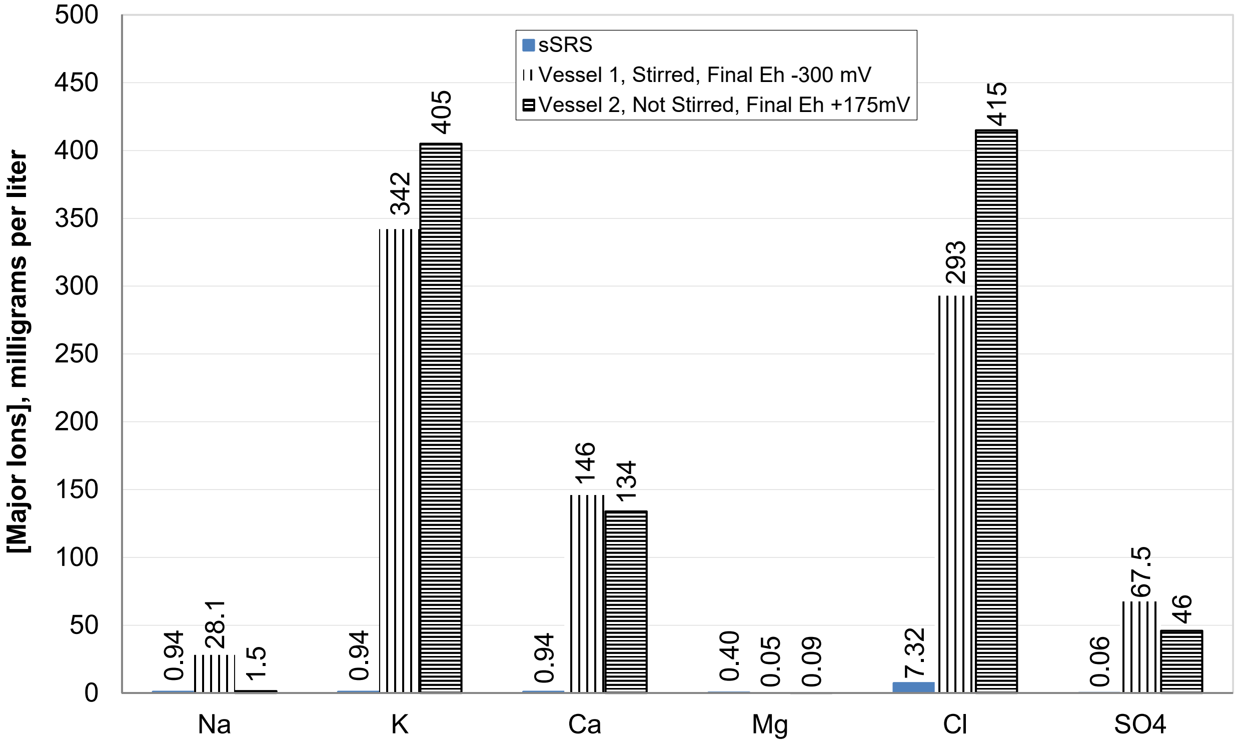

Figure 3-6. **Major ions in sSRS water and pulverized-grout–conditioned water samples**

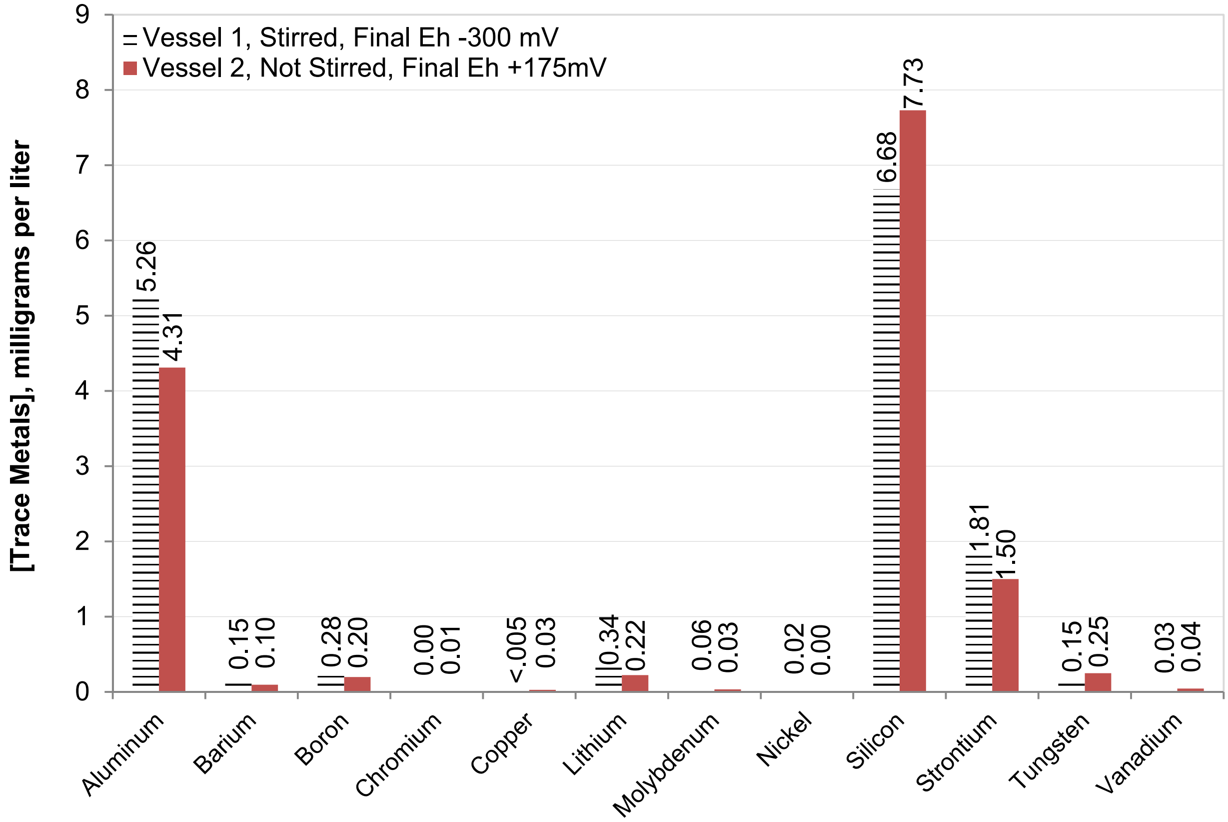

Figure 3-7. **Trace metals detected in pulverized-grout–conditioned water samples**

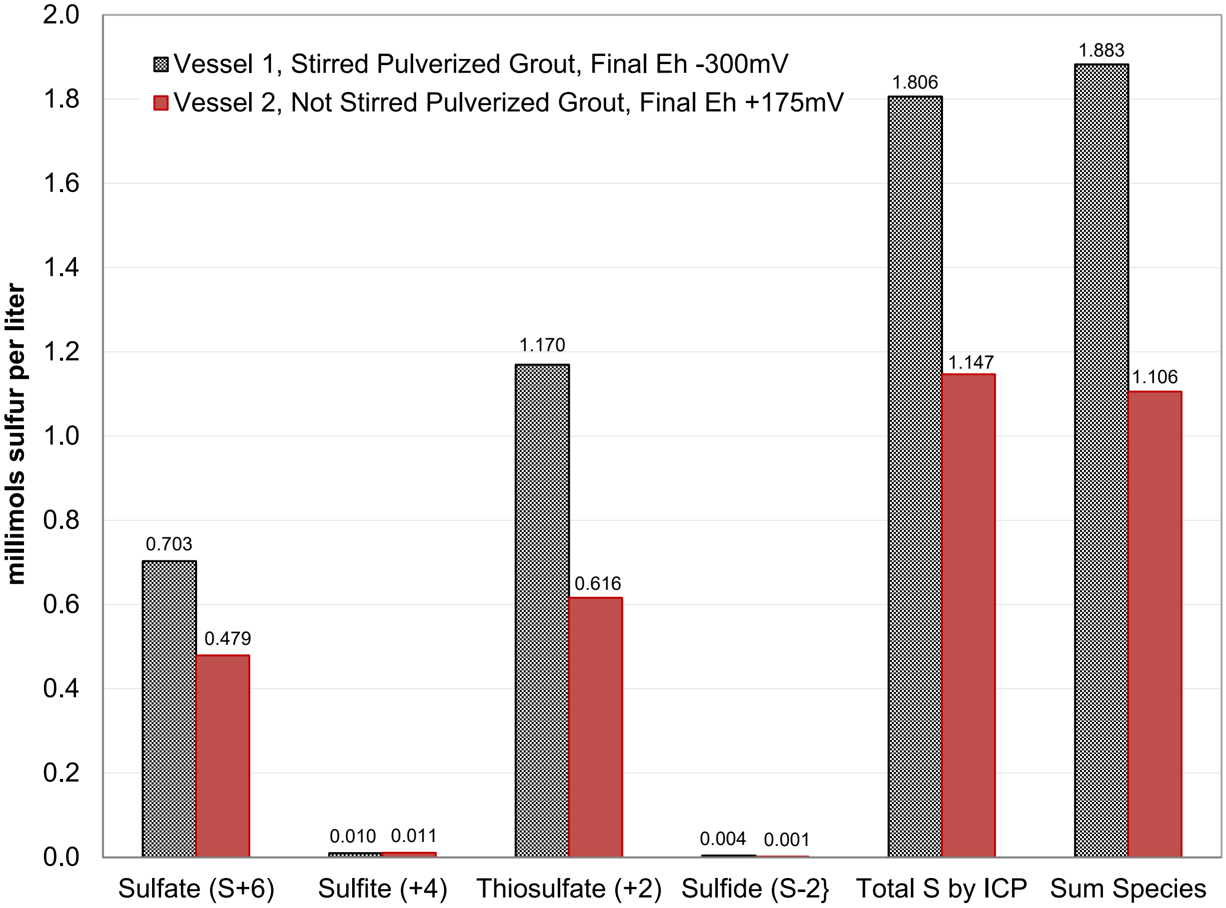

Figure 3-8. **Sulfur speciation analyses for pulverized grout-conditioned water samples**

4 TESTS OF INDIVIDUAL CEMENTITIOUS MATERIAL COMPONENTS OF TANK GROUT

Water-conditioning tests were performed using samples of the individual cementitious material components of Reducing Tank Grout LP#8-016. These tests were performed to investigate how individual grout components modify the chemistry of synthetic Savannah River Site (sSRS) water, and therefore, they are not physical analog models of the anticipated performance of reducing tank grout. Water-conditioning tests were performed using the same Grade 120 slag, Class F fly ash, and Portland cement that was used to prepare the laboratory grout specimen described by Walter and Dinwiddie (2019).

4.1 Grade 120 Slag Tests

Two tests were performed using only Grade 120 slag. The first test was performed by placing 100 g of slag above a 7-μm pore-size nylon mesh filter fabric that was loosely placed over a platinum-coated niobium support screen in a 4-port reaction vessel. The reaction vessel was then filled with 556 g of sSRS water. This test, begun on June 20, 2019, resulted in the slag forming a solid layer, approximately 1-cm-thick, above the support screen. Because this solid slag layer likely restricted stirring of the solution in the reaction vessel, a second slag-only test, begun on July 18, 2019, was performed by placing 100 g of slag in a nylon mesh bag that was secured with Trilene fishing line. The bag was set to rest on the support screen to facilitate circulation of water around the sample. The reaction vessel was then filled with 546 g of sSRS water.

When sSRS water was added, the reaction vessels were overfilled to eliminate head space, and then the dissolved oxygen (DO), pH, and oxidation–reduction potential (ORP) probes were inserted in three of the four ports. Any overflow or water displaced from the vessel by the probes was collected in an underlying aluminum tray. The mass of water that had been added to a reaction vessel was determined by measuring the mass of the tared tray and subtracting that net mass of water from the total water volume that had been used to overfill the reaction vessel, assuming a water density of 1 g/mL. After the reaction vessel was filled with sSRS water and measurement probes had been sealed into three ports, a rubber septum stopper was placed over the fourth port. DO, pH, and ORP were measured using the probes described in Section 2.

The first slag (unbagged) test was terminated after more than 16 days had elapsed, on July 5, 2019, when a water sample was collected after the Eh had stabilized at approximately −434 mV (Figures 4-1 and 4-2). The second slag (bagged) test was terminated after 36 days had elapsed, on August 23, 2019, when a water sample was collected. Water samples were collected by inserting two syringe needles through the rubber septum stopper that sealed the fourth port. One needle delivered ultra-pure nitrogen gas to the vessel to displace the water sample and the other needle was used to collect water. A water sample that was analyzed for sulfur species and ferrous iron was collected in a 5-mL syringe, sealed with a syringe valve. A water sample analyzed for trace metals and major ions was collected in a 1-liter Tedlar bag. These water sampling techniques were also used for the other single grout component and mixture water-conditioning tests described in this report.

