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September 25, 2015
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U.S. Nuclear Regulatory Commission
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Mail Stop TWFN 8F8
Washington, DC 20555

Subject: Intermediate Milestone 17860.04.004.515: Tank Grout Water Conditioning Tests—Status Report

Dear Mr. Heath:

This letter transmits the subject intermediate milestone, prepared by the Center for Nuclear Waste Regulatory Analyses staff as part of the task order titled Technical Assistance for the Review of the U.S. Department of Energy's (DOE's) Non-High-Level Waste Determinations. This report documents fiscal year 2015 activities related to experiments on the capacity of reducing grout to condition the chemistry of infiltrating water. These chemical effects, particularly reduction, are considered by DOE to be beneficial to the tanks' ability to isolate radionuclides for long time periods. The work included dynamic flow tests to simulate flow through fast pathways, such as cracks and annular spaces, and static tests to evaluate the maximum reducing capacity of the grout. Much of the work this year involved refining the experimental apparatus for the dynamic flow tests to improve measurements of dissolved oxygen and to reduce oxygen diffusion into the flow loop. With these refinements, the experimental program can advance during the next fiscal year using both dynamic and static tests.

The report is attached in Microsoft® Word and PDF versions. We also will make the report available to the U.S. Nuclear Regulatory Commission staff in a convenient location on the CNWRA-hosted shared drive.



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Mr. Maurice Heath
September 25, 2015
Page 2

If you have any questions regarding this report, please contact Dr. Gary Walter at (210) 522-3805 or me at (210) 522-5582.

Sincerely,



David Pickett, Ph.D., P.G.
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DP/ar
Enclosures
SHAREPOINT: DOE Non-High Level Waste Determinations 17860.04\Fiscal Year 2015

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TANK GROUT WATER CONDITIONING TESTS— STATUS REPORT

Prepared for

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

Prepared by

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September 2015

ABSTRACT

This report describes proactive work related to tank grout water conditioning performed during fiscal year 2015 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 the waste tanks at the Savannah River Site 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, and dissolved oxygen content of the infiltrating water, all of which can affect the release of radionuclides from the residual waste in the tanks. The initial tests were designed to simulate flow of water through a narrow aperture pathway, such as a crack or annular space between the grout and a pipe or tank wall. These tests are referred to as dynamic flow tests. Additional testing under static (no flow) conditions was performed to investigate the reducing capacity of the grout.

The dynamic flow tests, in which simulated Savannah River Site (sSRS) groundwater was flowed past tank grout core specimens, indicated that the tank grout rapidly increased the pH of the sSRS water on contact with the core, but that the grout had little effect on the dissolved oxygen concentration and only slightly lowered the Eh. However, these tests were affected by oxygen diffusion through the flexible tubing used in the peristaltic pump, resulting in relatively high dissolved oxygen concentrations in the flow loop.

Chemical analyses of effluent from the core flow cell indicated that contact with the core significantly increased the concentration of major cations and sulfate, and added mg/L (ppm) concentrations of aluminum, barium, boron, silicon, and strontium. Analysis of sulfur species indicated that oxidation of reduced sulfur species (presumably metal sulfides) in the grout was the source of the increased sulfate. Slight reduction of hexavalent chromium, added to the sSRS water as a redox indicator, was also observed. Modification of the sSRS water chemistry decreased with increased contact time between the sSRS water and the grout core.

Static tests on sub-samples from the grout cores in a fixed volume of sSRS water and with the dissolved oxygen concentration reduced to the detection limit of the dissolved oxygen probe {nominally 0.004 mg/L [0.004 ppm]}, indicated that the grout could produce strongly reducing conditions in the sSRS water. The difference in results between the dynamic and static tests with respect to the reducing capacity of the grout may be due to increased water-grout contact area and time in the static test apparatus, as well as the significantly reduced dissolved oxygen concentrations in the static tests.

To further investigate the reducing capacity of the grout under dynamic flow conditions, additional tests on intact core specimens using the revised dynamic flow loop apparatus are proposed. These tests will be performed with much lower dissolved oxygen concentrations in the flow loop. Static tests will also be designed to investigate the effect of grout surface area and grout-mass-to-water ratios on Eh. The residual reductive capacity of the cores will be determined by slicing the cores into cross-section discs and then subsampling based on distance from the perimeter.

