

FISCAL YEAR 2016 TANK GROUT WATER-CONDITIONING TESTS—STATUS REPORT

Prepared for

**U.S. Nuclear Regulatory Commission
Contract No. NRC-HQ-12-C-02-0089**

Prepared by

**G.R. Walter
C.L. Dinwiddie**

**Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas**

January 2017

ABSTRACT

This report describes proactive work related to tank grout water conditioning that was performed during fiscal year 2016 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 investigate how contact between groundwater and tank grout similar to that being used to fill underground waste tanks at the Savannah River Site (SRS) would modify the chemistry of groundwater that might infiltrate through cracks or other fast pathways in the tank grout. The work specifically focused on how the grout would affect the pH, oxidation-reduction potential (Eh), and dissolved oxygen (DO) concentrations of the infiltrating water, all of which can affect the release of radionuclides from residual waste in the tanks.

Static water conditioning tests were performed on samples of a grout specimen in May and June 2016. The static water conditioning tests all resulted in Eh values in the range of -50 to -100 mV after a few days of reaction. None of the tests indicated that the Eh would approach -500 mV as suggested by geochemical models (e.g., SRR-CWDA-2010-00128, Rev. 1). The tests suggest that Eh is insensitive to DO at concentrations less than approximately 0.01 mg/L [0.01 ppm]. At greater DO concentrations, Eh appears to be controlled by DO rather than by any redox couples that may evolve from the reducing grout. Unlike the results of water analyses reported for the FY 2015 dynamic test (Walter and Necsoiu, 2015), the water samples analyzed from the FY 2016 static tests did not reveal the presence of oxidizable species, such as reduced sulfur, that would control Eh. Grout reactivity does, however, appear to be related to the grout surface area that is in contact with simulated SRS water. The inflections in Eh evolution observed during the May 2016 static tests were not observed during the June 2016 tests. Additional static tests should be performed on crushed grout samples having a greater surface area-to-volume ratio to further investigate the effect of surface area on water conditioning.

Because the Eh appears to be controlled by DO at concentrations greater than 0.01 mg/L [0.01 ppm], it is important to determine if tank grout can consume DO in meteoric or groundwater that is infiltrating it, and thus lower the DO concentration to levels at which redox couples in the grout can control the Eh. A dynamic flow test conducted in FY 2016 was an initial attempt to address this question. Any oxygen consumption by the grout during this test was less than the measurement error between the DO probes (approximately 3 percent DO saturation).

During future work, it may be possible to reduce the measurement differences between DO probes so that more accurate measurements of oxygen consumption under dynamic flow conditions can be performed. Additional dynamic tests using crushed grout should also be performed during FY 2017. The FY 2016 tests were performed on a grout specimen that was prepared with Grade 100 blast furnace slag cement; however, SRS recently switched to use of finer and more reactive Grade 120 slag cement in all of their grouts. A grout specimen has been prepared using the Grade 120 slag cement and should be tested during FY 2017.

REFERENCES

SRR-CWDA-2010-00128. “Performance Assessment for the H-Area Tank Farm at the Savannah River Site.” SRR-CWDA-2010-00128, Revision 1. November 2012.

Walter, G.R. and D.M. Necsoiu. “Tank Grout Water Conditioning Tests—Status Report.” Report to Nuclear Regulatory Commission IM17860.04.004.515. September 2015.

CONTENTS

	Page
Section	
ABSTRACT	iii
PREVIOUS REPORTS IN SERIES	v
FIGURES	vi
TABLE	vi
ACKNOWLEDGMENTS	vii
1 INTRODUCTION	1
2 MODIFICATIONS TO TEST APPARATUS AND EXPERIMENTAL DESIGN	2
3 STATIC TESTS	2
3.1 Grout Preparation	2
3.2 May 2016 Static Groundwater Conditioning Tests	4
3.3 June 2016 Static Tests	8
3.4 Results of Chemical Analyses	10
4 DYNAMIC TEST OF OXYGEN CONSUMPTION	13
5 SUMMARY AND RECOMMENDATIONS	15
6 REFERENCES	16

PREVIOUS REPORTS IN SERIES

Number	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

FIGURES

Figure	Page
1 Grout Cubes Used During Static Tests	5
2 Apparatus Used to Perform Static Water Conditioning Tests	6
3 DO Concentration Evolution During Static Tests 1–3, May 11–26, 2016.....	7
4 Eh Evolution During Static Tests 1–3, May 11–26, 2016	7
5 Results of DO and Eh Measurements During Static Test 4, June 9–14, 2016.....	9
6 Results of DO and Eh Measurements During Static Test 5, June 15–17, 2016.....	9
7 Results of DO and Eh Measurements During Static Test 6, June 20–23, 2016.....	10
8 Major Constituent Concentrations in Test 4 and Test 5 Water Samples Compared With Their Concentrations in sSRS Water.....	12
9 Comparison of Secondary and Trace Constituent Concentrations Detected in Static Test Conditioned Water Samples.....	12
10 Schematic Diagram of Dynamic Test Apparatus.....	14
11 Measured DO Concentrations (as Percent Saturation) During the Dynamic Flow Test.....	15

TABLE

Table	Page
1 Nominal Small-Scale Reducing Tank Grout LP#8-16 Component Quantities per Batch.....	3

ACKNOWLEDGMENTS

This report documents independent, confirmatory work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA®) for the U.S. Nuclear Regulatory Commission (NRC) under Contract No. NRC-HQ-12-C-02-0089. The studies and analyses reported here were performed on behalf of the NRC Office of Nuclear Material Safety and Safeguards, Division of Decommissioning, Uranium Recovery, and Waste Programs. The report is an independent product of CNWRA and does not necessarily reflect the view or regulatory position of NRC.

The authors gratefully acknowledge the technical review of James Prikryl, the editorial and programmatic reviews of Gordon Wittmeyer and Osvaldo Pensado, and the assistance of Arturo Ramos 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 Geosciences and Engineering Division Quality Assurance Manual. Analyses by the Chemistry and Chemical Engineering Division at Southwest Research Institute® were conducted under an ISO 9001:2008-certified quality system. Sources for other data should be consulted for determining the level of quality for those data. Scientific Notebooks 1229, 1263, and 1289 (Walter and Dinwiddie, 2016a,b; Walter, 2015) were used to document experimental conditions and in-process entries associated with this work.

ANALYSES AND CODES: None

REFERENCES:

Walter, G.R. "Task 2: Tank Grout Water Conditioning Tests Continued." Scientific Notebook 1263. San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. 2015.

Walter, G.R. and C.L. Dinwiddie. "Task 2: Tank Grout Water Conditioning Tests." Scientific Notebook 1229. San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. 2016a.

Walter, G.R. and C.L. Dinwiddie. "Task 2: Tank Grout Water Conditioning Tests." Scientific Notebook 1289. San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. 2016b.

1 INTRODUCTION

This report describes proactive work related to tank grout water conditioning that was performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA®) during fiscal year 2016 (FY 2016) 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 investigate how contact with tank grout similar to that being used to fill the waste tanks at the Savannah River Site (SRS) would modify the chemistry of groundwater that might infiltrate through cracks and other fast pathways in the tank grout. The work focused on how the grout would affect the pH, oxidation-reduction potential (Eh), and dissolved oxygen (DO) concentrations of the infiltrating water, all of which can affect the release of radionuclides from the residual waste in the tanks.

Previous tests performed during FY 2015 were initially designed to simulate water flow through a narrow aperture pathway, such as a crack or annular space between the grout and a pipe or tank wall. The reducing grout tested during FY 2015 had been cored from the weathered and aged intermediate-scale grout monolith (Walter et al., 2010), and therefore consisted of an early generation reducing grout prototype dissimilar to that being used to fill and stabilize waste tanks at SRS today. These tests, which were performed by flowing synthetic SRS (sSRS) water past intact grout cores in a flow loop, were affected by persistently elevated DO that may have resulted in measured Eh values that were higher than expected based on geochemical modeling (e.g., SRR-CWDA-2010-00128, Rev. 1). The effect of DO on Eh was confirmed by FY 2015 static tests during which DO was reduced to less than the detection limit of the DO probe {nominally 0.004 mg/L [0.004 ppm]} and Eh decreased from an initial value of approximately +320 mV to -180 mV (Walter and Necsoiu, 2015).