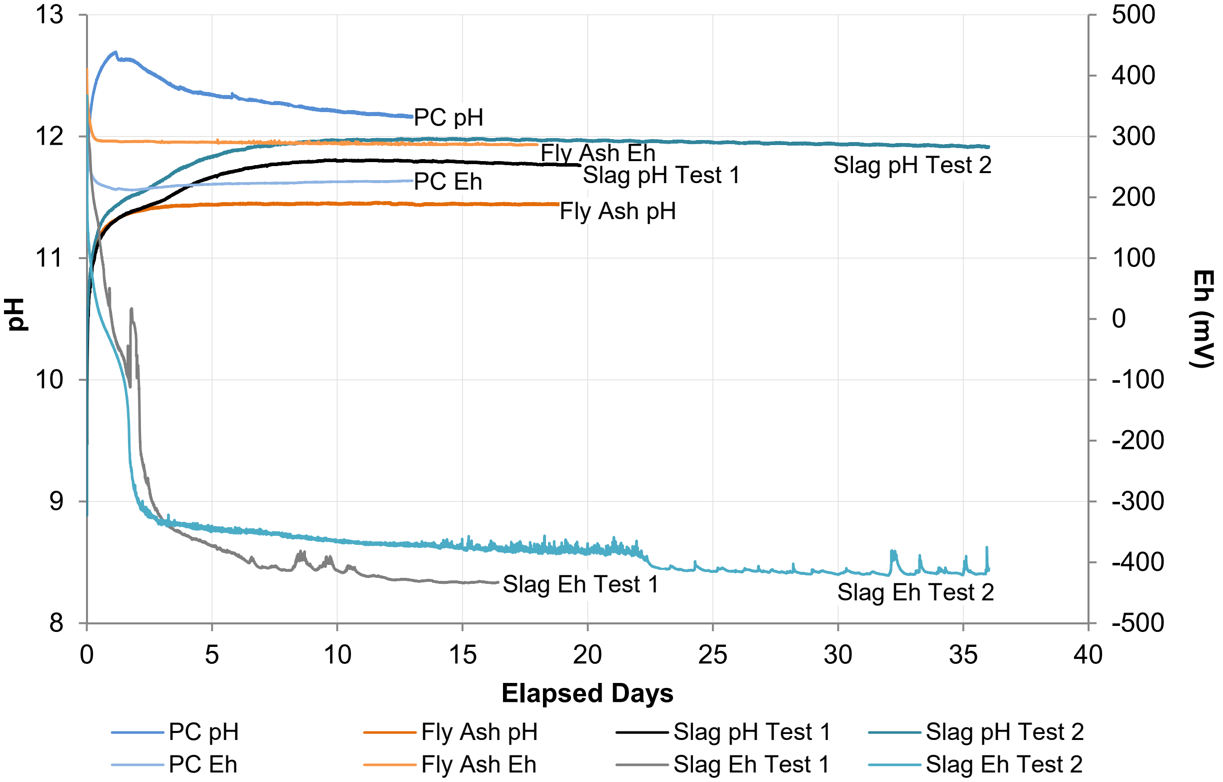

Figure 4-1. **pH and Eh data from individual grout-component water-conditioning tests**

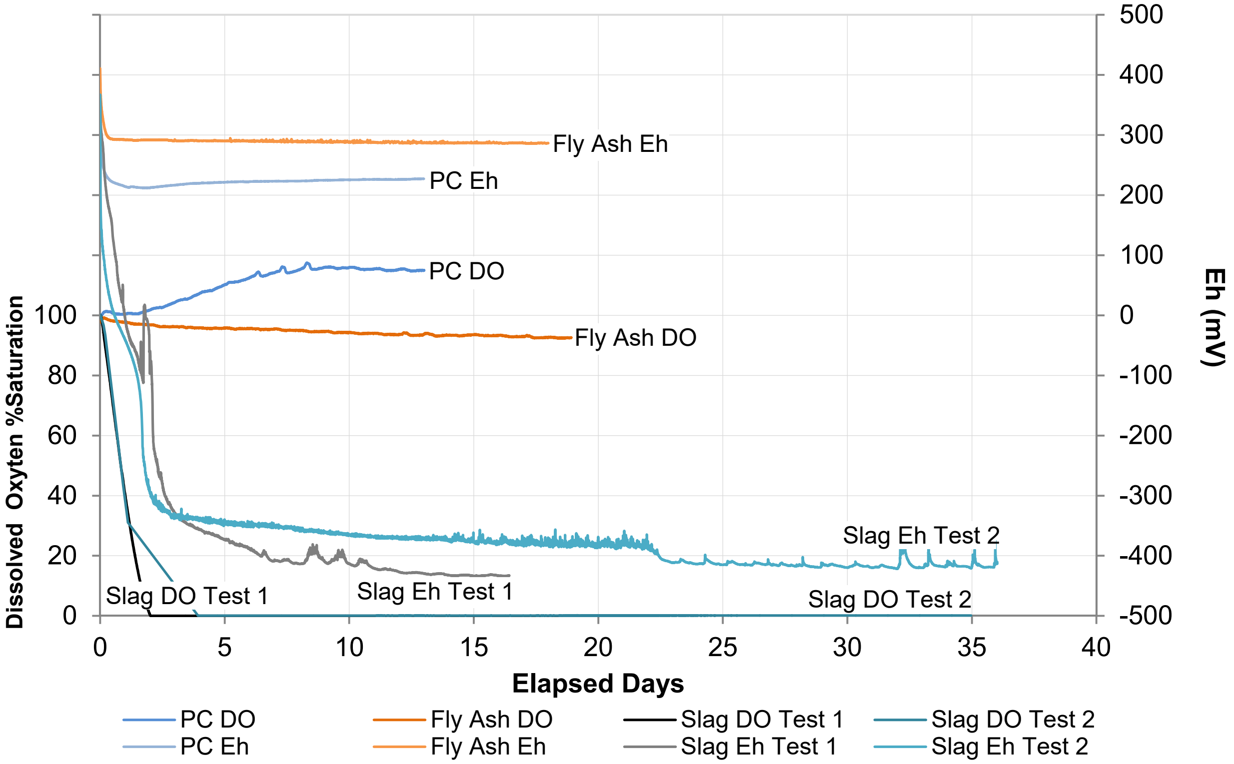

Figure 4-2. **DO and Eh data from individual grout-component water-conditioning tests**

4.2 Class F Fly Ash Test

The Class F fly ash test was performed by placing 103 g of fly ash above a 7-µm pore-size nylon mesh filter fabric that was loosely placed over a platinum-coated niobium support screen in a 4-port reaction vessel. The reaction vessel was overfilled with sSRS water to eliminate head space, and then DO, pH, and ORP probes were inserted into the vessel as described previously for the slag tests. The fourth port of the reaction vessel was sealed with a rubber septum stopper. The reaction vessel contained 532 g of sSRS water during the test. The fly ash test began on June 21, 2019, and ended 15 days later on July 5, 2019, when a water sample was collected. DO, pH, and ORP data continued to be collected for several more days (Figures 4-1 and 4-2). The fly ash had formed a soft paste by the end of the test.

Pabalan et al. (2009) suggested that over the long-term, fly ash is also a potential source of reducing species. Magnetite is often present at several weight percent in commercial fly ash. Additionally, fly ash may contain unburned carbon up to 4 to 5 weight percent. Atkins et al. (1989) documented experiments of up to 1 to 2 years duration for which fly ash containing carbon did not affect the Eh of cement−fly ash blends, but over the longer term, the reducing potential of unburned carbon in fly ash may come into effect. Testing the unburned carbon content and magnetite content of the Class F fly ash used by U.S. Department of Energy (DOE) for tank closure operations could be informative about the potential for its long-term influence as a source of reduction capacity.

4.3 Portland Cement Test

The Portland cement test was performed by placing 100 g of Portland cement in a 7-µm nylon mesh bag secured with Trilene fishing line. The bag was placed on the platinum-coated niobium support screen in the 4-port reaction vessel. The reaction vessel was overfilled with sSRS water to eliminate head space, and then DO, pH, and ORP probes were inserted into the vessel. The fourth port of the reaction vessel was sealed with a rubber septum stopper. The reaction vessel contained 565 g of sSRS water during the test. The Portland cement test began on July 18, 2019 and ended 13 days later on July 31, 2019 (Figures 4-1 and 4-2). The cement formed a hard mass inside the nylon bag by the end of the test.

4.4 DO, pH, and Eh Evolution During Individual Grout-Component Tests

The pH and Eh measured during the individual grout-component tests are shown in Figure 4-1, and the DO with Eh data are shown in Figure 4-2. Only the single-component slag tests exhibited a significant decrease in DO and Eh. Although the Class F fly ash and Portland cement tests both exhibited small decreases in Eh after interaction with sSRS water began, the Eh of the water during both of those tests remained positive. DO exceeding 100 percent saturation during the Portland cement test (Figure 4-2) may have been due to a DO probe malfunction, although subsequent tests using the same probe did not encounter a similar anomaly. During the slag tests, DO decreased rapidly to below the detection limit of the probe and the Eh gradually decreased to within the range of −400 to −430 mV (Figure 4-2). Eh was observed to decrease much more rapidly in the slag-only water-conditioning tests than during previous grout water-conditioning tests.

4.5 Chemistry of Conditioned Water Collected from Individual Grout-Component Tests

Water samples that had been collected from the reaction vessels at the end of each test were analyzed using the methods listed in Section 2. The distribution of major ions in the water samples collected from individual grout-component tests is illustrated in Figure 4-3.

Although each of the cementitious grout components contributes to a significant increase in the dissolved solids in the reacted water, there are major differences in the contributions from the individual grout components. Fly ash caused a significant increase in sulfate (SO_4) while the major ions contributed by Portland cement were potassium (K) and calcium (Ca).

Slag produced modest increases in all major ions, except magnesium (Mg). The results from the individual grout-component tests are generally consistent with the results for the tests performed with pulverized grout (Figure 3-6), although the dissolved concentrations observed for the pulverized grout tests were generally lower. The distribution of trace metals in the water samples collected from the individual grout-component tests are illustrated in Figure 4-4. Except for strontium, which was very high in the Portland cement, the general distribution of metals was similar to that from the tests of pulverized grout (Figure 3-7), although the concentrations were somewhat higher for barium (Ba) and lithium (Li) in all of the individual grout-component tests.

The dissolved sulfur species detected in the water samples collected from the individual grout-component tests are illustrated in Figure 4-5. Only the fly ash and slag tests resulted in significant dissolved sulfur concentrations. The fly ash test, which maintained oxidizing conditions throughout, resulted in a relatively high sulfate concentration, but little in the way of reduced sulfur species. In contrast, the slag tests, which produced strongly reducing conditions, resulted in significant sulfide concentrations along with lesser concentrations of other less-reduced sulfur species (sulfite and thiosulfate). The presence of sulfate, sulfite, and thiosulfate in the presence of sulfide in the slag samples is likely due to slow redox reactions in the reaction vessel, or oxidation of the samples in the syringe or during the analytical process. In comparison to the individual grout-component test results (Figure 4-5), the dominant reduced sulfur species detected in the pulverized grout tests was thiosulfate with very little sulfide (Figure 3-8). The lowest Eh attained during the pulverized grout tests was −303 mV, whereas the lowest Eh attained during the slag-only tests was approximately −434 mV. These results are consistent with the observation that reduced sulfur species play an important role in controlling the Eh in the contact water. The differences between the total sulfur measured by inductively coupled plasma (ICP) and the sum of species by ion chromatography may be due to differences in the accuracy and precision of the two methods.

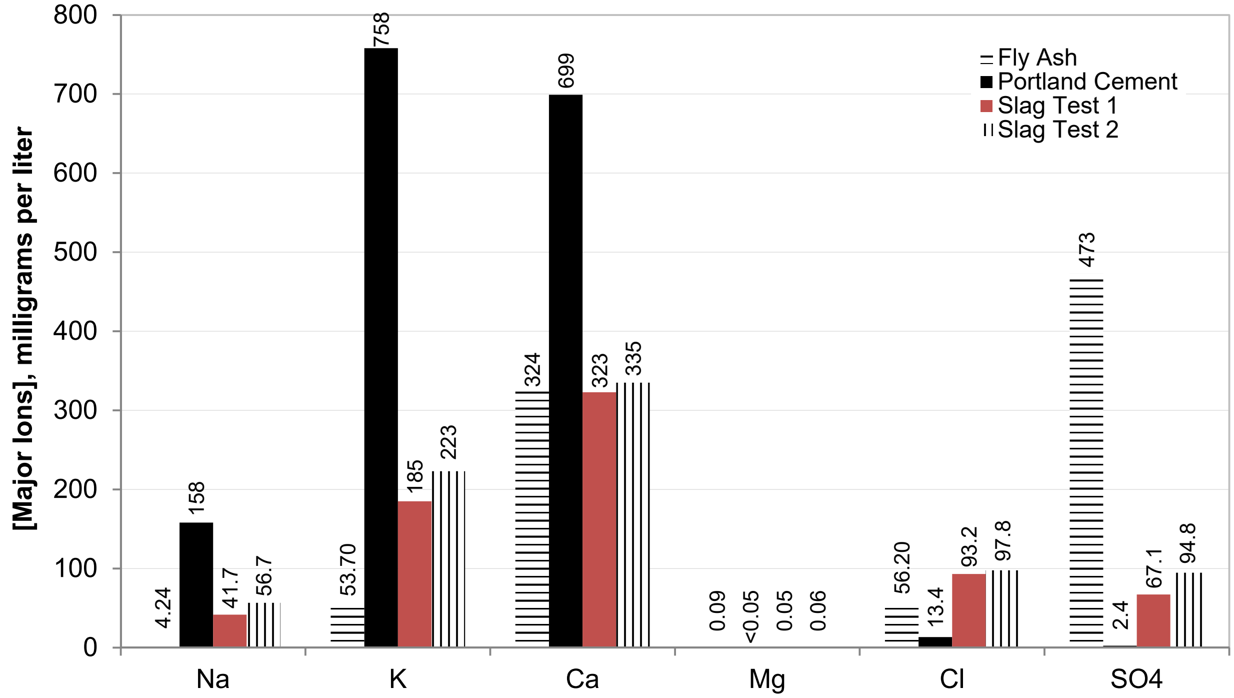

Figure 4-3. **Major ions in water samples collected from individual grout-component tests**

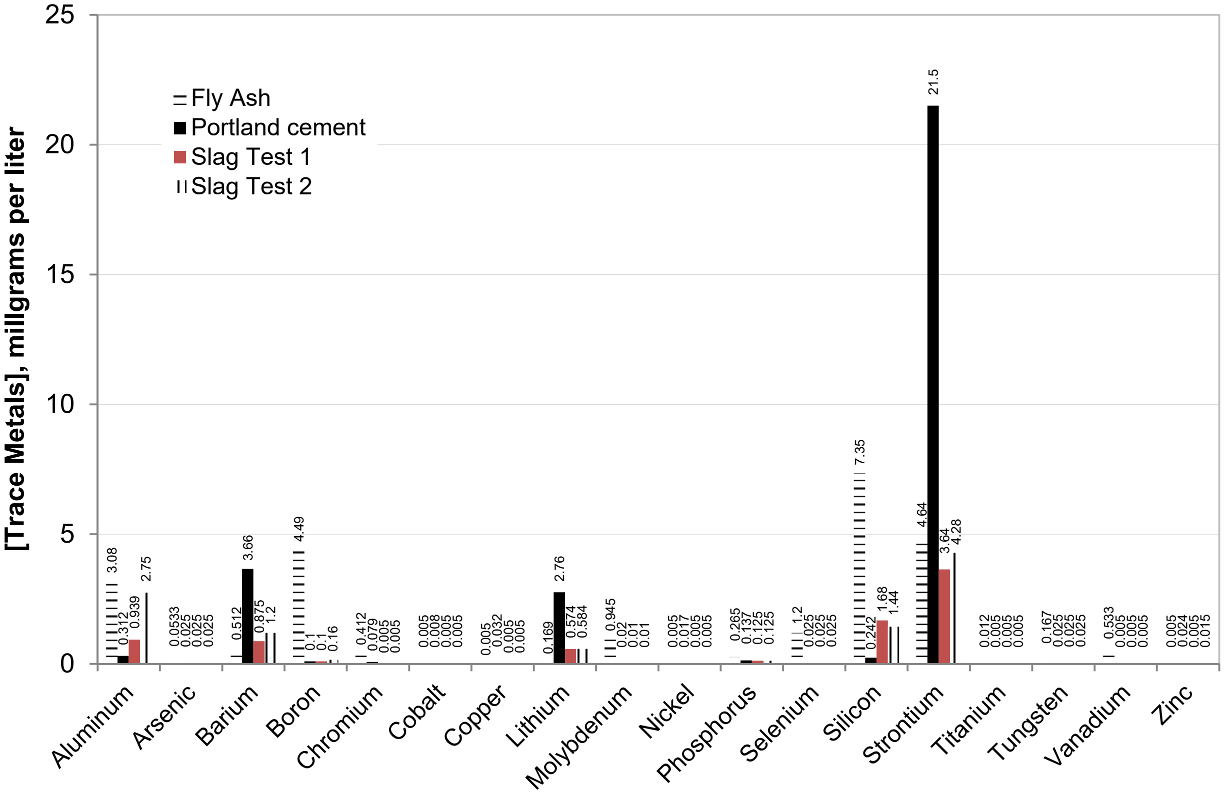

Figure 4-4. **Trace metals detected in water samples collected from the individual grout-component water-conditioning tests**