CONTENTS

Section	Page
ABSTRACT	ii
FIGURES	iv
TABLES	vi
ACKNOWLEDGMENTS	vii
ACRONYMNS/ABBREVIATIONS.....	viii
1 INTRODUCTION.....	1-1
2 GENERAL DYNAMIC FLOW TEST DESIGN	2-1
2.1 Core Collection.....	2-1
2.2 Preparation of Simulated Savannah River Site Groundwater	2-1
3 RESULTS.....	3-1
3.1 Test 1, Core 11, Middle Section	3-1
3.1.1 Test Equipment and Procedures	3-1
3.1.2 Core 11 Middle Section Closed-Loop, Aerated Test Results	3-3
3.1.3 Core 11 Middle Section Closed-Loop, Deaerated Test	3-9
3.2 Core 12 Middle Section Close-Loop, Aerated Test	3-9
3.3 Investigation of Source of Dissolved Oxygen.....	3-10
3.4 Reconfigured Dynamic Flow Apparatus	3-17
3.5 Summary of Dynamic Flow Tests.....	3-18
4 STATIC TEST DESIGN	4-1
4.1 Preliminary Static Test	4-1
4.2 July 30-August 3 2015 Static Test.....	4-1
4.3 Summary of Static Tests	4-4
5 SUMMARY AND RECOMMENDATIONS.....	5-1
6 REFERENCES.....	6-1

FIGURES

Figure	Page
2-1	General Configuration of Tank Grout Water Conditions Tests.....2-2
2-2	Collection and Preparation of Core Samples2-3
3-1	Flow Loop Apparatus Used for Core 11, Middle Section Closed-Loop Aerated Test3-2
3-2	Configuration of the Dissolved Oxygen Flow Cell Used in Core 11 Middle Section Tests in November and December 20143-2
3-3	Core 11, Middle Section, Closed-Loop Pretest Measurements Prior to Placing Core in Flow Loop.....3-4
3-4	Core 11, Middle Section, Closed-Loop, Aerated Measurements Versus Flow Loop System Volumes (1 System Volume Approximately Equals 1 Day).....3-5
3-5	Comparison of Major Ion Concentrations Before and After Contact With Grout Core, Core 11 Middle Section Closed-Loop Aerated Test.....3-7
3-6	Comparison of Metals in Water Samples Before and After Contact With Grout Core, Core 11 Middle Section Closed-Loop Aerated Test.....3-7
3-7	Sulfur Molar Speciation in Contact Water, Core 11 Middle Section Closed-Loop Aerated Test.....3-8
3-8	Comparison of Hexavalent and Total Chromium Concentration in sSRS Water and Water Contacted With Grout3-10
3-9	pH, DO, and Eh Measured During Core 11 Middle Section Closed-Loop, Deaerated Test3-11
3-10	Pretest Measurements of pH, DO, and Eh for Core 12 Middle Section Closed-Loop, Aerated Test.....3-12
3-11	pH, DO, and Eh Measured During Core 12 Middle Section Closed-Loop, Aerated Test.....3-13
3-12	Revised Flow Loop Configuration Used in June–July Deaerated Dynamic Flow Test.....3-15
3-13	Results of July 6–7, 2015 Deaerated Dynamic Flow Test Showing Changes in Dissolved Oxygen (DO) and Eh Before and After the Core Cell3-15
3-14	Comparison of Major Constituents in Water Samples Before and After Contact With the Core for July 2015 Core 11 Deaerated Test3-16
3-15	Comparison of Major Constituents in Contact Water Samples Between December 2014 and July 2015 for Core 11 Test3-16
3-16	Metals Detected in Water Samples Before and After Contact With Core for July 2015 Core 11 Test3-18
3-17	Comparison of Metals Detected in December 2014 Contact Water Samples With Metals Detected in July 2015 Contact Water Samples for Core 11 Tests3-19
3-18	Sulfur Speciation in sSRS Water and Core Contact Water for the July 2015 Core 11 Test3-19
3-19	Comparison on Sulfur Speciation Between Contact Water for the December 2014 Core 11 Test With Contact for the July 2015 Test3-20
4-1	Preliminary Static Test Apparatus.....4-2
4-2	Pattern Used to Cut Core Cubes and Cubes From Core 11, Middle Section, Used in Preliminary Static Test4-2
4-3	Eh Based on ORP Measurements for Preliminary Static Test July 21–23, 2015.....4-3
4-4	Apparatus Used in July 30–August 3, 2015 Static Test on Core 104-3