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 the U.S. Department of Energy’s (DOE’s) performance assessment (PA) modeling (e.g., SRR-CWDA-2010-00128, Rev. 1), the DO concentration must be reduced to low levels at which redox couples other than O₂-H₂O control the Eh, such as Fe⁺²-Fe⁺³, Mn⁺²-Mn⁺⁴, and those of various sulfur species. Shallow groundwater at the SRS has DO concentrations in the range of 1 to 9 mg/L [1 to 9 ppm] (Strom and Kaback, 1992). To achieve the low Eh conditions assumed in PA modeling, DO must be removed from infiltrating groundwater by reaction with reductants in the tank grout.

Work performed during FY 2016 focused on modifying the grout water-conditioning experimental design to reduce DO concentrations in the test apparatus and conducting dynamic and static experiments to measure the rate of oxygen consumption and Eh reduction by the tank grout. The dynamic flow tests conducted during FY 2016 used a column packed with cubes extracted from a lab-prepared tank grout specimen. Static reaction tests were conducted using a flask containing the same or similar tank grout cubes. The tank grout specimens had been previously prepared using the same formula and materials sourced from DOE’s cementitious and aggregate material vendors, as well as the same admixtures that their contracted grout batch plant, Argos (Jackson, South Carolina), uses when preparing waste-tank stabilizing grout.

2 MODIFICATIONS TO TEST APPARATUS AND EXPERIMENTAL DESIGN

Dynamic flow tests performed during FY 2015 (Walter and Necsoiu, 2015) had revealed problems with oxygen infusing into the flow apparatus that likely affected the Eh of the effluent after contact with intact grout cores. During FY 2016, various tests were performed to evaluate the source of DO in the flow loop and to reduce oxygen infusion into the loop. To further reduce the potential for oxygen entering the flow loop, the peristaltic pump used in previous tests was replaced with an Agilent 1100 high-performance liquid chromatography (HPLC) pump and the flexible polyvinyl chloride (PVC) tubing was replaced with 1/8-in OD by 1/16-in ID Fluran® F-5500-A tubing (Saint-Gobain North America), which is reported by the manufacturer to have a lower permeability with respect to oxygen and other atmospheric gases than most PVC (Tygon) tubing. Preliminary tests with the revised flow loop indicated that DO concentrations entering the core flow cell could be reduced to approximately 0.2 mg/L [0.2 ppm] or to 2 to 3 percent of saturation {approximately 8.2 mg/L [8.2 ppm]}. Efforts to further reduce the influent DO concentrations were unsuccessful and little difference was found between using the HPLC pump and the peristaltic pump. Because the HPLC pump clogged after extensive use—perhaps due to the presence of grout particulates in the closed loop test—it was replaced with a peristaltic pump for some dynamic tests.

3 STATIC TESTS

Static tests were performed during May and June 2016 using a lab-created, bench-scale, flowable, zero-bleed specimen of low-paste, No. 8 stone reducing tank grout, prepared according to the same formula used by DOE to recently fill and stabilize waste tanks at SRS. The LP#8-16 reducing grout formula admixtures (SRNL-STI-2011-00551) were revised by Argos, DOE SRS's batch plant operator, before the tank grout formula (Table 1) was finalized. The final tank grout formula, as recorded on Argos's batch tickets (e.g., SRR-CWDA-2013-00026), was used to fill and stabilize SRS Tanks 18F, 19F, 5F, 6F, and 16H. DOE's procurement specification for tank grout (C-SPP-F-00055, Rev. 4) allows batch plant operator Argos leeway to vary admixture doses through prescribed ranges based on field conditions. During FY 2016, CNWRA used a tank grout specimen prepared with a high-range water reducer dose (Table 1) equivalent to that used in recent grout placed into SRS tanks that contained cooling coils (e.g., Tanks 5F, 6F, and 16H) to improve flowability around obstacles. The grout specimen tested by CNWRA during FY 2016 differs from tank grout batched for Tank 12H, however, because it was prepared with Grade 100 instead of Grade 120 slag cement.

3.1 Grout Preparation

At NRC's request, DOE provided vendor information for cementitious and aggregate materials acquired by DOE contractor Argos for batching tank grout. At CNWRA's request, these vendors provided 55-gal drums of Portland cement (Type I/II, ASTM C150 by Holcim US, Inc. of Birmingham, Alabama), blast furnace slag cement (Grade 100, ASTM C989 also by Holcim), and Class F Flyash (ASTM C618 by SEFA Group, Inc. of Lexington, South Carolina) for use in these experiments. Fine aggregate (ASTM C33 sand) provided by South Carolina Minerals, Inc. (North Augusta, South Carolina) was delivered in a bag on a pallet, moist to the touch, so was oven-dried prior to batch preparation to remove residual moisture. Coarse aggregate (No. 8 stone or pea gravel) provided by Aggregates USA (Grovetown, Georgia), was delivered in 55-gal drums. The stone and cementitious materials arrived dry and were not further dried. The sand, stone, and admixture suppliers are also the same vendors that DOE SRS and Argos

Table 1. Nominal Small-Scale Reducing Tank Grout LP#8-016* Component Quantities per Batch

Formula	Cementitious Materials				DI Water	w:c	Aggregate		Admixtures†		
	Portland Cement Type I/II‡	Slag Grade 100‡	Fly Ash Class F§	Total Cementitious Mass			Quartz Sand	Gravel No. 8¶	ADVA Cast 575	EXP-958	Recover Hydration Stabilizer
	grams								ml		
SRS Reducing Tank Grout	100	168	290.4	2954	323.2	0.58	1432	640	2	2	0.3

* Final formula based upon Argos batch tickets (SRR-CWDA-2013-00026)

† W.R. Grace and Company, Columbia, Maryland

‡ Holcim US, Inc., Birmingham, Alabama

§ SEFA Group, Inc., Lexington, South Carolina

|| South Carolina Minerals, Inc., North Augusta, South Carolina

¶ Aggregates USA, Grovetown, Georgia

use. Argos's eight cubic yard reducing grout formula (SRR-CWDA-2013-00026) was downscaled by a factor of 4536 to a volume suitable for preparing a bench-scale laboratory specimen.

On August 22, 2015, the cementitious materials identified in Table 1 were measured accordingly and premixed in a sealed, plastic Ziploc® bag until visually homogenized. The water and oven-dried sand were measured and blended together in an 8-qt Globe® SP08 counter-top commercial kitchen mixer until homogenized, and then the premixed cementitious materials were added to the wet sand and blending continued. Liquid admixtures were pipetted into the mixing bowl and blending continued. Lastly, gravel was measured and added to the bowl for blending. The fresh grout batch was poured into a cylindrical glass mold {70-mm [2.75-in] inner diameter by 254-mm [10-in] height}, which had a base that consisted of a plastic sheet secured to the glass with duct tape. The grout hydrated and hardened uncapped. Staff made no attempt to keep an oxygen-free environment during preparation of the grout, and it likely underwent some degree of oxidation during mixing and setting, particularly at the exposed surface of the column. The specimen was removed from its cylindrical glass mold after completely wrapping it in duct tape and hammering it until the glass shattered and broke free from the specimen without damaging it. Three static groundwater conditioning tests were performed on samples cut from this tank grout specimen.

Subsamples from the tank grout specimen were prepared by first cutting five 1.3-cm [0.5 in]-thick discs from the middle portion of the specimen with a wet rock saw to minimize edge effects related to aggregate settling and so forth. These discs were then cut into approximately 1-cm³ [~0.06-in³] cubes with a rock saw (Figure 1). The dimensions of the roughly cubic samples were measured with an accuracy of 0.1 cm [0.04 in], and each sample was numbered. Cubes 1 through 40 were placed into a 250-mL [8.5 oz] 4-neck flask (Figure 2). Cubes 41 through 50 were cut and measured but not used during the May 2016 static tests.