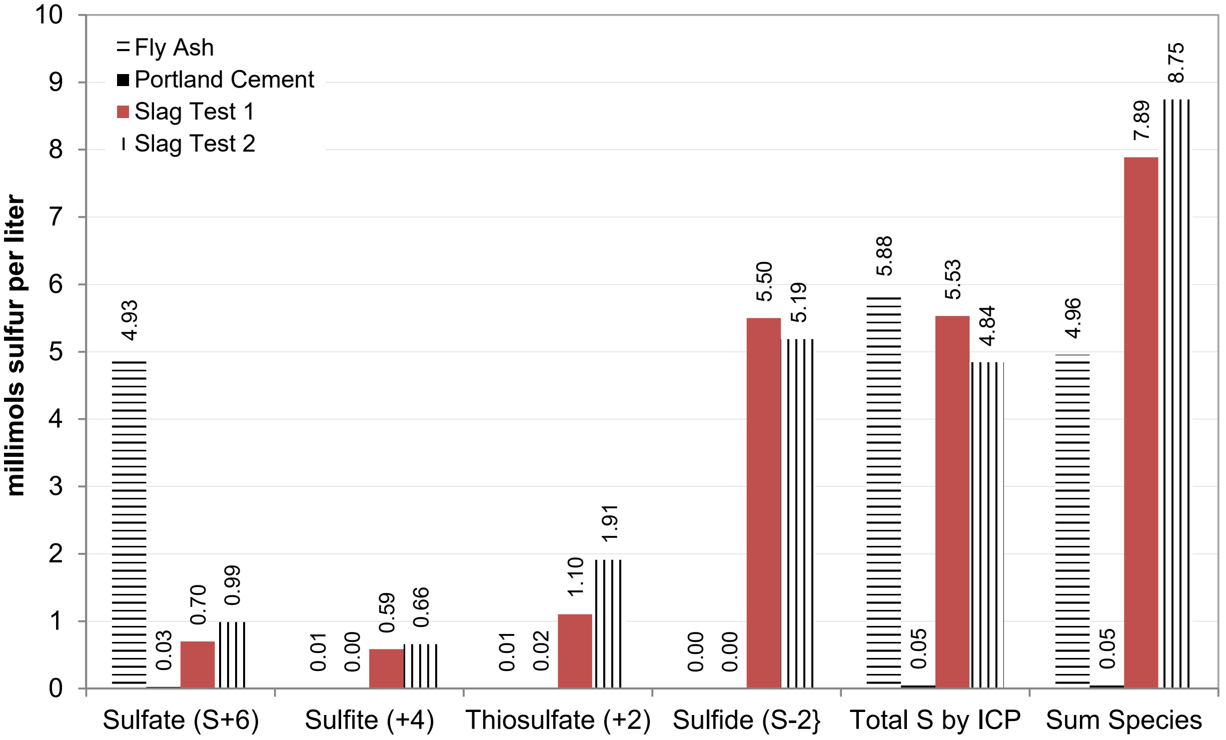

Figure 4-5. **Sulfur speciation analyses of water samples collected from individual grout-component tests**

5 WATER-CONDITIONING TESTS OF CEMENTITIOUS MATERIAL MIXTURES

Water-conditioning tests were also performed of cementitious material mixtures having mass ratios consistent with the Savannah River Site (SRS) Reducing Tank Grout LP#8-016 formula (SRR–CWDA–2013–00026), described in Walter and Dinwiddie (2019). These tests were performed to investigate the effect of the grout component mixtures on the redox chemistry of the contact water. Tests were performed of the following mixtures:

- Portland cement and Grade 120 slag
- Portland cement and Class F fly ash
- Class F fly ash and Grade 120 slag.

Staff measured the mass of the individual grout components until the targeted quantity of each was amassed in a tared beaker (see Table 5-1). The individual grout components were then poured together into a plastic bag, which was sealed and shaken to thoroughly combine the two materials. The mixed cementitious materials were then placed inside a 7-μm nylon mesh bag that was secured with Trilene fishing line. The bag was placed in the 4-port reaction vessel on the support screen and synthetic Savannah River Site (sSRS) water was added until it overflowed. The mass of sSRS water contained in the reaction vessel during each test is also listed in Table 5-1.

Table 5-1. Component masses and sSRS water mass used in mixed-component tests

Component 1	Component 2	Component 1 Mass (g)	Component 2 Mass (g)	Mixture Mass (g)	sSRS Water (g)
Portland cement	Grade 120 slag	37	63	100	538
Portland cement	Class F fly ash	26	74	100	535
Class F fly ash	Grade 120 slag	37	63	100	536

5.1 DO, pH, and Eh Evolution During Cementitious Material Mixture Tests

The pH and oxidation–reduction potential (Eh) measured during the cementitious material mixture tests are shown in Figure 5-1, and the dissolved oxygen (DO) with Eh data are shown in Figure 5-2. The maximum pH and minimum DO and Eh values attained during the individual grout component and cementitious material mixture tests are summarized in Table 5-2. The diagonal entries of the matrix in Table 5-2 summarize the results of the individual grout component tests, described in Section 4. The off-diagonal entries in Table 5-2 summarize the mixture tests. The lowest Eh reached during the tests is reported in Table 5-2 because some tests were affected by an increase in DO prior to their termination. Mixtures containing slag had reduced DO saturations and resulted in negative Eh values, but the lowest Eh values from mixture tests were greater (less negative) than those attained during the slag-only tests. This could be due either to chemical reactions that occurred between the slag and the other cementitious component in the mixture or to the lower slag-to-water mass ratio in the mixture tests relative to the slag-to-water mass ratio in the single component (i.e., slag only) tests.

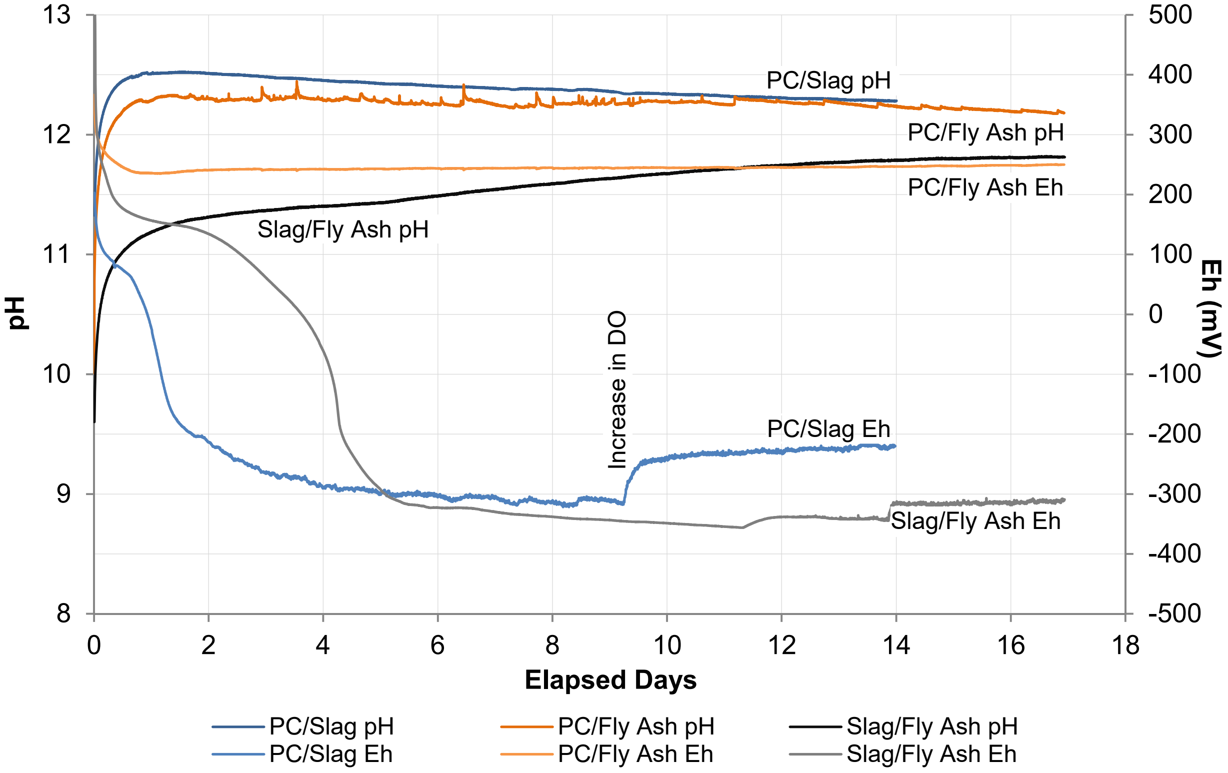

Figure 5-1. pH and Eh data from cementitious material mixture water-conditioning tests

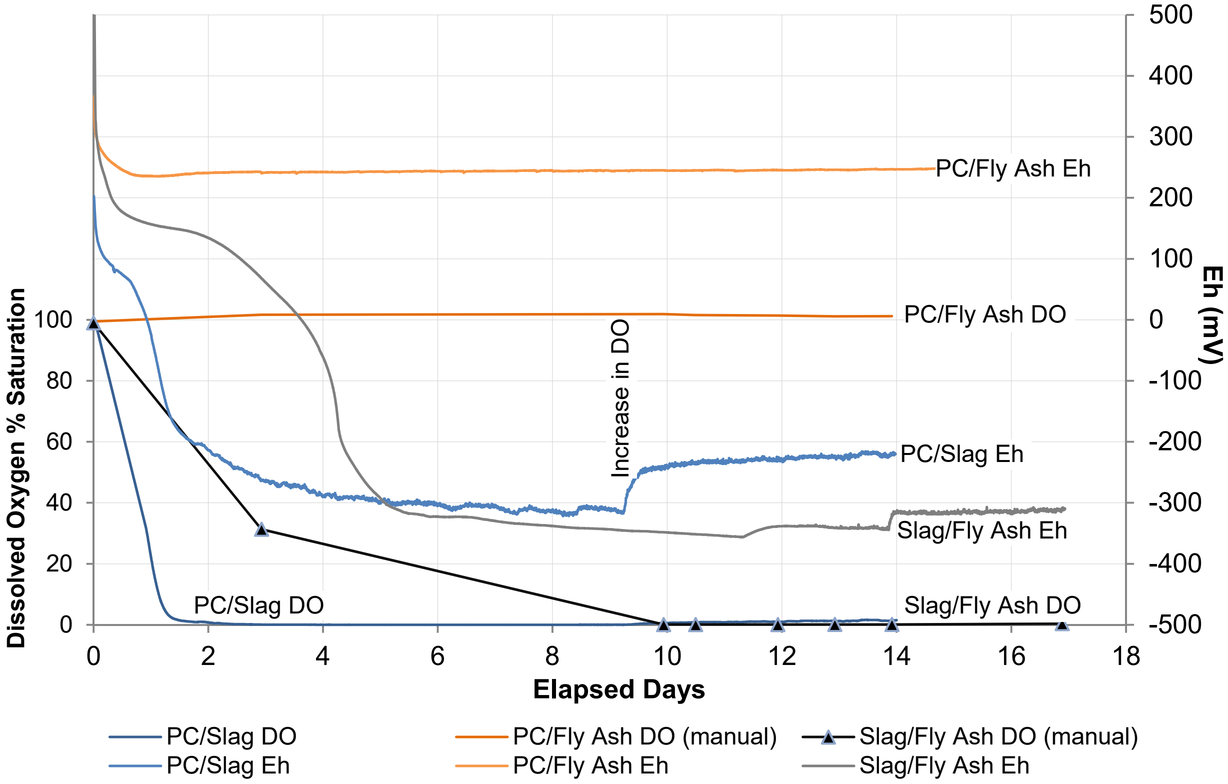

Figure 5-2. DO and Eh data from cementitious material mixture water-conditioning tests

Table 5-2. Chemical conditions in individual grout-component and mixture tests (diagonal entries summarize the individual grout-component tests and off-diagonal entries summarize the mixture tests)

Component	Portland cement	Class F fly ash	Grade 120 slag	
Portland cement	DO 114 percent pH 12.21 Eh +227 mV	No Entry	No Entry	
Class F fly ash	DO 100 percent pH 12.26 Eh +242 mV*	DO 83.48 percent pH 11.43 Eh +281 mV	No Entry	
Grade 120 slag	DO 1.46 percent* pH 12.27 Eh −313 mV*	DO 0.08 percent* pH 11.8 Eh −350*	Unbagged DO 0 percent pH 11.74 Eh −434 Mv	Bagged DO 0.14 percent pH 11.93 Eh −414 mV

*Minimum value during test

5.2 Chemistry of Conditioned Water Collected from Cementitious Material Mixture Tests

Water samples collected from the reaction vessels at the end of each test were analyzed using the methods listed in Section 2. The distribution of major ions in the water samples collected from the cementitious material mixture tests is illustrated in Figure 5-3. Although the results are generally similar to those obtained from the individual grout-component tests (Figure 4-3), mixtures containing Portland cement had much lower sulfate and total sulfur concentrations than did the individual component tests for Class F fly ash and Grade 120 slag (Figure 5-4). Thus, the presence of Portland cement in the mixtures appears to suppress the formation of dissolved sulfur in the contact water. However, this finding conflicts with statements in Pabalan et al. (2009) that alkaline materials, such as Portland cement, are necessary to activate reduced sulfur in the slag.