FIGURES (continued)

Figure		Page
4-5	Chips of Core 10 Used in July 30–August 3, 2015 Static Test.....	4-4
4-6	DO and Eh Measured During Static Test on Core 10, Bottom Section July 30–August 3, 2015.....	4-5

TABLES

Table		Page
2-1	Recipe Used to Prepare Batch 1 sSRS Water	2-3
2-2	Target, Nominal, and Actual Concentrations in sSRS Batch 1	2-4
2-3	Recipe Used to Prepare Batch 2 sSRS Water	2-4
2-4	Target, Nominal, and Actual Concentrations in sSRS Batch 1	2-5

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The authors thank English Percy for technical review and David Pickett for programmatic review. The authors also thank Arturo Ramos for support in report preparation.

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. Sources for other data should be consulted for determining the level of quality for those data. Walter and Dinwiddie (2015) and Walter (2015) were used to document the experimental conditions and in-process entries.

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. 2015.

ACRONYMNS/ABBREVIATIONS

Br ⁺	bromide
Ca ⁺²	Calcium
Cl ⁻	chlorine
CO ₂	carbon dioxide
Cr	chromium
CNWRA [®]	Center for Nuclear Waste Regulatory Analyses
DO	dissolved oxygen
HCO ⁻¹ ₃	bicarbonate
HPLC	high-performance liquid chromatography
ID	internal diameter
meq	milliequivalents
Mg ⁺²	magnesium
mL	milliliters
mmol	millimols
Na ⁺	sodium
NaBr	sodium bromide
NRC	U.S. Nuclear Regulatory Commission
OD	outside diameter
ORP	Oxidation-Reduction Potential
PVC	poly vinyl chloride
sSRS	Simulated Savannah River Site

1 INTRODUCTION

This report describes proactive work related to tank grout water conditioning performed by the Center for Nuclear Waste Regulatory Analyses during fiscal year 2015 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 the waste tanks at the Savannah River Site 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, and dissolved oxygen content of the infiltrating water, all of which can affect the release of radionuclides from the residual waste in the tanks. The initial tests were designed to simulate flow of water through a narrow aperture pathway, such as a crack or annular space between the grout and a pipe or tank wall. These tests are referred to as dynamic flow tests. Based on the results of these tests, additional testing under static (no flow) conditions was performed to investigate the reducing capacity of the grout.

2 GENERAL DYNAMIC FLOW TEST DESIGN

The general design of the dynamic flow tests is illustrated in Figure 2-1, although various modifications were made as the testing evolved. Simulated Savannah River Site (sSRS) groundwater, described in Section 2.2, was circulated through an acrylic flow cell containing a core sample from the Intermediate Scale Grout Monolith of Walter et al. (2010) and then through a sequence of flow cells in which the pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), and bromide (Br) were measured. The water was introduced from a reservoir that could be sparged with either atmospheric air to produce aerated water or a gas mixture of nitrogen and 388 ppmv carbon dioxide (custom gas mix primary standard from AirGas) to produce deaerated water. Water was pumped from the reservoir using an ISMATEC peristaltic pump capable of flow rates of 0.1 to 10 milliliters (mL) [0.0033 to 0.33 fl oz] per minute. The flow system was set up so that it could be operated in either an open-loop or closed-loop configuration. In the open-loop configuration, water flowed past the core sample and then to waste (once-through test). In the closed-loop configuration, water could be recirculated through the flow loop.

2.1 Core Collection

The core samples were collected from the Intermediate Scale-Grout Monolith on September 11, 2014, by wet coring the monolith at three locations. Each core was approximately 76 cm [30 in] long and represented the entire thickness of the Intermediate Scale-Grout Monolith. The core samples were dried, then cut into 23-cm [9-in] subsamples using a wet diamond rock saw, redried, and sealed in Mylar bags containing an oxygen absorbing packet (300 cc, OxygenAbsorbers.com). The entire process from core collection to sealing in the Mylar bags required approximate 2 hours. The steps in the core collection process are shown in Figure 2-2.