3.2 May 2016 Static Groundwater Conditioning Tests

Three static water conditioning tests (Tests 1–3) were performed using the apparatus described in Walter and Necsoiu (2015) and shown in Figure 2. DO was measured using a Hamilton VisiFerm D120 optical DO probe and the oxidation–reduction potential (ORP) was measured with a Weiss Research gel-filled double-junction ORP probe. The measured ORP was with respect to Ag:AgCl potential and adjusted to Eh by adding 200 mV to the measured potential.

The first static tank grout water conditioning test (Test 1) was begun on May 11, 2016, by placing grout cubes 1 through 40 in the sparging flask and adding 200 mL [6.8 oz] of sSRS groundwater to the flask. The total mass of the 40 grout cubes was 139.7 g [0.31 lb], and their bulk volume and surface area that were estimated based on the dimensions of each cube were 53.0 cm³ [3.2 in³] and 295 cm² [46 in²]. The flask was then sparged with a gas mixture of nitrogen and 388 parts per million by volume (ppmv) carbon dioxide (custom gas mix primary standard from Airgas®) to remove DO and to stir the water in the sparging flask. Test 1 lasted from 12:29 (military time) on May 11, 2016, until 09:39 on May 17, 2016, at which time the sparging gas tank had been emptied and the Eh had stabilized at -76 mV.

Prior to beginning Test 2, 100 mL [3.4 oz] of sSRS water remaining in the flask was removed and replaced with 150 mL [5.1 oz] of fresh sSRS water on May 18, 2016. Test 2 using the same grout cubes was then begun at 09:50 on May 19, 2016, by sparging the flask contents with deaeration gas while measuring DO and ORP. Test 2 lasted until 15:30 on May 23, 2016, at which time Eh had stabilized at values between -14 and -16 mV.



Figure 1. Grout Cubes Used During Static Tests

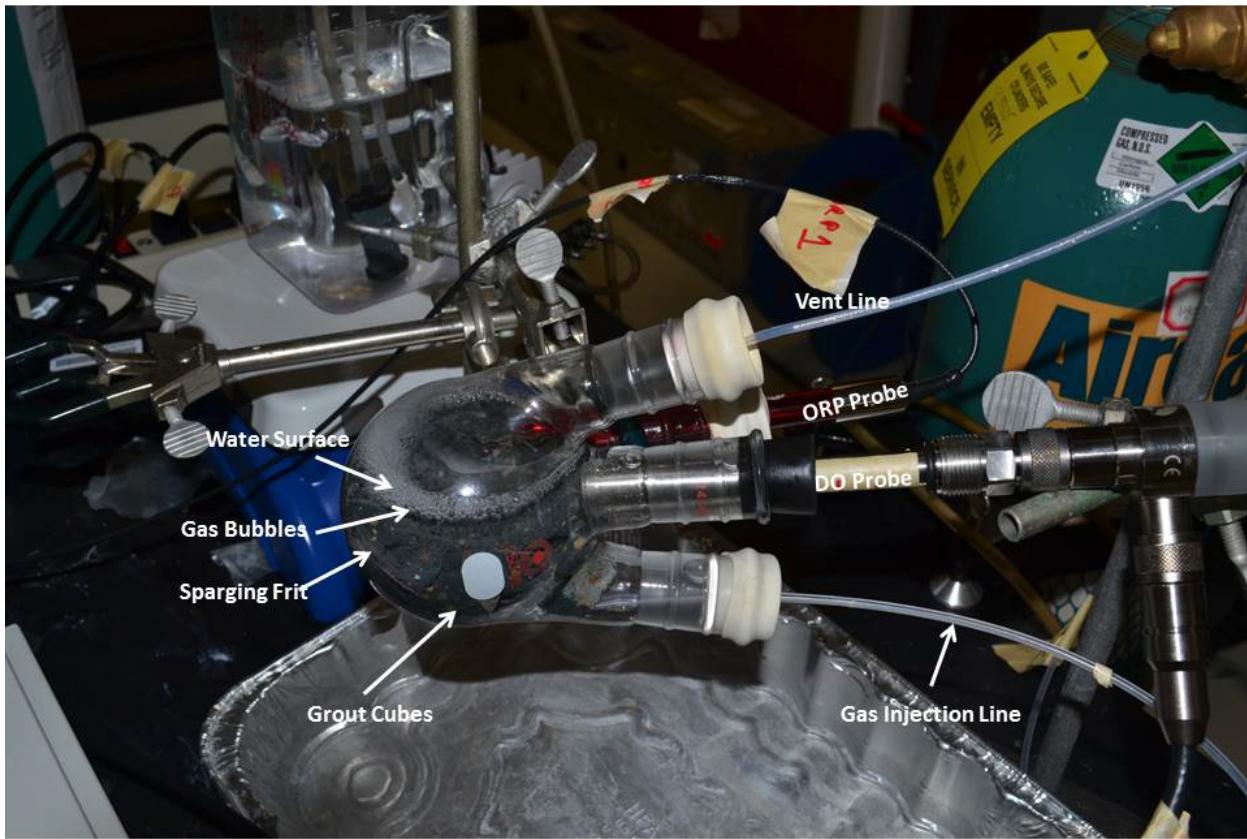


Figure 2. Apparatus Used to Perform Static Water Conditioning Tests

Prior to beginning Test 3, 172 mL [5.8 oz] of sSRS water remaining in the flask was removed and the grout cubes were also temporarily removed. After returning the grout cubes to the flask, 200 mL [6.8 oz] of fresh sSRS water was added to it. The ORP probe was recalibrated against a +200 mV standard. Test 3 was then begun at 16:00 on May 23, 2016. Test 3 lasted until 18:08 on May 26, 2016, at which time the sparging gas tank had been depleted.

The rate of DO decrease during each May 2016 test is shown in Figure 3. The DO concentration was reduced to less than 0.008 mg/L [0.008 ppm] (the lower limit of measurement) within the first 10 minutes of sparging during Tests 1 and 2, and within the first 30 minutes of sparging during Test 3. The slower rate of DO decrease during Test 3 was likely due to introduction of air into the grout when the cubes were temporarily removed from the flask in preparation for Test 3, and subsequent outgassing during the test, as evidenced by formation of tiny gas bubbles on the DO probe during Test 3.

The evolution of Eh during each May 2016 test, as derived from ORP measurements, is shown in Figure 4. The lowest Eh (-77 mV) was attained during Test 1. The Eh during Tests 2 and 3 stabilized between 0 and -20 mV except for some anomalously lower values at the end of Test 3. The sudden decrease in Eh toward the end of Test 3 may be associated with depletion of the sparging gas and decreased mixing within the sparging flask.

Each test was characterized by a rapid decrease in Eh during the first 0.4 days. The early rapid decrease in Eh does not appear to be associated with the decrease in DO that occurred during the first 10 to 30 minutes of sparging. The Eh curve for Test 1 displays three inflection points,