The distribution of trace metals in the water samples collected from the cementitious material mixture tests are illustrated in Figure 5-5. The results are generally similar to those obtained from the individual grout-component tests (Figure 4-4), indicating that interactions between the various grout components do not affect the dissolved metal concentrations.

The dissolved sulfur species detected in the water samples collected from the cementitious material mixture tests are illustrated in Figure 5-6. In Figure 5-6, the difference between the total sulfur by inductively coupled plasma (ICP) and the sum of sulfur species by ion chromatography may be due to differences in the accuracy and precision of the two methods. As mentioned previously, only the slag-containing mixtures resulted in significant dissolved sulfur concentrations. The slag/fly ash mixture resulted in the highest total dissolved sulfur concentration and the highest concentrations of reduced sulfur species. The total sulfur and reduced sulfur concentrations in the Portland cement/slag mixture were lower, even though the mass fraction of slag was the same in each test (Table 5-2) and the mixture particulate mass-to-water ratio was approximately the same. This suggests that Portland cement may suppress the production of reduced sulfur in the contact water. This finding appears to conflict with the assertion in Pabalan et al. (2009, p. 8-11) that the fraction of reacted slag will be low unless activated by a material such as Portland cement.

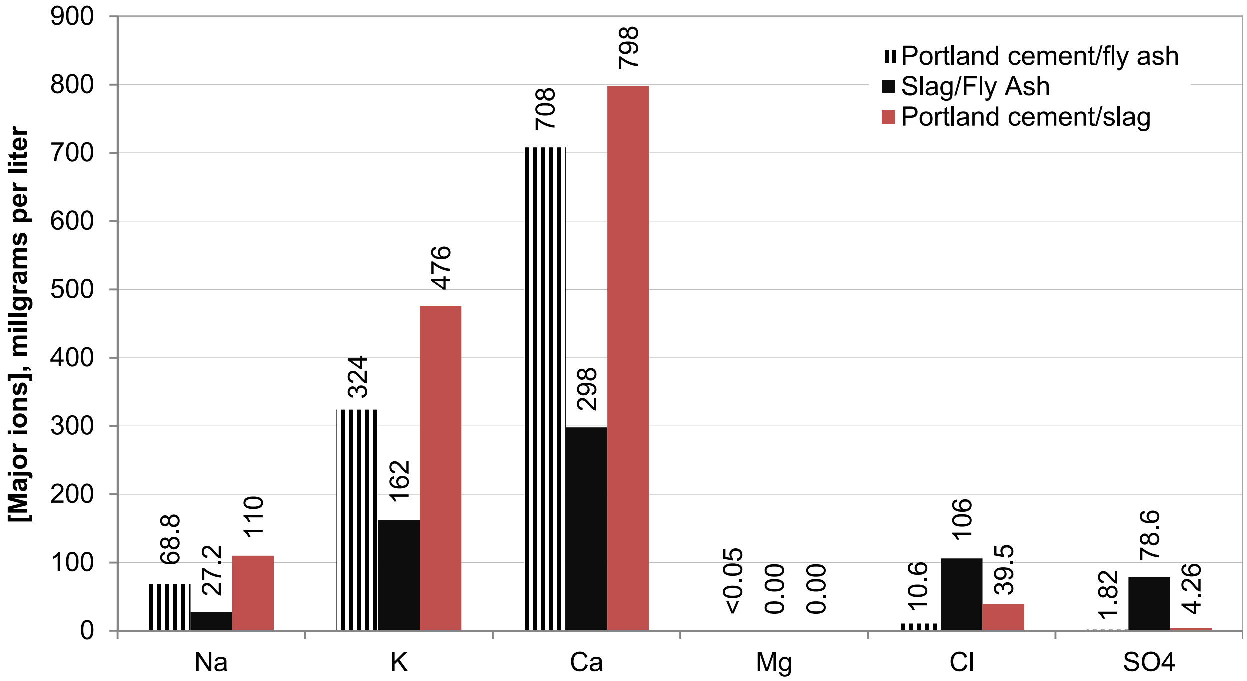

Figure 5-3. **Major ion concentrations in water samples collected from cementitious material mixture water-conditioning tests**

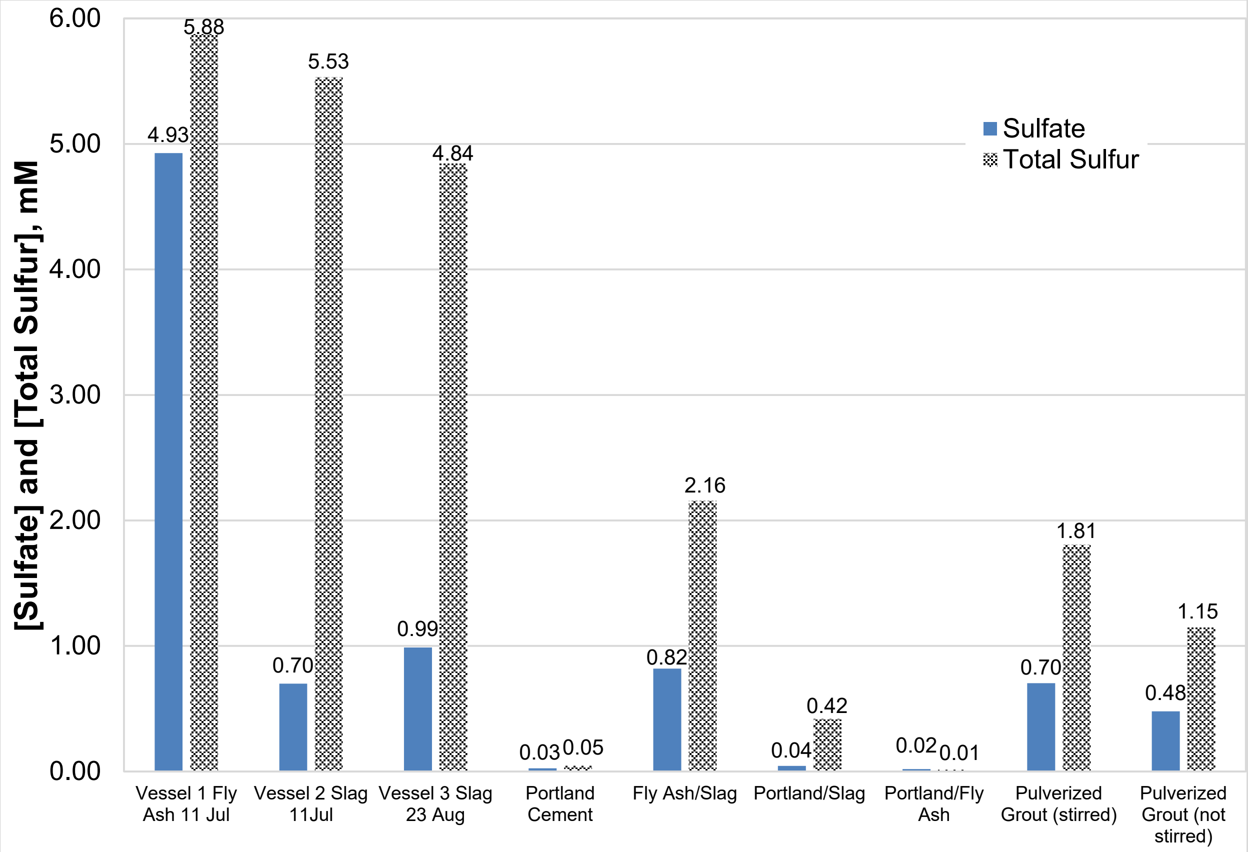

Figure 5-4. **Comparison of sulfate and total sulfur in water samples collected from all FY 2019 water-conditioning tests**

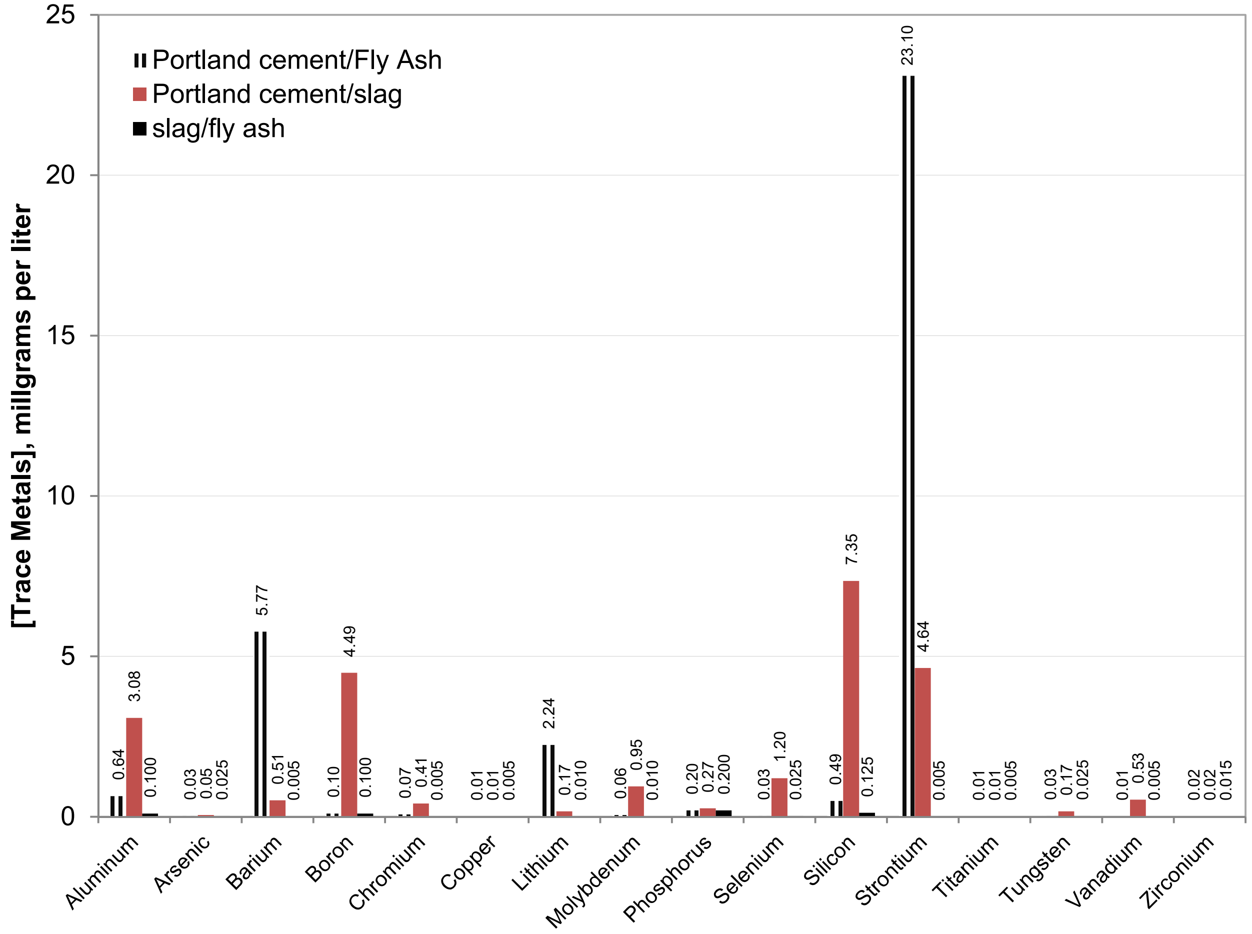

Figure 5-5. **Trace metals detected in water samples collected from the cementitious material mixture water conditioning tests**

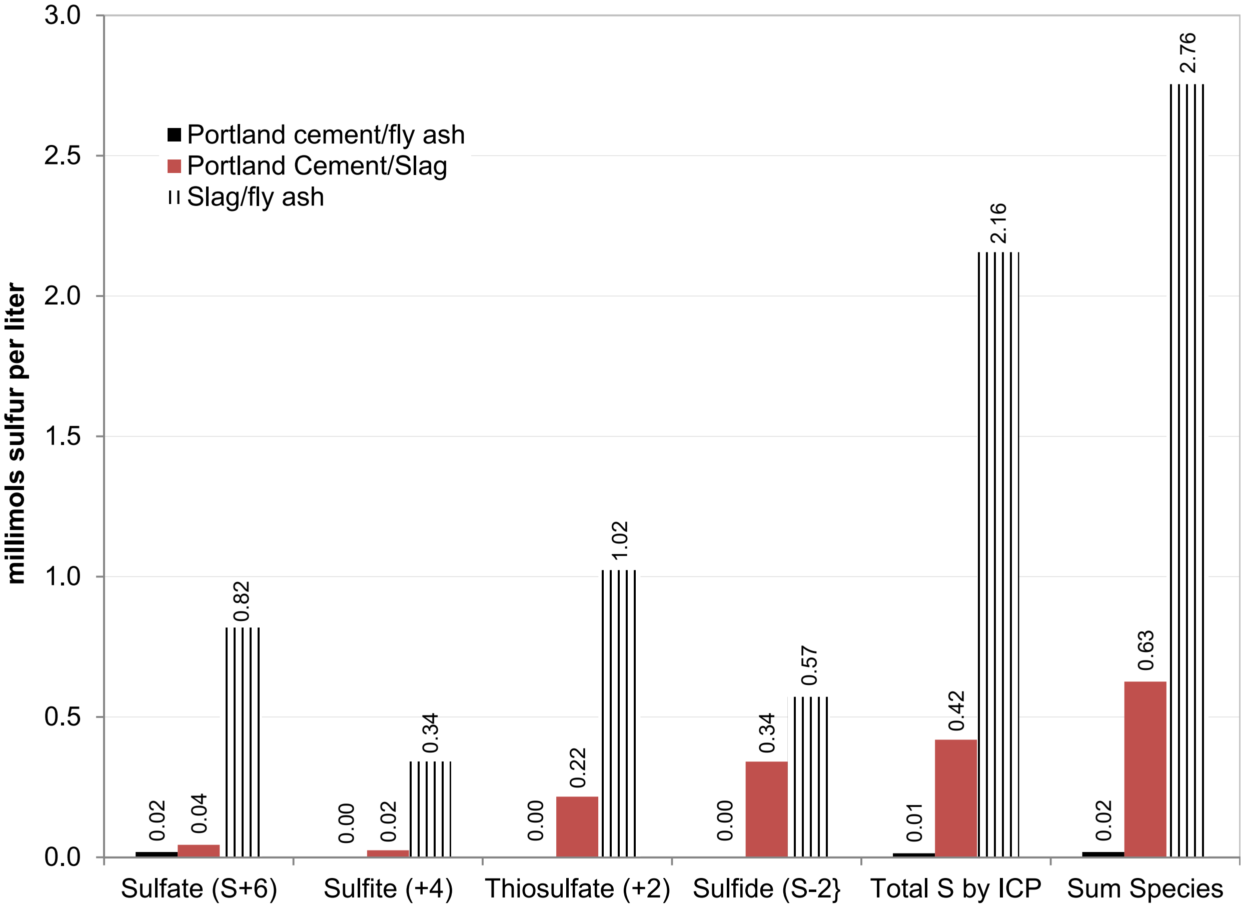

Figure 5-6. **Sulfur speciation analyses of water samples collected from cementitious material mixture tests**