2.2 Preparation of Simulated Savannah River Site Groundwater

The sSRS groundwater was prepared to represent the major ion chemistry of a groundwater sample from well P27D as reported by Strom and Kaback (1992). Two 20-L [5.3-gal] batches of sSRS water were prepared in 20-L [5.3-gal] carboys using reagent grade chemicals. The batches were prepared from 1 L [0.26 gal] concentrated stock solutions by pipetting the required volume of the stock solutions into the prefilled carboy containing deionized water. The carboy used for Batch 1 was filled with deionized water while weighing the pretared carboy on an industrial scale (Ohaus 3000 Series) until the weight reached 20 +/- 0.1 kg [44 +/- 0.2 lbs].

The recipe used to prepare Batch 1 is listed in Table 2-1 and the target, nominal, and analytically measured salt concentrations are listed in Table 2-2.

In addition to the constituents in the sSRS groundwater, 0.5 mL [0.017 fl oz] of a 5 M sodium bromide (NaBr) standard and 15 mL [0.51 fl oz] of potassium chromate (K_2CrO_4) were added to Batch 1. The sodium bromide was added to act as an inert tracer with a target concentration of 10 mg/L and the potassium chromate was added as a redox indicator with a target concentration of 0.05 mg/L. Bromide was omitted from later batches for reasons discussed in Section 3.2.1.

No attempt was made to match the pH and bicarbonate (HCO_3^-) reported for the P27D water because these were regarded as being controlled by the carbon dioxide (CO_2) concentration in the vadose zone above the shallow groundwater at the Savannah River Site. Assuming that the

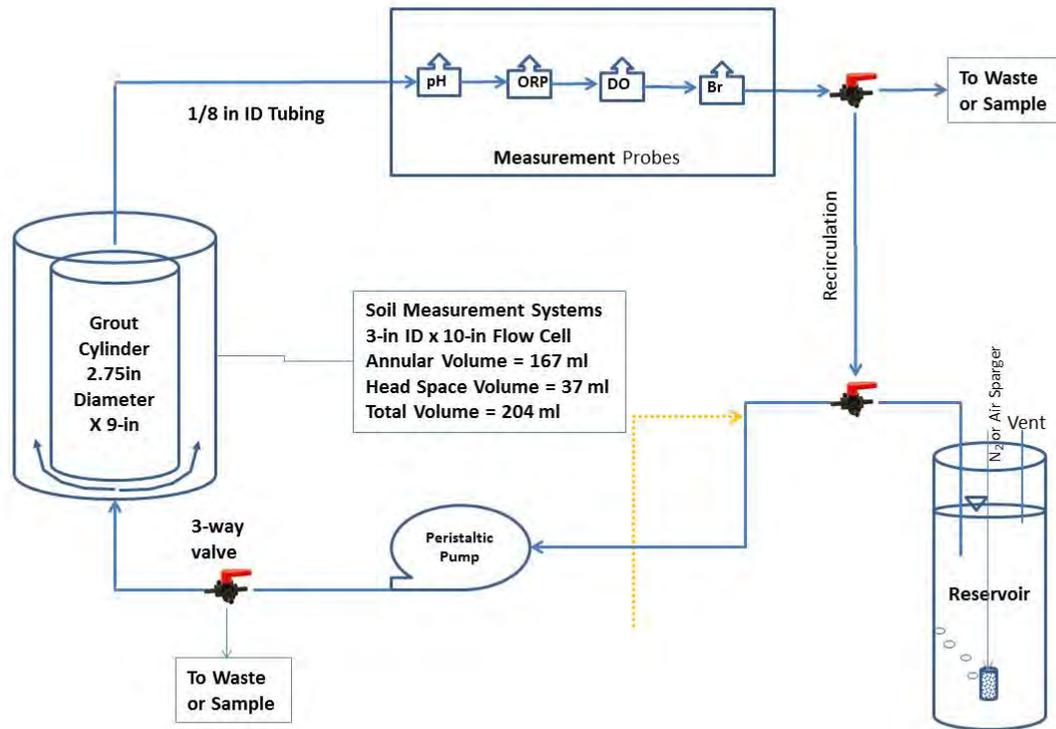


Figure 2-1. General Configuration of Tank Grout Water Conditions Tests

$$P_{CO_2} = \frac{[HCO_3^-][H^+]}{K_1 K_H} \quad (2-1)$$

[HCO_3^-] – molarity of HCO_3^- [M]
 [H_2CO_3] – molarity of H_2CO_3 [M]
 [H^+] – hydrogen ion activity or 10^{-pH}
 and