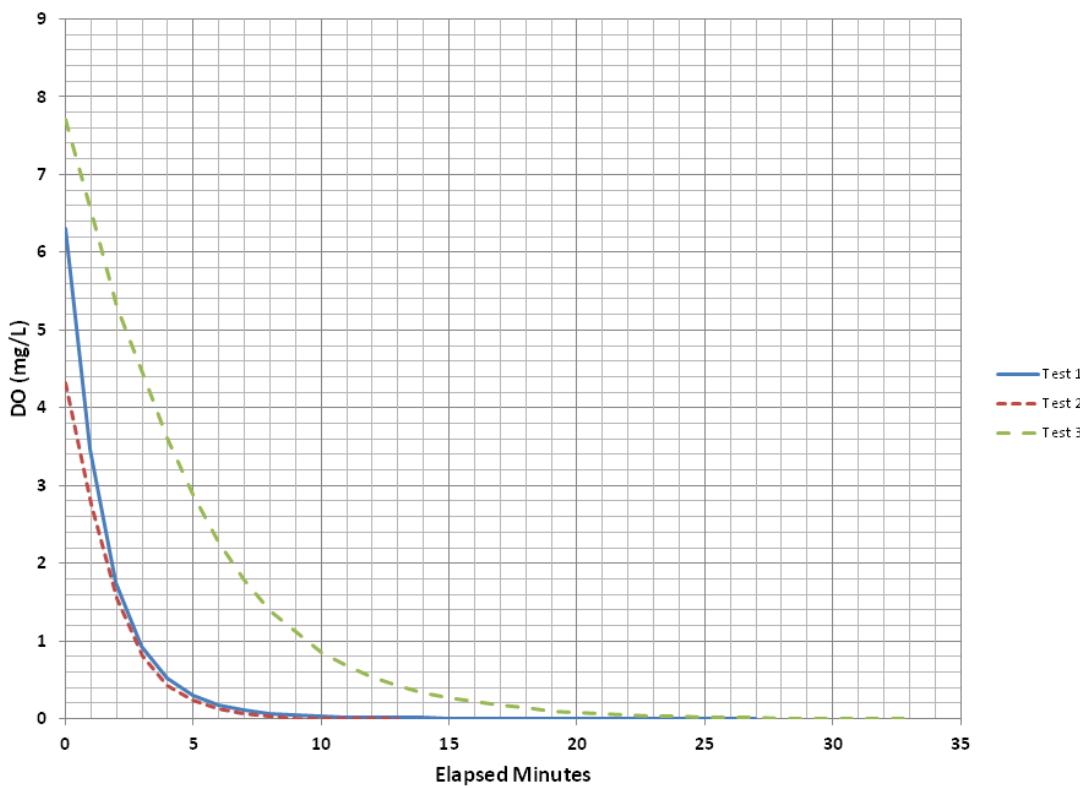


Figure 3. DO Concentration Evolution During Static Tests 1–3, May 11–26, 2016

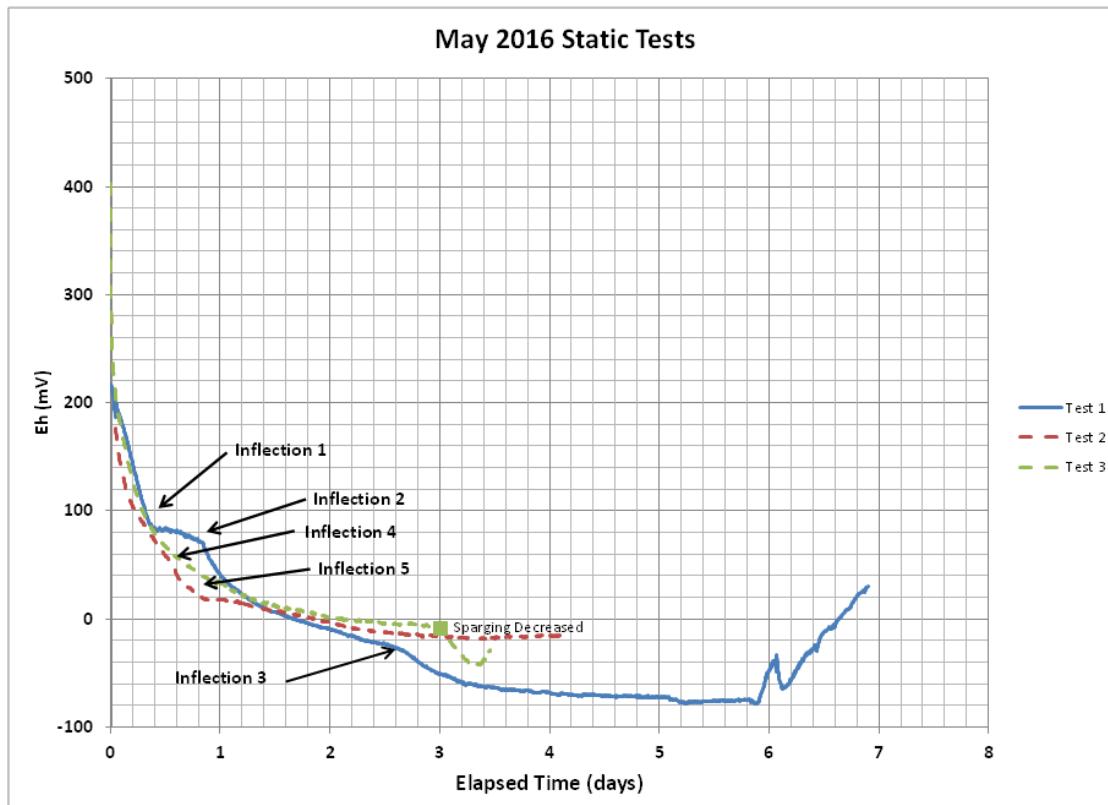


Figure 4. Eh Evolution During Static Tests 1–3, May 11–26, 2016

the first at approximately 0.4 days resulting in a lower rate of Eh decrease, the second starting at 0.8 days resulting in a faster rate of decrease, and the third starting at 2.6 days, again resulting in a faster rate of decrease followed by gradual stabilization. The curve for Test 2 displays two subtle inflections (inflections 4 and 5 in Figure 4) that occurred during the first day of the test and may correlate with inflections 1 and 2 during Test 1. Test 3 had a smooth rate of Eh decrease except at the very end of the test, as noted previously. We speculate that these inflections may relate to the onset or depletion of specific redox couples associated with reducing elements in the tank grout. These particular redox couples may have been depleted during the tests, resulting in a reduction in some of the reducing capacity of the tank grout between Tests 1 and 2. That Eh stabilized at approximately the same value during Tests 2 and 3 indicated that the tank grout retained some reducing properties over the course of the tests.

3.3 June 2016 Static Tests

Three static tests performed in June 2016 (Tests 4–6) were conducted to evaluate repeatability of results relative to those from the May 2016 static tests, particularly with respect to the inflections in the Eh response. The June tests were performed by placing grout cubes 1 through 50 in the sparging flask. This resulted in a mix of previously reacted cubes with fresh cubes. The total mass, bulk volume, and surface area of grout were 180.4 g [0.40 lb], 73 cm³ [4.5 in³], and 373 cm² [58 in²]. The three tests were performed using the same grout cubes during each test; 200 mL [6.8 oz] of sSRS water were added to the sparging flask during each test and the flask was sparged with the gas mixture used previously. Water samples were collected from the sparging flask for chemical analyses at the end of Tests 4 and 5.

Test 4 lasted from 11:14 on June 9 until 10:05 on June 14, 2016 (Figure 5). Early during Test 4, some oxygen leaked into the sparging flask, as indicated by the DO concentration increasing to approximately 0.08 mg/L [0.08 ppm] (Figure 5). The source of the DO is not known. The Eh initially stabilized at approximately –43 mV. A sudden increase in Eh occurred on June 13, 2016, just prior to Day 4 when the sparging gas was briefly turned off and back on, which caused overpressurization and one of four skirted septum stoppers popped off and introduced oxygen. The stopper was quickly replaced, after which Eh declined further until the end of the test on Day 5. The Eh disturbance on Day 4 resulted in an approximate doubling of the DO concentration, from 0.07 mg/L [0.07 ppm] to 0.15 mg/L [0.15 ppm] as observed in the data record, but the resumption of sparging reduced the DO concentration to its undisturbed level within 20 minutes. This result suggests that Eh is not very sensitive to DO at low concentrations.

Test 5 lasted from 11:12 on June 15 until 15:19 on June 17, 2016 (Figure 6). The ORP data collection system failed during this test so that only manual records of the ORP (Eh) are available. As during the May 2016 static tests, the DO concentration decreased to the detection level {approximately 0.008 mg/L [0.008 ppm]} within the first hour of the test and remained there for the duration of the test. The Eh decreased continuously during the test and reached –29 mV when the test was terminated after 2 days.