6 EDS AND XRD ANALYSES OF FLY ASH AND SLAG CEMENTS

Samples of Class F fly ash, and Grades 100 and 120 slag were provided to Southwest Research Institute® (SwRI®) Mechanical Engineering Division, Materials Engineering Department staff for energy dispersive X-ray spectroscopy (EDS) elemental analyses to semi-quantitatively determine the percentage of the elemental composition (Figures 6-1, 6-4,and 6-6, and Tables 6-1 to 6-3) and X-ray diffraction (XRD) analyses to determine mineralogy (Figures 6-2, 6-3, 6-5, 6-7, and 6-8). Such analyses are typically coupled. Data were obtained from a spot analysis of one area on each sample, so tabulated EDS chemical composition is reported to one decimal point. Jade version 3.1 (Materials Data, Inc. or MDI, Livermore, California) XRD interpretation software, which remains in use at SwRI, is a relatively old, capability-limited version of the software: peak picking is manual, rather than automated. Using Jade version 3.1, Rietveld Refinement is only possible when the weight percent's of the minerals present are known. In what follows, we demonstrate the differences between preliminary interpretations of XRD results obtained by SwRI's Mechanical Engineering Division staff in San Antonio (Figures 6-2, 6-5, and 6-7), and improved interpretations obtained by SwRI's Space Science and Engineering staff while visiting the University of Oklahoma, where a newer software version, Jade 2010 was borrowed for these analyses (Figures 6-3 and 6-8). Ongoing updates to this interpretation software from 2019 forward will be known as Jade Pro.

Minerals fit to the fly ash spectra included: berlinite, mullite, albite, luogufengite, hematite, aluminohydrocalcite, and wollastonite. Grade 100 slag (ASTM C989 from Holcim US, Inc. of Birmingham, Alabama), which was previously used to prepare grout for closing some of the Savannah River Site (SRS) waste tanks, produced no XRD peaks (F7465, Figure 6-5), because it consists of amorphous glassy particles (cf., Atkins and Glasser, 1992). Minerals fit to the Grade 120 slag spectra included: gypsum, calcite, pyrophylite, periclase, and nacrite. Some underfit peaks of Grade 120 slag (F7466, Figure 6-8) may be clays; they did not fit minerals in the database. Reduced-sulfur-bearing minerals were not identified in the fly ash and Grade 120 slag samples using Jade 2010 (Figures 6-3 and 6-8), although the oxide percentages indicated considerable SO_3. The $P_3O_{14}N_3H_4$ identification in Grade 120 slag (Figure 6-8) is unlikely; high background noise complicated identification of low-angle peaks. That U.S. Department of Energy's (DOE's) Grade 100 slag was amorphous and Grade 120 slag is crystalline is a significant difference that may impact grout water-conditioning results.

Future work may include XRD analyses of powdered grout samples prepared with (i) Grade 100 and (ii) Grade 120 slags, because after hydration reactions occur, the mineralogy evident in the two reducing grouts would be expected to differ from that in the cementitious grout components. To understand the independent mineralogy of both the fine and coarse aggregates that are used to prepare the tank grouts, and therefore their influence on the results of powdered grout mineralogical analyses, XRD analyses of powdered samples of the (i) sand and (ii) pea gravel may also be performed. To understand the mineralogy of aggregate-free, clean cap grout (C–SPP–Z–00012), which DOE placed into Lifts 5 and 6 of the primary and annulus of Tank 16 because of its enhanced flowability, XRD analyses of powdered clean cap grout samples may also be undertaken. Pozzolanic and cementitious material components of clean cap grout include slag cement (45 weight percent), Class F fly ash (45 weight percent), and Portland Type I/II cement (10 weight percent); water is the only other ingredient. Powdering indurated material samples for EDS and XRD analyses will require access to and use of a ball mill, or equivalent. Future EDS and XRD work also depends on SwRI's potential acquisition of MDI's Jade Pro mineralogy interpretation software, which allows the user to rapidly pick XRD peaks and identify the minerals present.

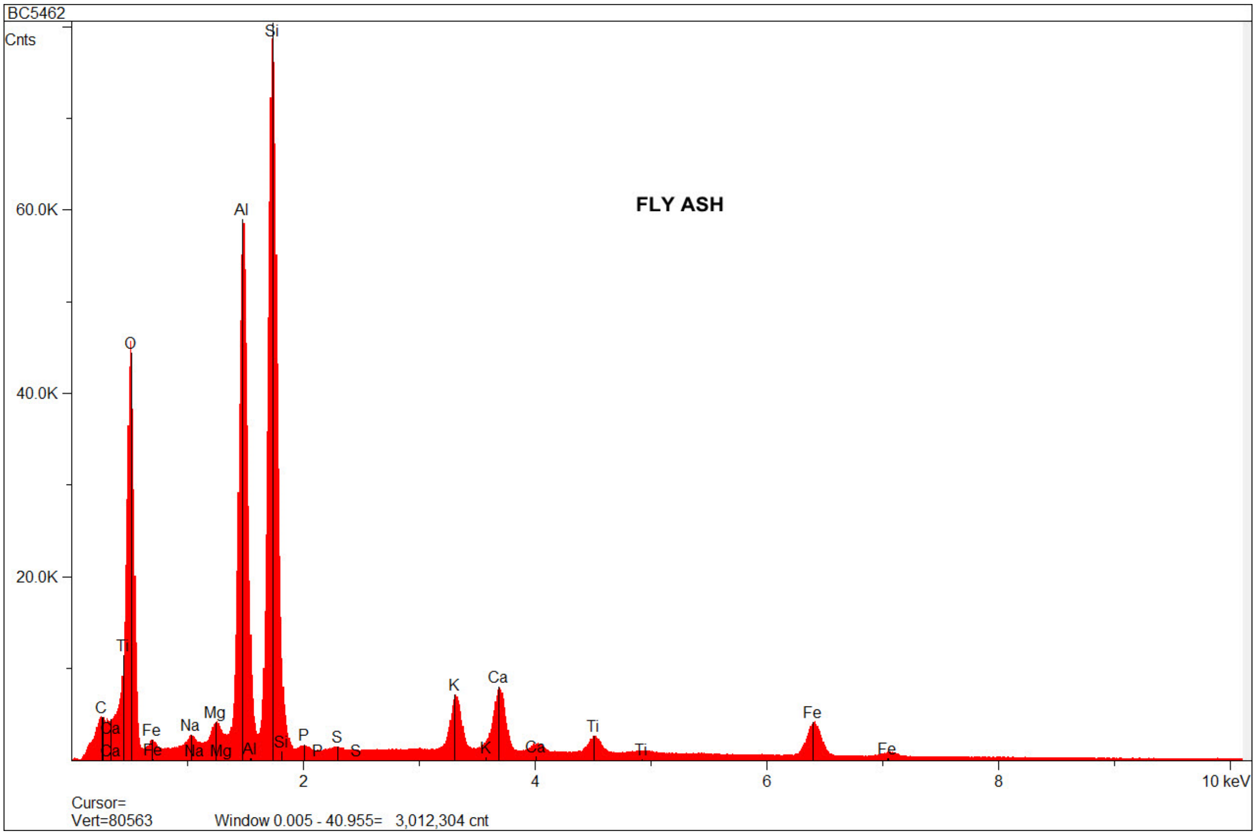

Figure 6-1. EDS electromagnetic emission spectrum of Class F fly ash (BC5462)

Table 6-1. EDS chemical composition analysis report for Class F fly ash (BC5462)

Element	Line	Intensity (c/s)	Atomic %	Conc. (wt.%)
Na	Ka	33.70	1.0	0.8
Mg	Ka	80.41	1.6	1.3
Al	Ka	1,744.41	29.7	26.6
Si	Ka	2,440.22	52.8	49.2
P	Ka	9.33	0.3	0.3
S	Ka	13.67	0.3	0.3
K	Ka	225.94	3.8	5.0
Ca	Ka	276.30	4.7	6.3
Ti	Ka	78.55	1.4	2.3
Fe	Ka	175.36	4.3	8.0
		Total:	99.9	98.1

kV 20.0
Takeoff Angle 35.0°
Elapsed Livetime 300.0

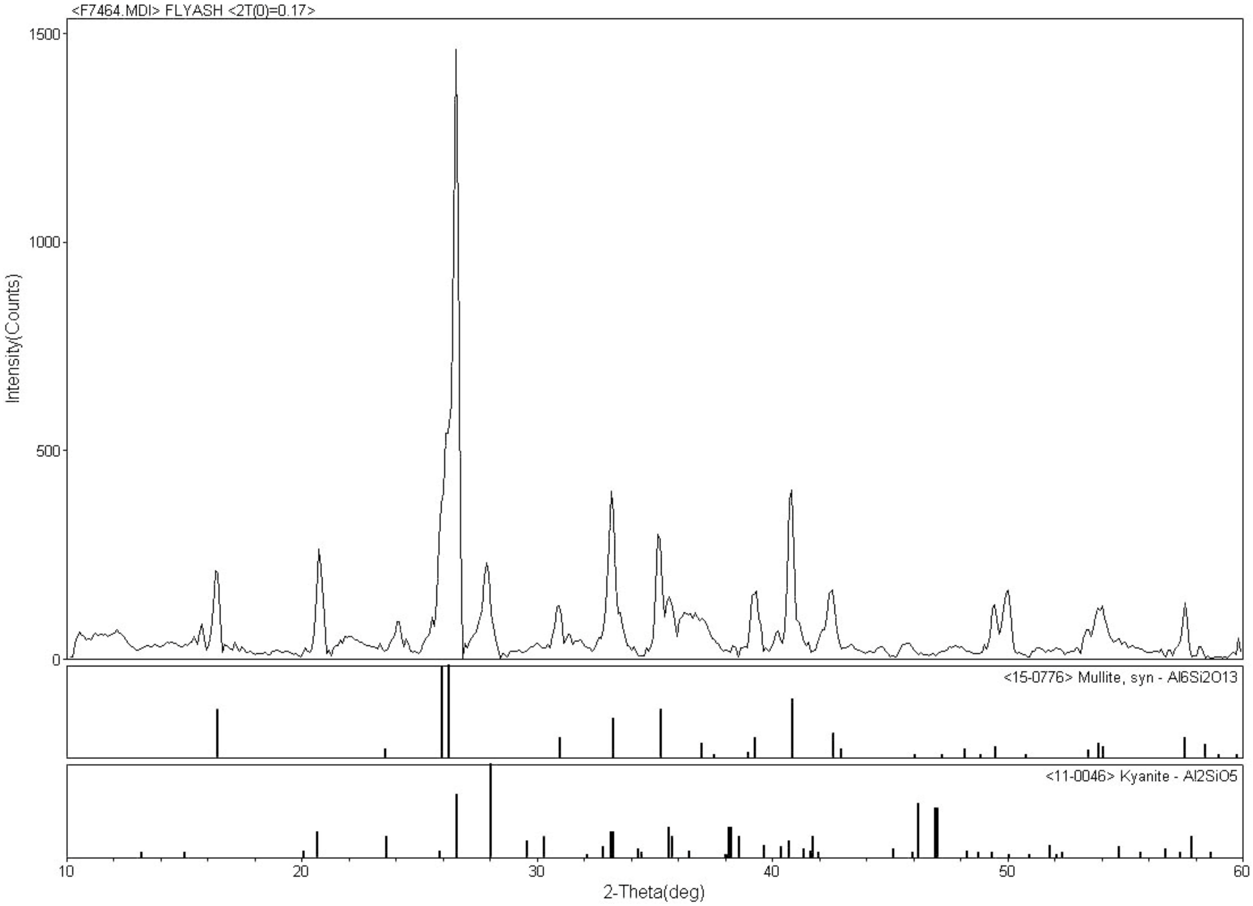

Figure 6-2. X-ray powder diffractogram of Class F fly ash (F7464). Preliminary mineral identifications using Jade version 3.1 included the aluminum silicates mullite ($Al_6Si_2O_{13}$) and kyanite (Al_2SiO_5)

WPF Report

Scan ID: F7464.MDI • FLYASH

Scan Parameters: 10.0°/60.0°/0.1°/12(s), I(p)=2707.9/13.9, Cu, Friday, August 23, 2019, 8:51 AM

Control File: J:\F7464.wrk.xml

☑ Zero Offset = -0.2005 (0.025) ☐ Displacement = 0.0 ☐ Distance Slack = 0.0

☑ Kα2 Peaks Present (Variable-Slit) ☐ Kα2/Kα1 Ratio = 0.5 ☐ X-Ray Polarization = 1.0

Geometry: Diffractometer Lp Fitted-Range: 10.0 - 60.0° BG-Model: Polynomial (2) λ: 1.54059 Å (Cu)

PSF: pseudo-Voigt Broadening: Individual FWHM Curve Instrument: Constant FWHM = 0.1°

Phase ID (9)	Chemical Formula	PDF-#	Wt% (esd)	RIR	µ
Mullite (PO)	$Al_{1.97}Cr_{.25}Si_{.78}O_{5.22}$	98-000-3514	23.6 (1.8)	0.60	164.3
Berlinite (PO)	$AlPO_4$	98-000-9785	29.2 (2.1)	2.28	175.6
Albite (PO) (?)	$Na(Si_3Al)O_8$	98-000-1590	18.1 (1.6)	0.82	83.3
Hematite (PO) (?)	Fe_2O_3	98-000-1193	2.5 (0.5)	2.23	1192.8
Luogufengite (PO)	Fe_2O_3	04-011-7764	2.9 (0.6)	1.61	1140.4
Albite - low (PO)	$Na(AlSi_3O_8)$	98-000-0041	5.7 (0.8)	0.92	85.9
Alumohydrocalcite (PO)	$CaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O$	00-042-0592	1.1 (0.3)	(1.0)	73.5
Wollastonite-2M | calciumcatena-silicate,β-	$CaSiO_3$	04-010-2581	0.7 (0.3)	1.00	219.6
Mullite (PO)	$Al_{2.35}Si_{0.64}O_{4.82}$	01-073-1253	16.2 (1.5)	0.39	101.4

XRF(Wt%): Fe2O3=5.4%, Cr2O3=2.6%, CaO=0.5%, P2O5=23.1%, SiO2=27.2%, Al2O3=47.6%, Na2O=2.8%, CO2=0.3%

Refinement Halted (R/E=2.74), ♣ Round=4, Iter=12, P=124, R=11.88% (E=4.34%, EPS=0.5)

J:\F7464.MDI

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Figure 6-3. X-ray powder diffraction analysis of Class F fly ash (F7464); interpretations accomplished using Jade 2010 (Materials Data, Inc.)