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-6.3} \quad (2-2)$$

$$K_H = \frac{[H_2CO_3]}{P_{CO_2}} = 10^{-1.5} \quad (2-3)$$



(A)



(B)



(C)



(D)



(E)



(F)

Figure 2-2. Collection and Preparation of Core Samples: (A) Wet Coring of Intermediate Scale Grout Monolith; (B) Removal of Core From Monolith; (C) Marking of Core After Retrieval; (D) Cutting of Core in Laboratory; (E) Core Before Sealing in Mylar Bag; (F) Core Samples in Mylar Bags

Table 2-1. Recipe Used to Prepare Batch 1 sSRS Water		
Reagent	Mass in 1 L Stock Solution (g)	Volume Added to 20 L Carboy (mL)
NaBr	514.45	0.5
KCl	0.94	20
CaSO ₄ ·2H ₂ O	2.26	10
MgCl ₂ ·6H ₂ O	3.43	20
CaCl ₂ ·2H ₂ O	8.20	20
K ₂ CrO ₄	0.25	15
sSRS = Simulated Savannah River Site 1 g = 0.035 oz 1 mL = 0.034 fl oz		

Constituent	Target (mg/L) [*]	Nominal (mg/L) [†]	Actual (mg/L) [‡]
Na	0.97	2.88	3.53 [§]
K	0.49	0.49	0.53
Ca	2.50	2.50	2.37
Mg	0.41	0.41	0.38
Cl	3.33	5.53	5.34
SO ₄	0.63	0.63	0.52
Hexavalent Cr (Cr ⁺⁶)	None	0.05	0.0498
HCO ₃	6	NA	Not Measured
Br	None	10	Not Measured
pH	5.4	NA	6.15 [¶]

^{*}Target concentration based on well P27D (Strom and Kaback, 1992)
[†]Nominal concentration based on mass added to 20 L Carboy
[‡]Actual concentration based on laboratory analysis
[§]Sodium exceeds nominal due to addition of sodium fluorescein dye.
^{||}Not included in target specification
[¶]Initial measurement in aerated flow cell test DATE
 1 mg/L = 1 ppm
 sSRS = Simulated Savannah River Site

bicarbonate concentration reported in the P27D groundwater is controlled by the CO₂ partial pressure:

Using the reported HCO₃ concentration of 6 mg/L [6 ppm] or 9.8×10^{-5} M and pH of 5.6 [$10^{-5.6}$ M], and substituting Eqs (2-2) and (2-3) into Eq (2-1) gives a P_{CO2} of 1.6×10^{-2} atm or 16,000 ppmv. This value is much higher than the ambient atmospheric CO₂ concentration of approximately 380 ppmv, but not unusually high for soil, in which the CO₂ concentration can be 3,000 to 30,000 ppmv (e.g., Bohn et al., 1985). In any event, the pH and hence the carbonate content of the water was modified almost immediately after contact with the grout core, as will be discussed in Section 3.1.2, Batch 2 was prepared using the same target and nominal concentrations as Batch 1 except that NaBr was replaced with NaCl. The Batch 2 Recipe is listed in Table 2-3 and the target, nominal, and actual concentrations are listed in Table 2-4. The excess sodium and chloride in the final sSRS water based on the laboratory analysis may have been due to a malfunctioning de-ionized water system used to prepare the solution.