Test 6 lasted from 11:36 on June 20 until 17:49 on June 23, 2016 (Figure 7). Again, DO decreased rapidly during the first hour of the test and remained less than 0.01 mg/L [0.01 ppm] until approximately 1 day after sparging stopped, shortly before Day 3 of the test. The Eh decreased during the first 3.5 days, eventually reaching approximately –100 mV at Day 3.5, even though sparging stopped shortly before Day 3. In this test, Eh, but not DO, was affected by several changes to the sparging rate. The first change occurred at approximately Day 1.1 when the source for the sparging gas was inexplicably turned off during the evening after the

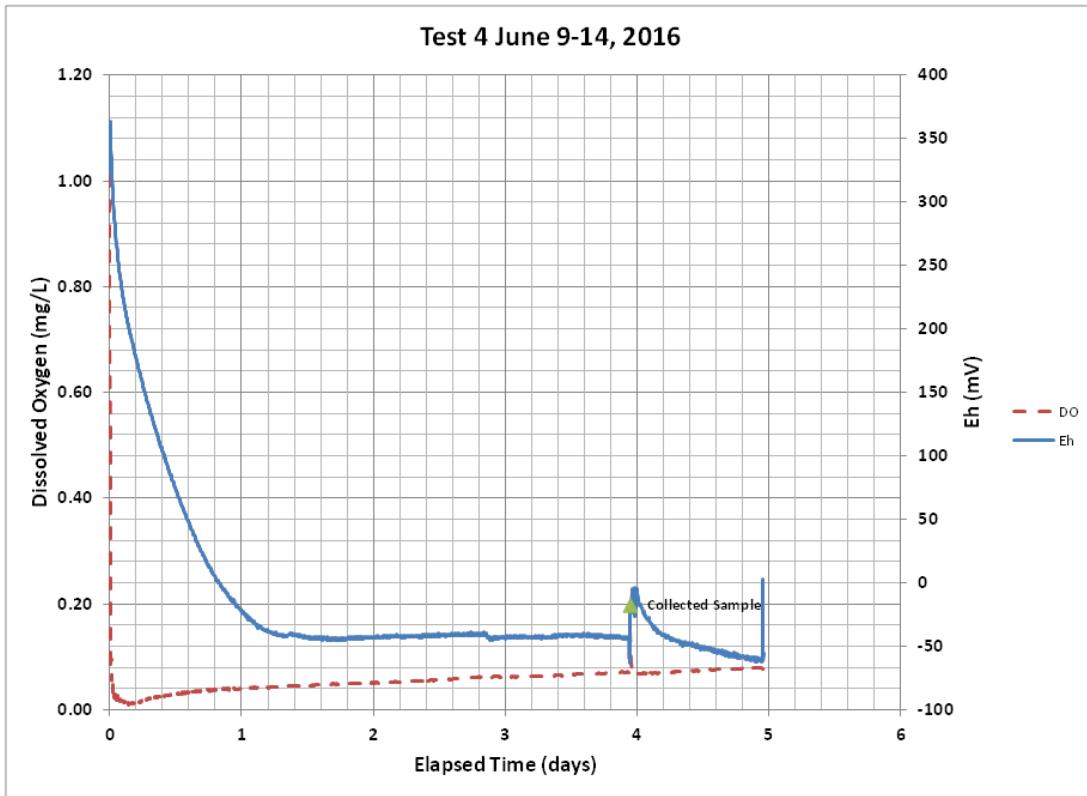


Figure 5. Results of DO and Eh Measurements During Static Test 4, June 9–14, 2016

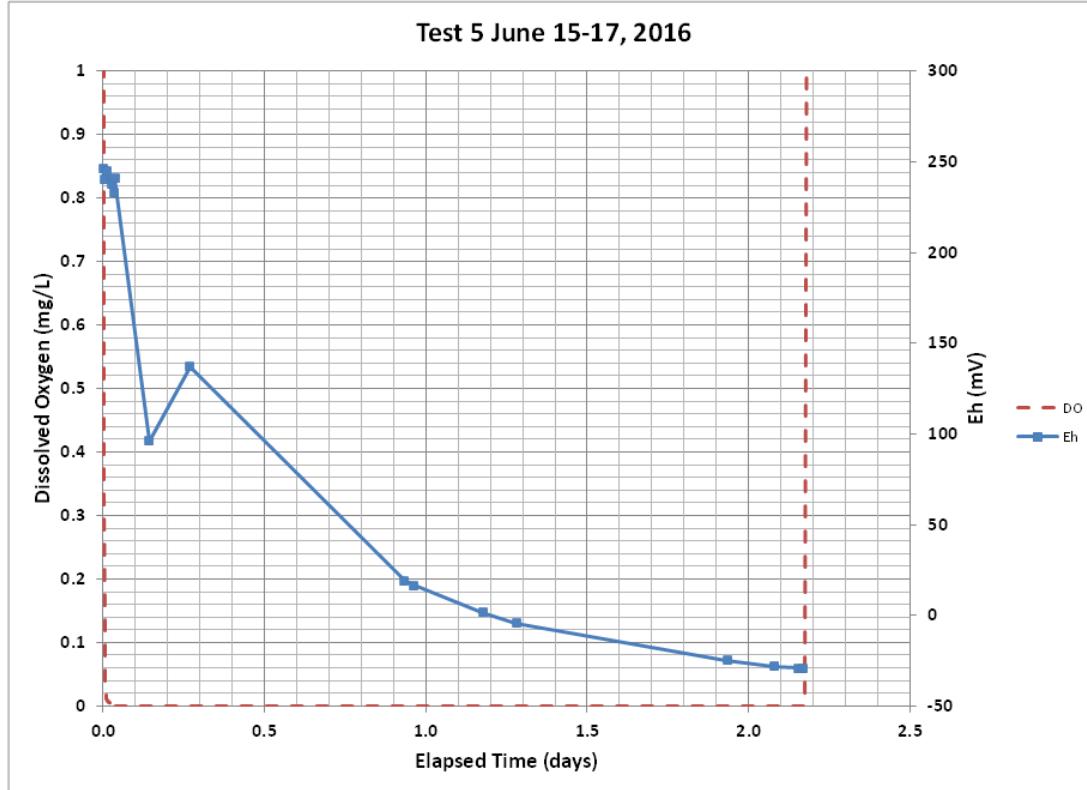


Figure 6. Results of DO and Eh Measurements During Static Test 5, June 15–17, 2016

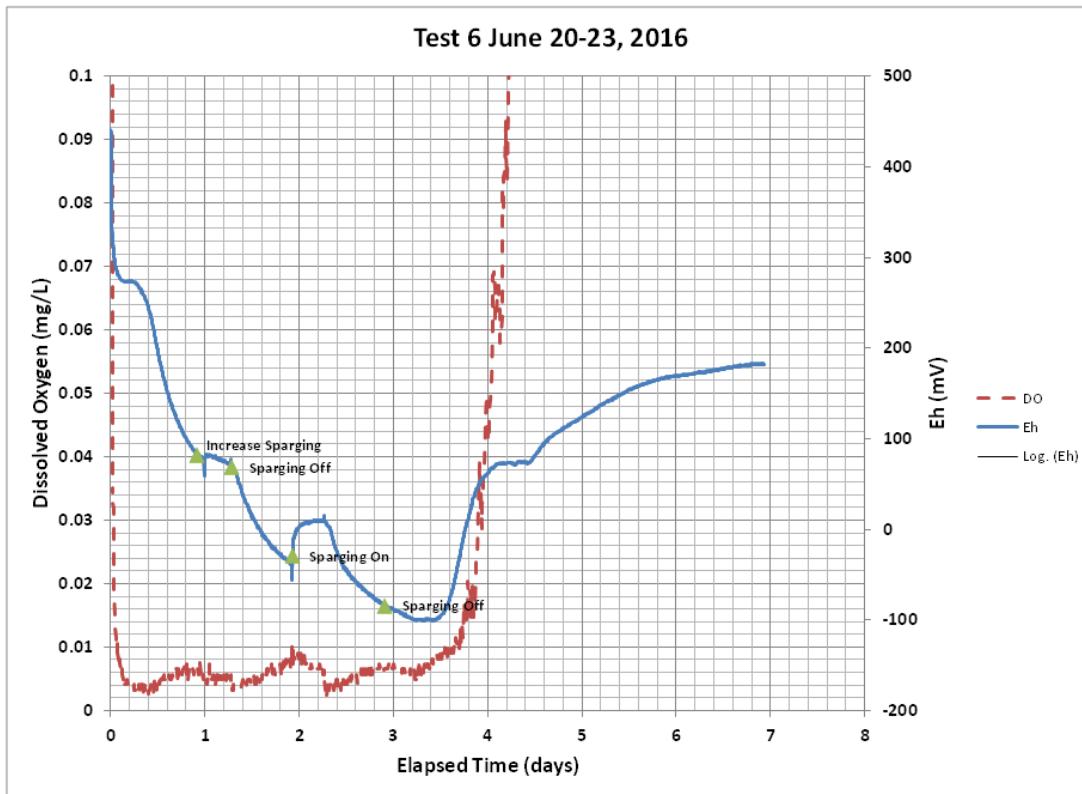


Figure 7. Results of DO and Eh Measurements During Static Test 6, June 20–23, 2016