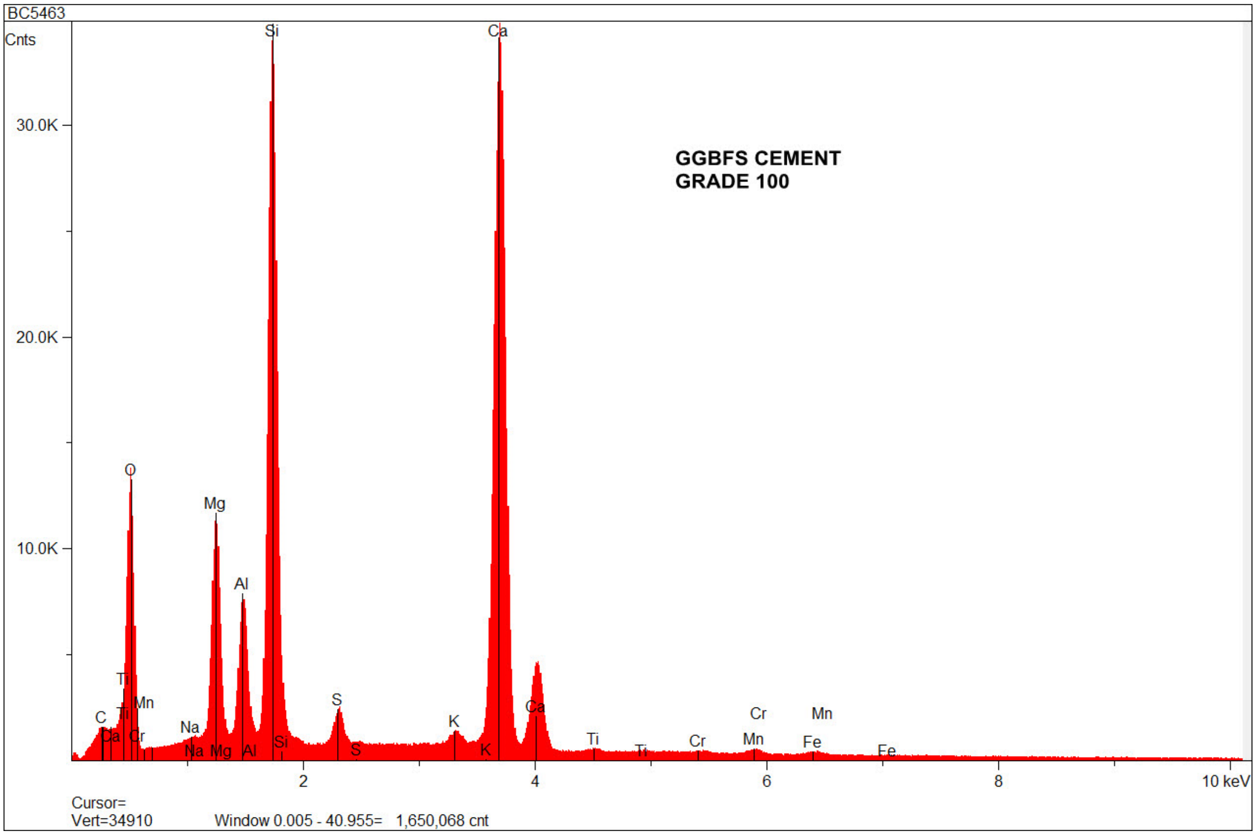


Figure 6-4. EDS electromagnetic emission spectrum of Grade 100 slag cement (BC5463)

Table 6-2. EDS chemical composition analysis report for Grade 100 slag cement (BC5463)

Element	Line	Intensity (c/s)	Atomic %	Conc (wt.%)
Na	Ka	8.73	0.6	0.4
Mg	Ka	314.80	13.4	10.0
Al	Ka	209.86	8.0	6.7
Si	Ka	1,042.06	36.5	31.6
S	Ka	60.14	2.1	2.0
K	Ka	24.29	0.7	0.8
Ca	Ka	1,299.26	37.6	46.5
Ti	Ka	7.17	0.3	0.4
Cr	Ka	5.59	0.2	0.3
Mn	Ka	10.48	0.4	0.7
Fe	Ka	7.11	0.3	0.6
		Total:	100.1	100.0

kV 20.0
Takeoff Angle 35.0°
Elapsed Livetime 300.0

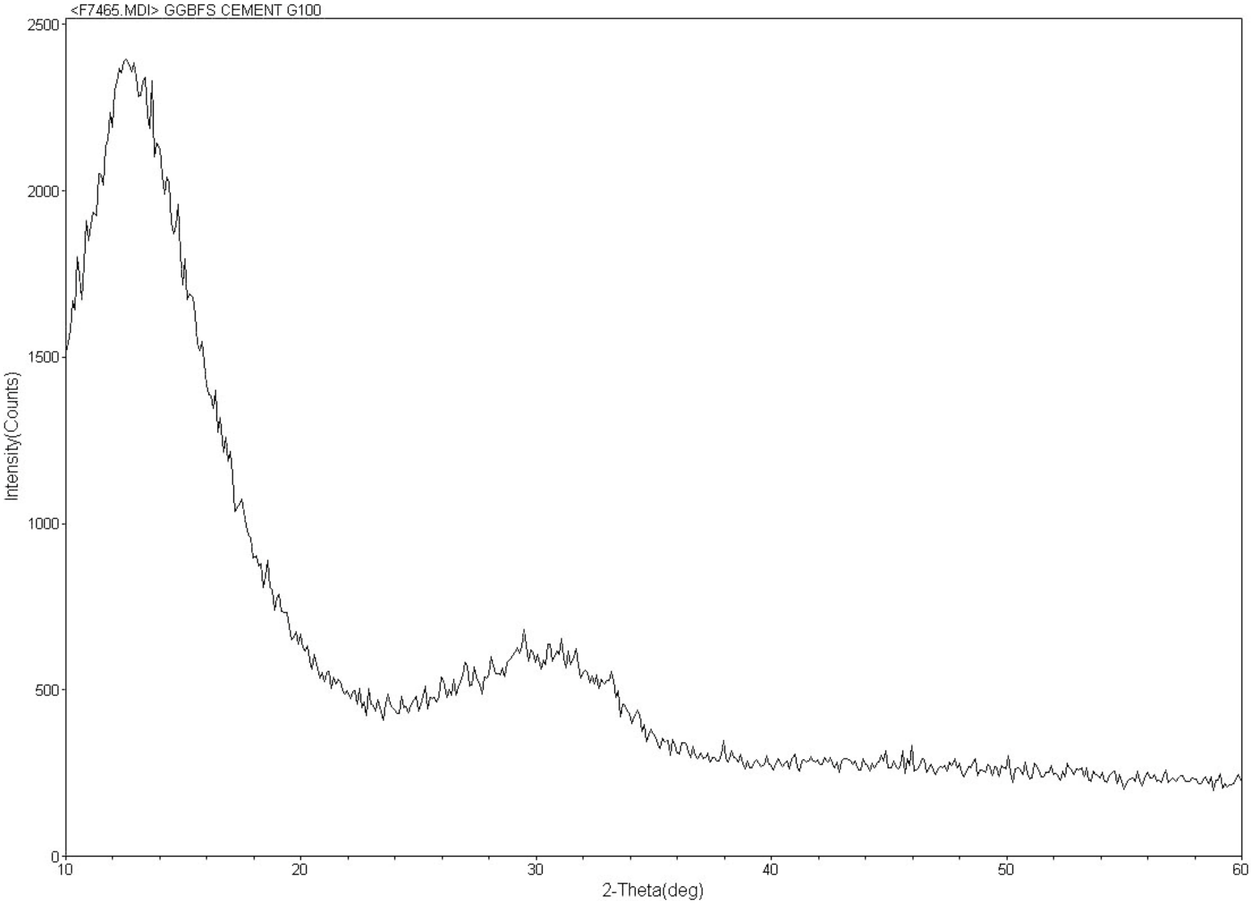


Figure 6-5. **X-ray powder diffractogram of amorphous Grade 100 slag cement (F7465) that produced no sharp peaks**

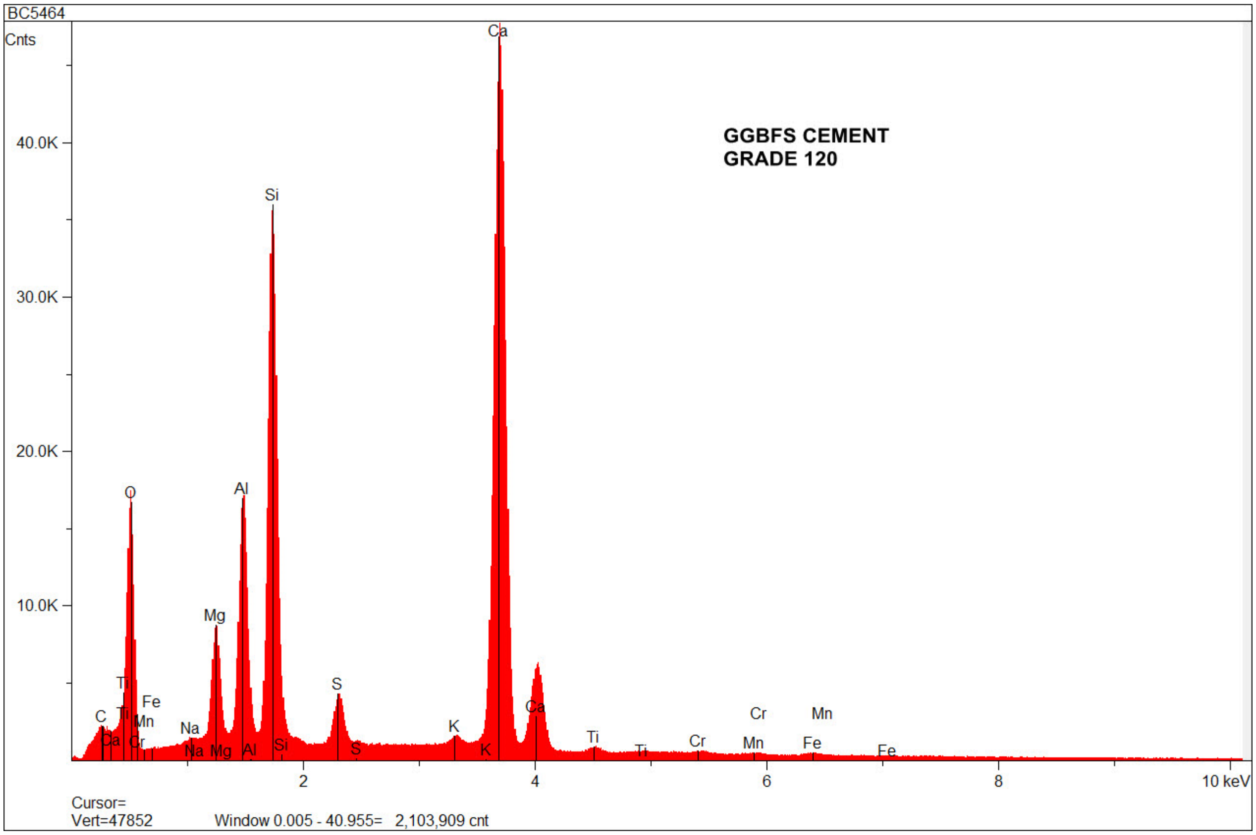


Figure 6-6. EDS electromagnetic emission spectrum of Grade 120 slag cement (BC5464)

Table 6-3. EDS chemical composition analysis report for Grade 120 slag cement (BC5464)