Reagent	Mass in 1 L Stock Solution (g)	Volume Added to 20 L Carboy (mL)
NaCl	0.62	80
KCl	0.94	20
CaSO ₄ ·2H ₂ O	2.26	10
MgCl ₂ ·6H ₂ O	3.43	20
K ₂ CrO ₄	0.25	15

sSRS = Simulated Savannah River Site
 1 g = 0.035 oz
 1 mL = 0.034 fl oz

Constituent	Target (mg/L)[*]	Nominal (mg/L)[†]	Actual (mg/L)[‡]
Na	0.97	0.97	3.34
K	0.49	0.49	0.67
Ca	2.50	2.50	3.04
Mg	0.41	0.41	0.44
Cl	3.33	7.12	10.8
SO ₄	0.63	0.63	0.61
Hexavalent Cr (Cr ⁺⁶)	0.05	0.05	0.048
HCO ₃	6	NA [§]	Not Measured
pH	5.4	NA [§]	6.3

^{*}Target concentration based on well P27D (Strom and Kaback, 1992)
[†]Nominal concentration based on mass added to 20 L Carboy
[‡]Actual concentration based on laboratory analysis
[§]Not included in target specification
^{||}Initial measurement in deaerated flow cell test
1 mg/L = 1 ppm
sSRS = Simulated Savannah River Site

3 RESULTS

This section describes the procedures used for and results of the dynamic tank grout water conditioning tests performed between November 6, 2014, and August 2015.

3.1 Test 1, Core 11, Middle Section

Testing of the middle section of Core 11 started on November 6, 2014, using the apparatus shown in Figure 3-1. The testing was performed first using aerated Simulated Savannah River Site (sSRS) water and then using deaerated sSRS water.

3.1.1 Test Equipment and Procedures

The changes in water chemistry were measured in terms of pH and oxidation-reduction potential (ORP) with bromide (Br) concentration measured as a tracer. pH was measured using a Weiss Research gel-filled, double junction pH probe connected to a Hanna Instruments pH mini-controller (Model 931700). The pH probe was calibrated in NIST traceable pH standards of pH 4.00, 7, .01, 10.01, and 12.45. ORP was measured using a Weiss Research gel-filled double junction ORP probe connected to a Hanna Instruments ORP mini-controller (Model 932700). The ORP probe was standardized using a +200 mv versus Ag|AgCl ORP standard from Ricca Chemical Co. The Br concentration was measured with a Weiss Research double-junction bromide specific electrode and monitored with a Hanna Instruments pH mini-controller (Model 931700). The Br concentration was determined from a correlation between the pH reading on the Hanna controller and the values measured in standard solutions containing Br concentrations of 1, 5, 10, and 20 mg/L [ppm]. The pH, ORP, and Br probes were placed in Lazar Research Laboratories acrylic microflow cells connected in the flow loop. Output from the pH, ORP and bromide probes was recorded on a personal computer connected to an Agilent data logger (Model 34970A) and also recorded manually.

Dissolved oxygen (DO) concentrations were measured using Oakton galvanic DO probes and Oakton DO + 6 meters. The DO probes were calibrated by setting the reading to 100 percent oxygen saturation with the probe exposed to air and then 0 percent oxygen saturation with the probe submerged in a Zero Oxygen Standard (Ricca Chemical Co.) The DO probes were placed in a 100 mL 3-neck flask connected in the flow loop (Figure 3-2). The DO readings were recorded manually.

The components of the flow loop were connected with 1/8-in [3.175 mm] outside diameter (OD) by 1/16-in [1.59 mm] internal diameter (ID) poly vinyl chloride (PVC) tubing. Flow through the loop was induced using a 3-channel ISMATEC peristaltic pump capable of flow rates between 0.1 and 10 mL/minute [3.3×10^{-3} to 0.33 fl oz/min]. The water in the loop was drawn from the 1 L [34 fl oz] Wolff bottle (Figure 3-1) containing sSRS water that was aerated using an aquarium pump to bubble air through the water. The reservoir was isolated from the flow loop to perform closed-loop tests. Alternatively, the reservoir continuously fed the flow loop during open loop tests with the water discharged to waste. Water flowed from the peristaltic pump to the core flow cell. The acrylic core flow cell (Soil Measurement Systems) had an ID of 7.62 cm [3 in] and length of 25.4 cm [10 in]. The grout core, with a diameter of 6.99 cm [2.75 in] and length of 22.9 cm [9 in], was placed in the core flow cell. The resulting annular space between the core and the inner wall of the core flow cell was 0.32 cm [0.125 in]. Water flowed from the core cell to the pH, ORP, DO, and bromide probes and then was either recirculated through the flow loop or discharged to waste. The total water volume in the flow loop was approximately