investigators left the laboratory. This change caused a relatively rapid decrease in Eh until the sparging gas was turned back on during the morning of Day 2. Resumption of sparging caused a sudden increase in Eh followed by further decline in Eh until Day 3.5, even though sparging was stopped shortly before Day 3. The DO did not increase significantly until shortly before Day 4.

The events that occurred during Test 6 provide some insight into the relationship between DO and Eh, and into the effect of sparging on the Eh measurements in the static test apparatus. Sparging serves two purposes during static tests: first it reduces DO concentrations and second it mixes the water in the sparging flask to maintain equilibrium between the ORP probe and the bulk fluid in the flask. The fluctuations in Eh observed during Test 6 in the absence of significant changes in DO indicate the Eh is not sensitive to DO concentrations less than approximately 0.01 mg/L [0.01 ppm], but is sensitive at higher concentrations. The results also indicate that the Eh measurements are affected to some extent by fluid mixing, as evidenced by the relatively rapid decrease in Eh when the sparging gas was turned off. This could be due to localized reducing conditions near the ORP electrode, as indicated by the decreases in Eh when sparging was stopped.

3.4 Results of Chemical Analyses

Water samples for chemical analysis were collected from the sparging flask on June 14 at the end of Test 4 and on June 17 at the end of Test 5. The samples were collected by forcing water from the sparging flask directly into a Tedlar bag using the sparging gas pressure without exposing the sample to the atmosphere. A sample of the sSRS water used during the static test was also collected on July 17, 2016. To prevent introduction of oxygen into the sample bags,

the samples were not filtered. The samples were analyzed by the Southwest Research Institute® Chemistry and Chemical Engineering Division for the following constituents:

- Chloride and sulfate by EPA Method 300¹
- Ferrous iron by SM 3500Fe-B²
- Sulfide, sulfite and thiosulfate by EPA 300M³
- Metals by EPA SW-846, Method 6010B

The major constituent concentrations measured in the static test conditioned water samples in relation to those in the sSRS water are illustrated in Figure 8. All major constituents increased significantly after the sSRS water contacted the grout. Large increases with respect to the sSRS water were measured for all major constituents, except magnesium, with the greatest increase in sulfate. Note that the conditioned water in the sparging flask was replaced with fresh sSRS water between Tests 4 and 5. The major constituent concentrations were lower in the sample collected after Test 5 than those in the sample collected after Test 4, indicating aging and leaching of soluble constituents from the grout. Such leaching was not observed in the water samples collected during the intact grout core dynamic test reported in Walter and Necsoiu (2015). The leaching observed in the static tests appears to be due to the greater surface area-to-water volume ratio of the grout cubes exposed to sSRS water during the static test ($1.9 \text{ cm}^2/\text{mL}$ [4.7 in^{-1}]) relative to that of the intact core in the FY 2015 dynamic test ($0.16 \text{ cm}^2/\text{mL}$ [0.41 in^{-1}]).

The concentrations of secondary constituents and trace metals measured in the Test 4 and Test 5 conditioned water samples are illustrated in Figure 9. As with the major constituents, secondary constituent concentrations were generally higher in the Test 4 conditioned water sample than in the Test 5 conditioned water sample. As with the results from the FY 2015 dynamic tests, no iron was detected in the conditioned water samples, despite the presumed presence of reduced iron in the grout. Manganese, another constituent in the grout with multiple oxidation states, was detected at concentrations slightly above the detection limit of 0.005 mg/L [ppm]. Manganese was not detected in the water samples collected during the dynamic test in FY 2015. No reduced sulfur species (sulfide, sulfite, and thiosulfate) were detected in the conditioned water samples. This contrasts with the results of the FY 2015 dynamic test during which thiosulfate was detected.

¹Determination of Inorganic Anions by Ion Chromatography

²Standard Methods for the Examination of Water and Wastewater,
<http://standardmethods.org/store/ProductView.cfm?ProductID=497>

³Determination of Inorganic Anions by Ion Chromatography

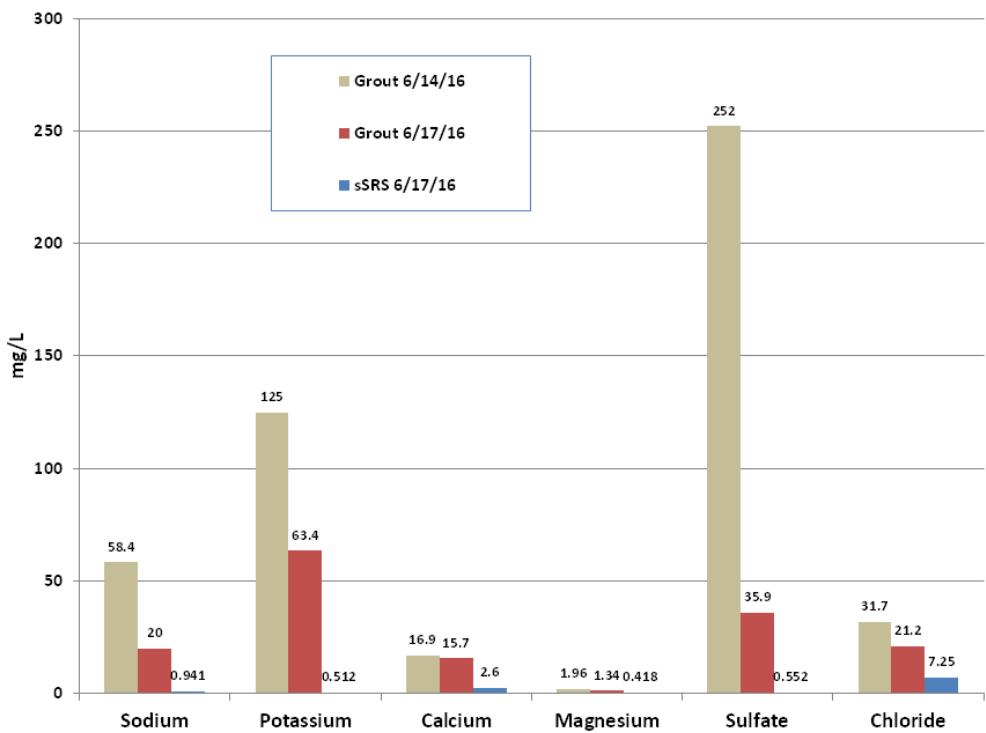


Figure 8. Major Constituent Concentrations in Test 4 and Test 5 Water Samples Compared With Their Concentrations in sSRS Water