Element	Line	Intensity (c/s)	Atomic %	Conc (wt.%)
Na	Ka	12.01	0.6	0.4
Mg	Ka	226.73	7.9	5.8
Al	Ka	486.26	14.4	11.8
Si	Ka	1,085.92	31.4	26.8
S	Ka	115.78	3.1	3.0
K	Ka	20.68	0.4	0.5
Ca	Ka	1,768.84	41.0	49.8
Ti	Ka	15.29	0.4	0.7
Cr	Ka	8.04	0.3	0.4
Mn	Ka	5.27	0.2	0.3
Fe	Ka	7.74	0.3	0.5
		Total:	100.0	100.0

kV 20.0
Takeoff Angle 35.0°
Elapsed Livetime 300.0

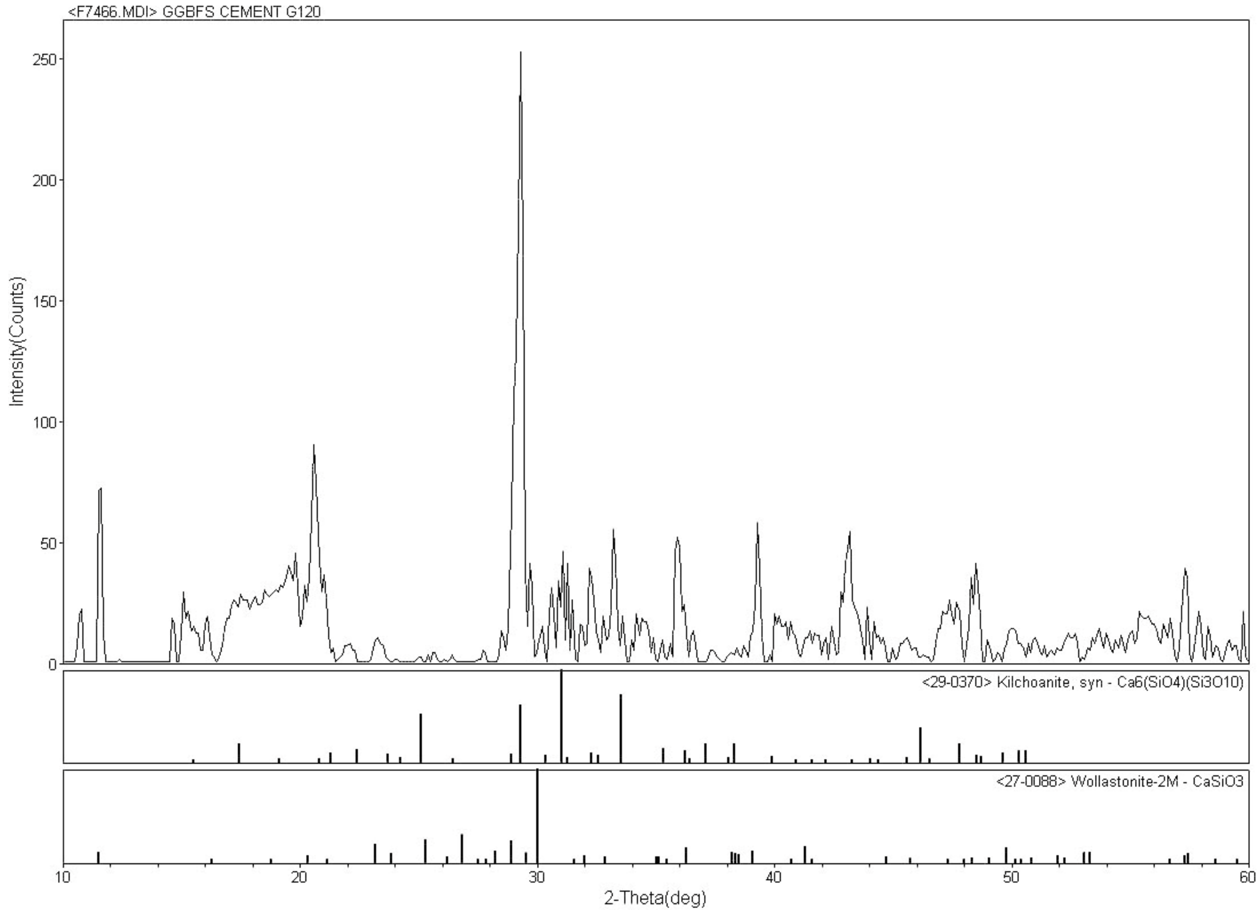
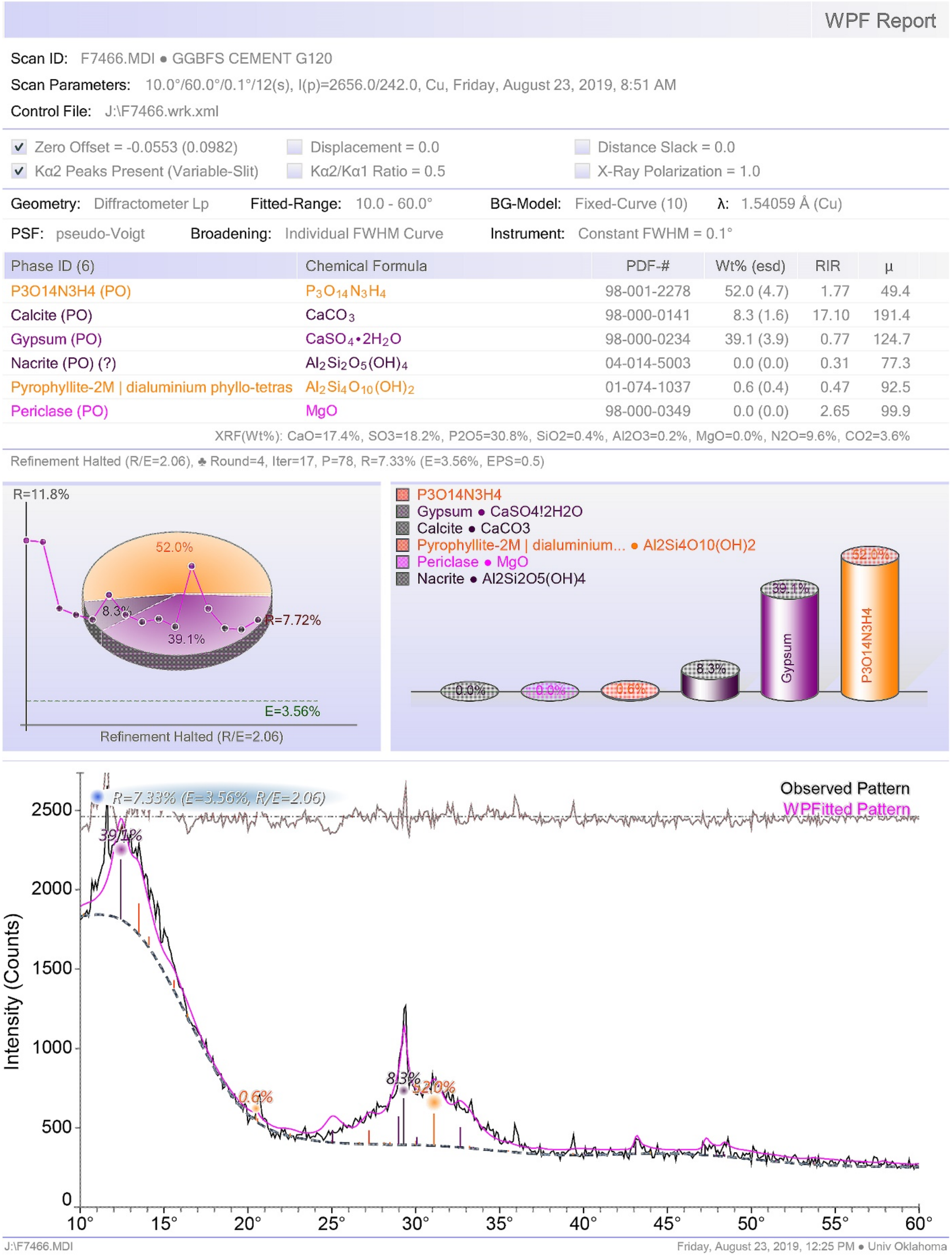


Figure 6-7. **X-ray powder diffractogram of Grade 120 slag cement (F7466). Preliminary mineral identifications using Jade version 3.1 included kilchoanite [$Ca_6(SiO_4)(Si_3O_{10})$] and wollastonite ($CaSiO_3$)**



WPF Report

Scan ID: F7466.MDI • GGBFS CEMENT G120

Scan Parameters: 10.0°/60.0°/0.1°/12(s), I(p)=2656.0/242.0, Cu, Friday, August 23, 2019, 8:51 AM

Control File: J:\F7466.wrk.xml

☑ Zero Offset = -0.0553 (0.0982) ☐ Displacement = 0.0 ☐ Distance Slack = 0.0

☑ Kα2 Peaks Present (Variable-Slit) ☐ Kα2/Kα1 Ratio = 0.5 ☐ X-Ray Polarization = 1.0

Geometry: Diffractometer Lp Fitted-Range: 10.0 - 60.0° BG-Model: Fixed-Curve (10) λ: 1.54059 Å (Cu)

PSF: pseudo-Voigt Broadening: Individual FWHM Curve Instrument: Constant FWHM = 0.1°

Phase ID (6)	Chemical Formula	PDF-#	Wt% (esd)	RIR	μ
P3O14N3H4 (PO)	$P_3O_{14}N_3H_4$	98-001-2278	52.0 (4.7)	1.77	49.4
Calcite (PO)	$CaCO_3$	98-000-0141	8.3 (1.6)	17.10	191.4
Gypsum (PO)	$CaSO_4 \cdot 2H_2O$	98-000-0234	39.1 (3.9)	0.77	124.7
Nacrite (PO) (?)	$Al_2Si_2O_5(OH)_4$	04-014-5003	0.0 (0.0)	0.31	77.3
Pyrophyllite-2M | dialuminium phyllo-tetras	$Al_2Si_4O_{10}(OH)_2$	01-074-1037	0.6 (0.4)	0.47	92.5
Periclase (PO)	MgO	98-000-0349	0.0 (0.0)	2.65	99.9

XRF(Wt%): CaO=17.4%, SO3=18.2%, P2O5=30.8%, SiO2=0.4%, Al2O3=0.2%, MgO=0.0%, N2O=9.6%, CO2=3.6%

Refinement Halted (R/E=2.06), ♣ Round=4, Iter=17, P=78, R=7.33% (E=3.56%, EPS=0.5)

J:\F7466.MDI

Friday, August 23, 2019, 12:25 PM • Univ Oklahoma

Figure 6-8. **X-ray powder diffraction analysis of Grade 120 slag cement (F7466); interpretations accomplished using Jade 2010 (Materials Data, Inc.). Identification of $P_3O_{14}N_3H_4$ is unlikely.**

7 SUMMARY AND INSIGHTS

Appendix A summarizes all water-conditioning experiments conducted to date, including three that are ongoing now.

During fiscal year (FY) 2019, water-conditioning tests were performed with pulverized grout, with individual grout components (Portland cement, Class F fly ash, and Grade 120 slag), and with cementitious material mixtures. FY 2019 tests indicated that slag is the only grout component that serves to consume dissolved oxygen (DO) and produce strongly reducing conditions in the contact water. Although the test of fly ash as a single component resulted in a modest decrease in DO, it did not result in reducing conditions. Tests of slag and slag mixtures resulted in significant concentrations of dissolved, reduced sulfur species in association with strongly reducing conditions.

The tests of slag as a single component resulted in the lowest minimum oxidation–reduction potential (Eh) values observed to date (i.e., −414 to −434 mV). Tests of slag mixtures (i.e., slag with Portland cement, and slag with fly ash) resulted in greater minimum Eh values (i.e., −313 to −350 mV), which could be due to chemical interactions between the slag and the other cementitious component, or to the lower slag-to-water mass ratio in the mixture tests.

The test of freshly pulverized reducing tank grout resulted in a minimum Eh of −303 mV, whereas a greater minimum Eh of −258 mV was observed when a cubed grout sample was tested during FY 2018 (Walter and Dinwiddie, 2019). Although the freshly pulverized grout sample, with its higher surface area-to-volume ratio, resulted in a slightly lower Eh value than did the cubed grout sample, the difference may not be significant. In fact, the lowest Eh observed in the pulverized sample test was attained after 140 days had elapsed, compared to the lesser 130 days it took for the cubed sample to attain its minimum Eh. Thus, the higher surface area-to-volume ratio of the pulverized sample did not increase the reaction rate. No conclusions have yet been reached about how the increased surface area of the pulverized grout samples *vis a vis* the cubed grout samples affects grout reactivity. Visual inspection of the pulverized tank grout samples suggests that sieving them into discrete size fractions may result in size class bins containing different chemical characteristics due to biased quantities of sand and pea gravel aggregate.

With respect to the redox-sensitive metals iron and manganese, ferrous iron (Fe^{+2}) was only detected in contact waters for the single-component slag tests and for the unstirred and previously reacted pulverized grout test, although total iron [based on inductively-coupled plasma (ICP) analyses] was less than the detection limit of 0.1 mg/L (except for the unstirred pulverized grout sample). Manganese was less than the ICP detection limit of 0.005 mg/L for all of FY 2019 water-conditioning tests.

None of the reducing tank grout water-conditioning tests performed during FY 2019 and FY 2020 have indicated that Eh would approach −500 mV, as has been suggested by geochemical models published by the U.S. DOE (e.g., SRR-CWDA-2010-00128, Rev. 1).

8 FUTURE WORK

During fiscal year (FY) 2019, staff reviewed recommendations of Pabalan et al. (2009), which were made before DOE decided on a final reducing tank-grout formulation and which are consistent with ongoing work performed under this task order. For example, Pabalan et al. (2009) described uncertainties regarding the long-term Eh of tank grout given the potential for (i) reduced sulfur species to react with iron oxides in Portland cement, (ii) the products of iron and steel corrosion to react with sulfide ion to form sulfide minerals, and (iii) manganese to participate in redox reactions with sulfide. The empirical test results reported here address some of these questions. For example, a test with a mixture of Portland cement and slag indicated that Portland cement had an effect on suppressing the production of dissolved reduced sulfur species, although the specific chemical reactions involved are not known. A more complete evaluation of the processes proposed by Pabalan et al. (2009) would require knowledge of the iron and manganese mineralogy of the grout constituents, as well as geochemical modeling. A summary table of the factors of importance to grout water-conditioning, testing status, and related potential future work is presented in Table 8-1. Refer to Appendix A for a summary of all water-conditioning experiments conducted to date.

Future water-conditioning work may include:

- Testing the effect of the slag-to-water mass ratio on the oxidation–reduction potential (Eh) and reduced sulfur species concentrations
- Retesting the water-conditioning effect of the Grade 120 slag and fly ash mixture for a longer duration while minimizing air ingress and oxygen levels
- Replication of the Table 5-2 slag-affected tests, but using Holcim's Grade 100 slag instead of Lehigh's Grade 120 slag
- Replication of Grade 120 cubed-grout tests, but using platinum-coated niobium screens
- Testing the effect of surface area on grout water-conditioning using relatively large grout samples (i.e., compared to the nominally 1-cm-scale cubed grout samples previously tested) in existing reaction vessels, given that the reactivity of tank grout may be related to the surface area in contact with water. Specific surface area may be measured precisely at Center for Nuclear Waste Regulatory Analyses (CNWRA®) using its Brunauer, Emmett and Teller (BET) instrument.
- Testing mixtures of all cementitious grout components [i.e., Portland cement, Class F fly ash, Grade 120 or Grade 100 slag, plus tank grout aggregates (i.e., sand and pea gravel) in LP#8-016 proportions (SRR–CWDA–2013–00026)]
- Testing mixtures of all cementitious material components of clean cap grout in formula-appropriate proportions [C–SPP–Z–00012; i.e., 10 weight percent Portland cement, 45 weight percent Class F fly ash, and 45 weight percent Grade 100 slag (as used in Tank 16) or Grade 120 slag (as may be used in the future)]
- Determine sulfide content of the Grade 100 and Grade 120 slags that have been and will be used to prepare Savannah River Site (SRS) grouts for tank closure operations, because sulfide may be the main source of reducing potential in tank grout
- Design studies to confirm that thiosulfate controls reducing grout Eh and to determine the poising capacity of Grades 100 and 120 slags used to prepare tank grouts (cf. Pabalan et al., 2009)

Table 8-1. Summary table of grout water-conditioning testing, status, and future work

Factor of Importance	Testing Status	Future Work
Effect of fast or discrete flow paths on redox	Dynamic flow column tests of intermediate-scale grout monolith core segment(s) to measure dissolved oxygen (DO)-consumption and Eh	Dynamic flow tests did not indicate significant consumption of DO or Eh reductions, but were somewhat inconclusive due to difficulty in preventing oxygen infusion into the test apparatus. No additional dynamic flow tests are planned.
Effect of individual grout constituents on redox	Testing of DO consumption and redox for Portland cement, fly ash, and Grade 120 GGBFS completed	Test Grade 100 GGBFS and evaluate effect of sand and pea gravel
Effect of interactions between grout constituents on redox	Testing of two constituent mixtures of Portland cement, fly ash, and GGBFS completed	Additional tests with sand and pea gravel
Effect of make-up water chemistry on grout redox	Bench-scale tank grout specimens have been prepared to date using deionized water	Prepare new tank grout specimens using synthetic Jackson, SC, well water or sSRS water with dilute rainwater-like chemistry
Effect of GGBFS mass ratio on Eh and poising	Preliminary results indicate Eh not effected	Additional tests to confirm preliminary results
Effect of tank grout/sSRS water contact area on reaction rate	Tests using nominally ~1 cm cubed grout and pulverized grout completed	Additional tests with cubed and larger grout samples to probe if and how the reactivity of grout is related to the grout surface area-to-mass ratio
Long-term poising capacity	Longest test to date lasted 170 days, with minimum Eh stabilizing after 140 days	Estimate ultimate reducing capacity based on sulfide content of GGBFS, retest samples after reaction with multiple water volumes

- Design studies to test the magnetite content and unburned carbon content of the vendor-provided Class F fly ash used by U.S. Department of Energy (DOE) for tank closure operations, to improve understanding of its long-term influence as a source of reducing species and reduction capacity in tank grout (cf. Pabalan et al., 2009).

A ball mill or equivalent mechanism may be used to powder indurated sample materials for energy dispersive X-ray spectroscopy (EDS) chemical analysis and X-ray diffraction (XRD) mineralogy analyses, including:

- Fine aggregate (ASTM C33 sand) from South Carolina Minerals, Inc. (North Augusta, South Carolina)
- Coarse aggregate (No. 8 stone or pea gravel) from Aggregates USA (Grovetown, Georgia)

- Tank grout composed, in part, of Grade 100, ASTM C989 ground granulated blast furnace slag cement (Holcim US, Inc.)
- Tank grout composed, in part, of Grade 120, ASTM C989 ground granulated blast furnace slag cement (Lehigh Cement Company, LLC, Fort Lauderdale, Florida)
- Clean cap grout (C–SPP–Z–00012) composed, in part, of Grade 100, ASTM C989 ground granulated blast furnace slag cement (Holcim US, Inc.), as was placed into Tank 16H
- Clean cap grout (C–SPP–Z–00012) composed, in part, of Grade 120, ASTM C989 ground granulated blast furnace slag cement (Lehigh Cement Company, LLC, Fort Lauderdale, Florida), as DOE may use in the future if the need for a more flowable tank fill arises.

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APPENDIX A

SUMMARY OF WATER-CONDITIONING EXPERIMENTS PERFORMED TO DATE

Table A–1. Summary of water-conditioning experiments performed to date

Experiment	Description
1	November–December 2014 water-conditioning ***dynamic flow*** tests: Simulated synthetic Savannah River Site (sSRS) water conditioning as water flowed through a narrow-aperture pathway between intact grout core in a column-based flow loop,* using a core removed from the ***intermediate-scale grout monolith***†. Grout rapidly increased the pH of sSRS water on contact but had little effect on dissolved oxygen (DO) and only slightly lowered oxidation–reduction potential (Eh) to +245 mV (Core 11) and +215 mV (Core 12). However, these tests were affected by oxygen diffusion through the flexible tubing used in the peristaltic pump, resulting in relatively high DO in the flow loop.
2	July–August 2015 ***static (i.e., no flow)*** water-conditioning tests, using cubed (Core 11) or chipped (Core 10) subsamples from the ***intermediate-scale grout monolith,*** were performed to investigate the reducing capacity of the grout.* With DO reduced to the detection limit of the DO probe, this grout produced strongly reducing conditions in sSRS contact water of −109 mV (previously used Core 11) and −180 (pristine Core 10).
3	May 2016 water-conditioning static tests (Tests 1–3)‡: Reacted fresh sSRS water with lab-prepared ***Grade 100-slag*** tank grout cubes (***LP#8-16 reducing grout***, C–SPP–F–00055, Rev. 4) inside glass, deaeration-gas-sparging flasks. Test 1 used fresh grout; Test 2 used Test 1's previously reacted grout; Test 3 used Test 2's twice-reacted grout. Sparging gas was mixture of nitrogen and 388 parts per million by volume (ppmv) carbon dioxide. Measured DO and Eh evolution with time.
4	June 2016 water-conditioning static tests (Tests 4–6)‡: Reacted fresh sSRS water with mixture of fresh and previously used, lab-prepared ***Grade 100-slag*** tank grout cubes inside glass, deaeration-gas-sparging flasks. Tests 4–6 each used/reused the same grout samples. Eh was not sensitive to DO at low oxygen concentrations {i.e., <0.01 mg/L [0.01 ppm]} but was sensitive to fluid mixing. Chemical analyses were performed on the conditioned sSRS water at the end of Tests 4 and 5 (i.e., chloride and sulfate by EPA Method 300; ferrous iron by Standard Method 3500Fe-B; sulfide, sulfite and thiosulfate by EPA 300M; and metals by EPA SW-846, Method 6010B). Analyses demonstrated leaching of soluble constituents. No iron or reduced sulfur species (sulfide, sulfite, and thiosulfate) were detected in the conditioned water, but manganese was detected.
5	June 2016 water-conditioning dynamic flow test‡: Reacted sSRS water with lab-prepared ***Grade 100-slag*** tank grout cubes packed into a flow loop, which had been used previously during Experiment 3 and 4 static tests; deaerated, low-DO sSRS water was injected into the flow column. Measured DO and Eh evolution with time to evaluate whether tank grout will consume DO and reduce its concentration. This dynamic column test provided no evidence that DO was consumed by the reducing tank grout.
6	November 2017 10-day DO consumption test: Reacted fresh sSRS water with ***Grade 100-slag*** tank grout cubes in a closed flask to investigate the capability of the grout to consume DO; DO decreased to approximately 1 percent of saturation after approximately 6 days. Eh remained relatively high (~300 mV) and pH never increased beyond 7.58, which was more neutral than anticipated. The grout had the capability to consume DO from sSRS water in the absence of active sparging. Eh remained high during the short duration of the test, and subsequent tests demonstrated that extended test durations may be required to achieve relatively low Eh values. It is not known why pH remained relatively low, given that pH rapidly increased to >10 during subsequent tests.

Table A–1. Summary of water-conditioning experiments performed to date

Experiment	Description
7	***Grade 120-slag*** tank grout cubes were reacted in custom, 4-neck reaction vessel with sSRS water under open, constant pCO_2 conditions for 31 days. Sparging gas was mixture of nitrogen and 385 parts per million by volume (ppmv) carbon dioxide; sSRS water underwent evaporation during the test and had to be partially replaced at 11 and 24 days into the test. DO saturation generally varied between approximately 2.5 and 3.5 percent during the test. Eh decreased to a minimum of −143 mV after approximately 17 days. pH 8.48 was measured near the end of the test. The relatively low alkaline pH measured near the end of the constant-pCO_2 test is likely the result of sparging with CO_2, which buffered the solution.
8	January 2018 ~130-day, closed-system water-conditioning test: ***Grade 120-slag*** tank grout cubes were reacted in custom, 4-neck reaction vessel with sSRS water under closed conditions (no sparging); magnetic stirring bar was separated from the cubes by a ***stainless-steel*** screen. Eh may have been influenced by chemical reactions with the stainless-steel screen used to support the grout cubes. DO ultimately decreased to the detection limit of the DO probe. Eh stabilized at approximately −258 mV after 120 days; pH rose to fluctuate between 11.25 and 11.35 units. The relatively high alkaline pH measured during this test was due to the reactivity of the tank grout.
9	Three ***blank, constant-pCO_2, open-system experiments*** of sSRS water-conditioning (absent tank grout) sparged with N_2/CO_2 gas: DO decreased to below the measurement limit of the probe during the first 24 hours of each test; tests were continued until each tank of sparging gas was exhausted (15 to 20 days). The first and last test were ***conducted with the stainless-steel screen*** in the reaction vessel; the other test was conducted ***absent the stainless-steel screen*** and resulted in a lower pH than measured in the vessels that contained the screen. With the stainless-steel screen in place, the minimum Eh measured was lower than for the test conducted without the stainless-steel screen. Stainless steel is thought to result in an artificial lowering of Eh.
10	August 2018 15-day ***closed-system blank experiment*** of sSRS water-conditioning absent tank grout: pH increased from approximately 5.9 at the beginning of the test to stabilize at approximately 6.26 after 4 days. Eh increased from approximately +470 mV at the start of the test to stabilize at approximately +545 mV. DO decreased from 97 percent at the beginning of the test to 91 percent at its end. This test was conducted in the presence of the ***stainless-steel screen***.
11	August 2018 ***blank, open-system experiment*** of sSRS water-conditioning absent tank grout, sparged with ultra-high-purity N_2 gas: This test used the same equipment and materials used in Experiment 10. Experiment 11 began immediately after Experiment 10 was terminated. A port in the reaction vessel was opened to the atmosphere, a small amount of water was removed to create headspace, and the aqueous solution in the vessel was sparged after insertion of a fritted diffusor through the open port. DO decreased to less than the detection limit of the probe within 90 min. pH increased from a low of 6.26 to stabilize at approximately 9.4 after a period of approximately 3 days, due to the purging of dissolved CO_2. Eh decreased from a high of approximately +545 mV when sparging began to a low of +248 mV when this experiment was terminated.
12	Three ***Grade 120-slag pulverized tank grout*** water-conditioning experiments were conducted to compare results obtained with those when using lower surface-area-to-volume ratio cubed grout. Pulverized grout was placed into nylon mesh filter fabric bags that were either suspended inside reaction vessels above a magnetic stirring bar or placed on the floor of the vessel in the absence of a stirring bar. A test of fresh, pulverized grout resulted in a minimum Eh of −303 mV after 140 days of grout–water interaction, which was lower than the minimum Eh of −258 mV observed during a 130-day test of cubed grout. Although a lower minimum Eh was observed when testing a pulverized sample with a larger surface area-to-volume ratio than the cubed sample, the difference between the two values may not be significant. The larger surface area-to-volume ratio of the pulverized sample did not appear to increase the reaction rate.

Table A–1. Summary of water-conditioning experiments performed to date

Experiment	Description
13	Two stirred, ***Grade 120 slag-only*** water-conditioning experiments: The slag component of reducing tank grout LP#8-016 was tested to investigate how it modifies the chemistry of synthetic Savannah River Site (sSRS) water. Slag was either placed above a platinum-coated niobium screen on nylon mesh filter fabric or was bagged in nylon mesh filter fabric and placed on the screen above a magnetic stirring bar. During these 16- and 36-day slag tests, DO decreased rapidly to below the detection limit of the probe and ***resulted in the lowest minimum Eh values*** (−414 to −434 mV) observed to date.
14	Stirred, ***Fly ash-only*** water-conditioning experiment: The fly ash component of reducing tank grout LP#8-016 was tested to investigate how it modifies the chemistry of synthetic Savannah River Site (sSRS) water. Mesh-bagged fly ash was placed on a platinum-coated niobium screen, located above a magnetic stirring bar. This 15-day test resulted in a modest decrease in DO and Eh, but Eh remained positive and did not produce reducing conditions.
15	Stirred, ***Portland cement-only*** water-conditioning experiment: The Portland cement component of reducing tank grout LP#8-016 was tested to investigate how it modifies the chemistry of synthetic Savannah River Site (sSRS) water. Mesh-bagged Portland cement was placed on a platinum-coated niobium screen, located above a magnetic stirring bar. This 13-day test resulted in a modest decrease in Eh, but Eh remained positive and did not produce reducing conditions. The DO response was cryptic and not well-understood.
16	Stirred, ***Portland cement + Grade 120 slag mixture*** water-conditioning experiment: Mixture experiments were performed to investigate the effect of the grout component mixtures on the redox chemistry of the contact water. Mesh-bagged cementitious material was placed on a platinum-coated niobium screen, located above a magnetic stirring bar. During this 14-day test, the minimum Eh was −313 mV. Less negative Eh values for slag mixture tests may be due to chemical interactions occurring between slag and the other tank grout component, or to the lower slag-to-water-mass ratio of the mixture tests. Slag is the only component of tank grout having both a significant effect on DO consumption and on producing strongly reducing conditions in the synthetic groundwater.
17	Stirred, ***Grade 120 slag + fly ash mixture*** water-conditioning experiment: Mixture experiments were performed to investigate the effect of the grout component mixtures on the redox chemistry of the contact water. Mesh-bagged cementitious material was placed on a platinum-coated niobium screen, located above a magnetic stirring bar. During this 17-day test, the minimum Eh was −350 mV. Less negative Eh values for slag mixture tests may be due to chemical interactions occurring between slag and the other tank grout component, or to the lower slag-to-water-mass ratio of the mixture tests. Slag is the only component of tank grout having both a significant effect on DO consumption and on producing strongly reducing conditions in the synthetic groundwater.
18	Stirred, ***Portland cement + fly ash mixture*** water-conditioning experiment: Mixture experiments were performed to investigate the effect of the grout component mixtures on the redox chemistry of the contact water. Mesh-bagged cementitious material was placed on a platinum-coated niobium screen, located above a magnetic stirring bar. This mixture did not consume DO and did not result in reducing conditions. During this 17-day test, the minimum Eh was +242 mV.

Table A–1. Summary of water-conditioning experiments performed to date	
Experiment	**Description**
19	Three stirred, closed-system experiments using fresh cubed tank grout samples are being conducted with **platinum-coated niobium support screens** in place of stainless-steel support screens. Platinum-coated niobium should be less reactive than stainless-steel. These are long-term tests that are proceeding very slowly.

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