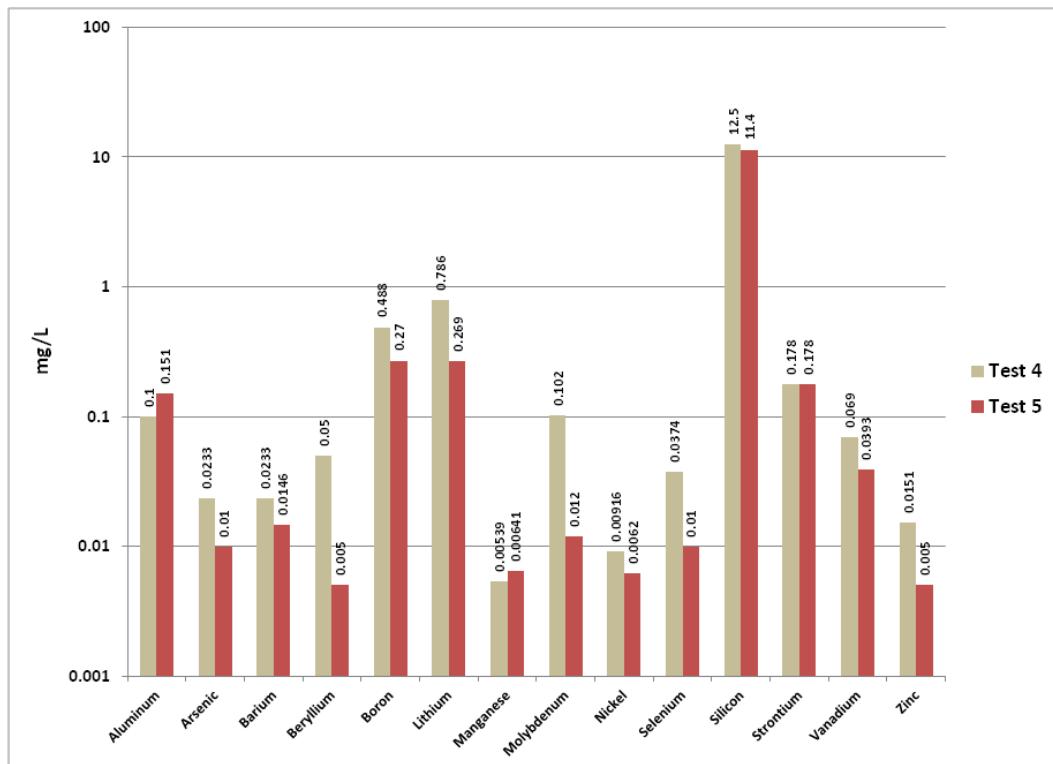


Figure 9. Comparison of Secondary and Trace Constituent Concentrations Detected in Static Test Conditioned Water Samples

4 DYNAMIC TEST OF OXYGEN CONSUMPTION

During FY 2016, a dynamic test was performed to evaluate the ability of the tank grout to consume DO and reduce its concentrations. Because the dynamic flow tests on intact core samples performed during FY 2015 did not reveal any significant reduction to DO concentrations, the tests performed during FY 2016 used a column packed with some of the tank grout cubes that had been used during the static tests, assuming that increasing the surface area of the grout in contact with the sSRS water would increase the reactivity of the grout. In a sense, these tests mimicked flow through a network of cracks in the tank grout.

The dynamic test was performed using the apparatus shown schematically in Figure 10. A reservoir continuously sparged with a gas mixture of nitrogen and 388 ppmv carbon dioxide provided a supply of deoxygenated, low DO sSRS water to the column. Water was pumped from the sparging reservoir using a peristaltic pump. DO concentrations were measured using solid state optical DO probes (Hamilton VisiFerm D120). The components of the test apparatus were connected using the Fluran tubing described in Section 2.

The column containing the tank grout cubes was a 30-cm [1-ft]-long by 2.54-cm [1-in]-internal diameter Pyrex tube {i.e., with a volume of 152 cm³ [4.9 in³]}. The lower (influent) and upper (effluent) ends of the tube were sealed with a skirted septum stopper. The flow was introduced into the column through a syringe needle and connected to the flow system with a Luer-lock connector. The effluent end of the column was also connected to the flow system with a syringe needle.

The June 6–7, 2016, dynamic column test was performed to evaluate the ability of the grout to consume DO. DO was the only measured parameter during this test because previous tests indicated that restricting oxygen infusion into the test apparatus was difficult when ORP and pH probes were included in the flow loop. The glass column was initially filled only with deionized water (no grout) to test the accuracy with which differences in DO could be measured between the influent and effluent of the column. The column was initially purged with deaerated, deionized water at a flow rate of 5 mL/min [0.16 oz/min] for 264 minutes {i.e., a water volume of 1320 mL [43 oz] was passed through the column}; then the flow loop was switched to recirculating mode. After approximately 1.5 hours, the influent and effluent DO probes agreed to within approximately 2 percent of DO saturation (i.e., 27.5 percent versus 25.8 percent).

The column was then emptied, and the tank grout cubes labeled 1 through 29 (Figure 1), which had been previously used during the May static tests, were placed in the column and the column and recirculation tubing were purged with deaerated sSRS water at a flow rate of 8 mL/min [0.26 oz/min] for 5 minutes {i.e., a water volume of 40 mL [1.3 oz] was passed through the grout-filled column}. Before recirculation began, the column was being filled with sSRS water, which was discharged to waste. Recirculation of water in the flow system at a flow rate of 2 mL/min [0.066 oz/min] began after 40 minutes had elapsed. The total mass of the 29 grout cubes was 81.8 g [0.18 lb], and their bulk volume and surface area, as estimated based on the dimensions of each cube, were 34 cm³ [2.1 in³] and 199 cm² [31 in²].

The resulting DO concentrations at the influent and effluent DO probes, recorded as percent saturation, are illustrated in Figure 11. DO probe 1 (DO1) was positioned at the influent end of the flow loop and DO probe 2 (DO2) was at the effluent end of the glass column, as shown in Figure 10. DO increased in the flow loop during recirculation and then stabilized with a constant difference between the effluent and influent concentrations of approximately –3 percent (Figure 11). The initial increase in DO concentration was either due to oxygen infusion through

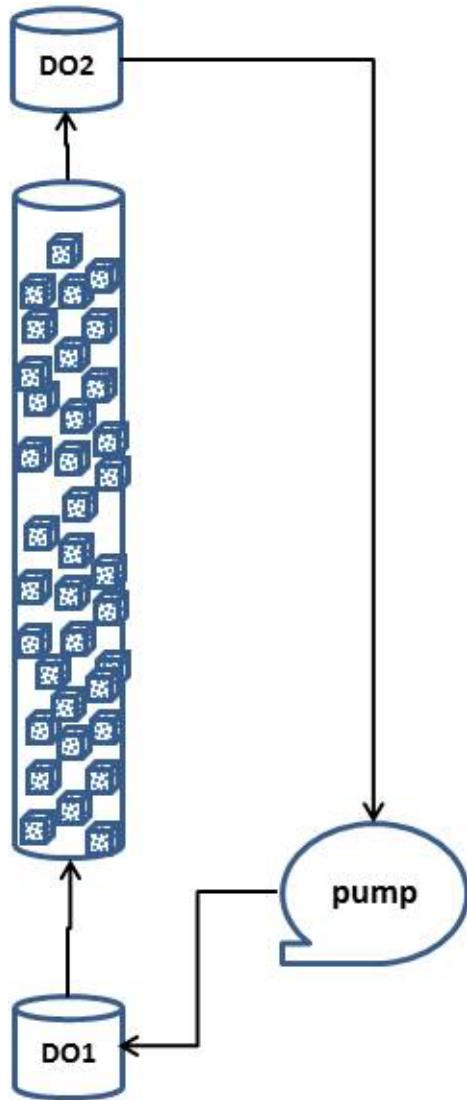


Figure 10. Schematic Diagram of Dynamic Test Apparatus

the Fluran tubing or oxygen being released from the grout cubes that were only partially saturated at the start of the test, or both. The DO concentration in the flow loop ultimately stabilized at approximately 45 percent saturation with a constant difference between the influent and effluent DO probes (Figure 11). Reasons for stabilization of DO concentration in the flow loop are either that the rate of DO consumption by the grout was equal to the infusion rate or that DO in the flow loop became constant and the initial increase was likely due to oxygen being released from the grout cubes. The latter alternative is more likely because it would be fortuitous that the DO consumption rate equaled the infusion rate. Further, given that the difference between the DO probes of approximately 3 percent was similar to that measured in the pre-test without grout in the column, we conclude that the dynamic column test provided no evidence that DO was being consumed by the grout.

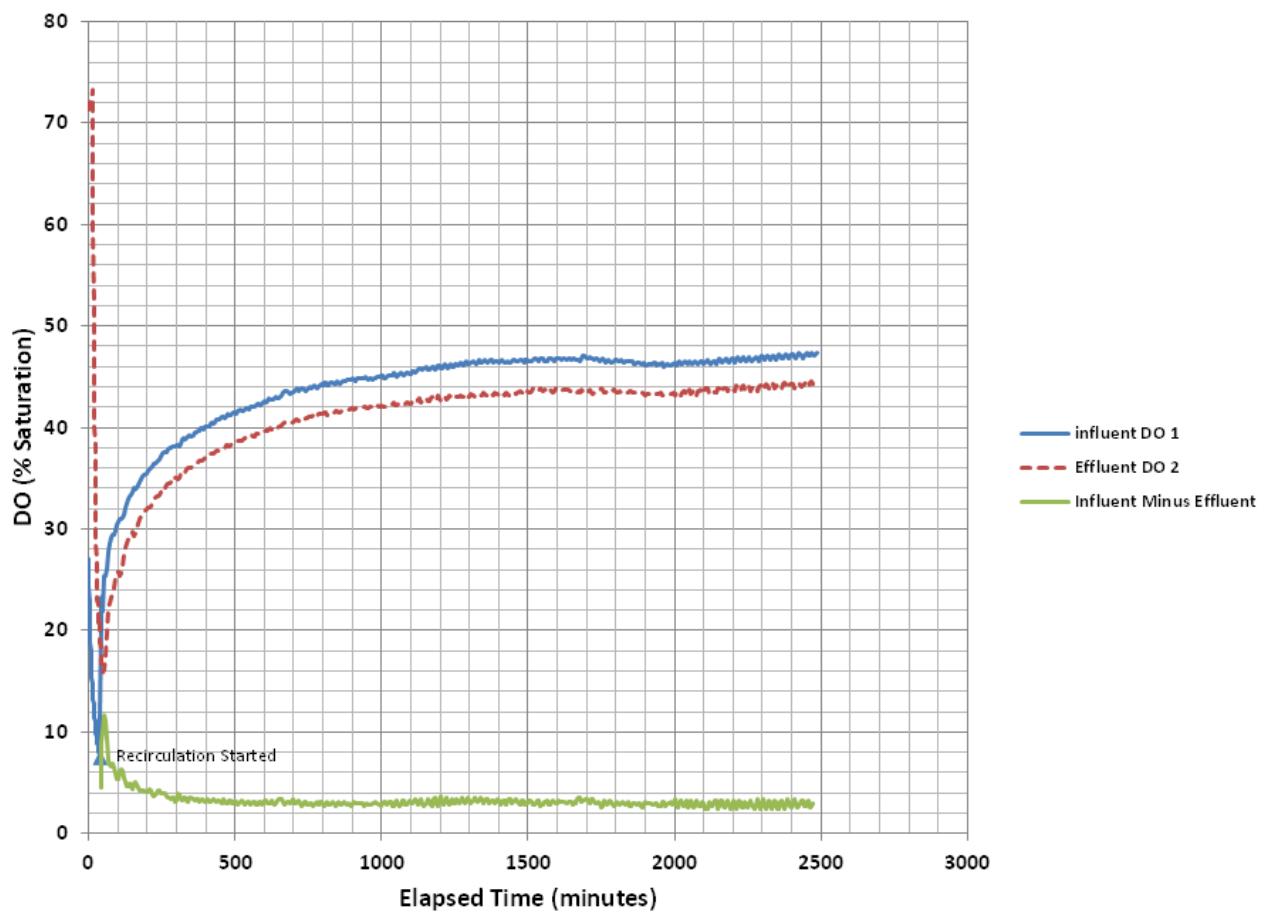


Figure 11. Measured DO Concentrations (as Percent Saturation) During the Dynamic Flow Test

5 SUMMARY AND RECOMMENDATIONS

All six static water conditioning tests performed during FY 2016 resulted in Eh values in the range of -50 to -100 mV after a few days of reaction. None of the tests indicated that Eh would approach -500 mV, as has been suggested by geochemical models (e.g., SRR-CWDA-2010-00128, Rev. 1). Static test results suggest that Eh is insensitive to DO at concentrations less than 0.01 mg/L [0.01 ppm]. At DO concentrations greater than 0.01 mg/L, Eh appears to be controlled by DO rather than by any redox couples that may evolve from the reducing grout. In a future report, CNWRA will include information from a literature review about redox couples that may control the Eh in tank grout. Unlike the water chemistry analytical results obtained from the FY 2015 dynamic test (Walter and Necsoiu, 2015), analysis of water samples collected from the FY 2016 static tests did not reveal the presence of oxidizable species, such as reduced sulfur, which would control Eh. The reactivity of the grout does, however, appear to be related to its surface area in contact with sSRS water. The inflections in Eh evolution observed during the May 2016 static tests were not observed during the June 2016 tests. Additional static tests should be performed during FY 2017 on crushed grout samples comprised of various particle size fractions to investigate the effect of surface area on water conditioning. In addition, dynamic flow tests should be performed to further investigate the ability of the grout to consume DO, which plays a major role in controlling the Eh in the water contacting the grout.

Because Eh appears to be controlled by DO at concentrations greater than 0.01 mg/L [0.01 ppm], it is important to determine if tank grout can consume DO in meteoric or groundwater infiltrating through it and thus lower the DO concentration to levels at which redox couples in the grout can control the Eh. The dynamic flow test conducted during FY 2016 was an initial attempt to address this question. Any oxygen consumption by the grout used in this test was less than the difference in DO saturations measured by the DO probes (approximately 3 percent DO saturation).

During future work, it may be possible to reduce the measurement differences between DO probes so that more accurate measurements of oxygen consumption under dynamic flow conditions can be performed. Additional dynamic tests using high surface area crushed grout should also be performed during FY 2017 to better understand surface area effects. The FY 2016 tests were performed on a tank grout specimen that was prepared with Grade 100 blast furnace slag cement; however, SRS recently switched to use of finer and more reactive Grade 120 slag cement in all their grouts. A tank grout specimen has been prepared with DOE's Grade 120 slag cement and should be tested during FY 2017.

6 REFERENCES

C-SPP-F-00055. Ganguly, A. "Furnishing and Delivery of Tank Closure Grout." Revision 4. Aiken, South Carolina: Savannah River Remediation, LLC. December 20, 2012.

SRR-CWDA-2010-00128. "Performance Assessment for the H-Area Tank Farm at the Savannah River Site." SRR-CWDA-2010-00128, Revision 1. November 2012.

SRR-CWDA-2013-00026. "Requested Pre-Visit Information in Support of U.S. Nuclear Regulatory Commission F-Tank Farm March 2014 Onsite Observation Visit." Revision 0. Attachments 3 and 4: Batch Tickets. March 13, 2014.

SRNL-STI-2011-00551. Stefanko, D.B. and C.A. Langton. "Tanks 18 and 19-F Structural Flowable Grout Fill Material Evaluation and Recommendations." Revision 1. Aiken, South Carolina: Savannah River National Laboratory. April 2013.

Strom, R.N. and D.S. Kaback. WSRC-RP-92-450, "SRP Baseline Hydrogeologic Investigation: Aquifer Characterization, Groundwater Geochemistry of the Savannah River Site and Vicinity." Aiken, South Carolina: Westinghouse Savannah River Company. 1992.

Walter, G.R. and D.M. Necsoiu. "Tank Grout Water Conditioning Tests—Status Report." Report to Nuclear Regulatory Commission IM17860.04.004.515. September 2015.

Walter, G.R., C.L. Dinwiddie, D. Bannon, J. Frels, and G. Bird. "Intermediate Scale Grout Monolith and Additional Mesoscale Grout Monolith Experiments: Results and Recommendations." San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. 2010.