Figure 3-1. Flow Loop Apparatus Used for Core 11, Middle Section Closed-Loop Aerated Test

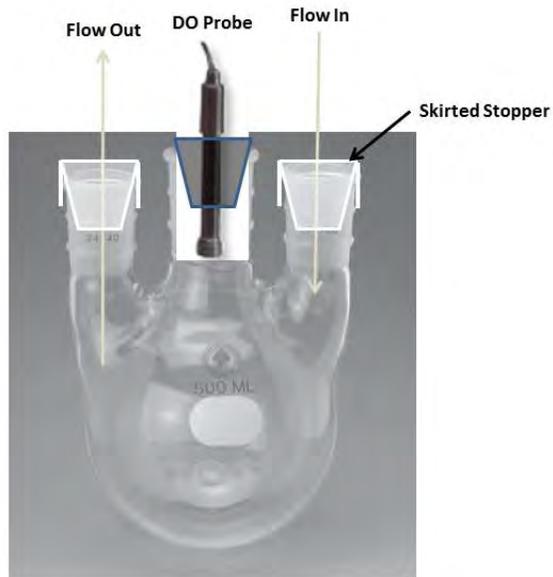


Figure 3-2. Configuration of the Dissolved Oxygen Flow Cell Used in Core 11 Middle Section Tests In November and December 2014

1,600 mL [54 fl oz]. Under closed-loop conditions, the water to grout mass ratio was 0.87 based on a dry core weight of 1,841 g [4.05 lbs].

3.1.2 Core 11 Middle Section Closed-Loop, Aerated Test Results

The closed-loop, aerated test was started at on November 7, 2014, by placing the grout core in the core flow cell and filling the flow loop with aerated sSRS water. After purging bubbles trapped in the flow loop, the flow rate was set at 1.1 mL/min [0.037 fl oz/min] and the water was recirculated through the reservoir and the flow loop. Flow through the core flow cell was from bottom to top during the first 10 days of the test, at which point the direction of flow was switched from top to bottom in an effort to minimize bubble accumulation in the core cell. The reservoir was replenished with aerated sSRS water at this time. The test was terminated on December 4, 2014.

Figure 3-3 shows the pH, Eh (calculated from ORP plus 200 mV), and DO measured in the flow loop prior to introducing the grout core while the sSRS water was pumped to waste. The pH, Eh (ORP plus 200 mV), and DO readings immediately before introducing the grout core were 6.54, 482 mV, and 6.76 mg/L [6.76 ppm], respectively. The bromide measurements proved to be unreliable, apparently because changes in the water chemistry affected the response of the Br selective electrode. Because of these uncertainties, the Br results will not be discussed.

Figure 3-4 shows the pH, Eh, and DO measurements made during the test. The pH of the water increased from 6.7 to 10.61 almost immediately after contacting the core and then stabilized at approximately 11.6 after one system volume (approximately 1 day). The Eh dropped rapidly from +763 mV at the start of the test to approximately +400 mV after 3 system volumes (approximately 3 days), then suddenly decreased to approximately +245 mV and remained steady for the rest of the test. The early, high Eh values are believed to have been influenced by a small air bubble trapped in the ORP probe flow cell because the rapid decrease in Eh coincided with removing this bubble.

DO decreased gradually from 6.7 mg/L [6.7 ppm] during the first 5 system volumes (approximately 5 days), then fluctuated around 5 mg/L [5 ppm] for the remainder of the test. The DO, and possibly the ORP, measurements were affected by small gas bubbles that formed in the flow loop, particularly in the 3-neck flask containing the DO probe. The DO measurements may also have been affected by drift in the performance of the DO probe and the relatively large volume and slow water circulation rate in the 100 ml [3.4 fl oz] 3-neck flask. The DO measurements will be discussed further in Section 3.1.3.

Two samples from the flow loop were collected on December 4, 2014, by pumping directly into a 1-L [34-fl oz], air-free Tedlar sample bag (SKC, Inc.). Duplicate samples of the sSRS stock solution were collected in 500-mL [17-fl oz] Nalgen bottles. The samples were analyzed by the Southwest Research Institute[®] Chemistry and Chemical Engineering Division for the following constituents:

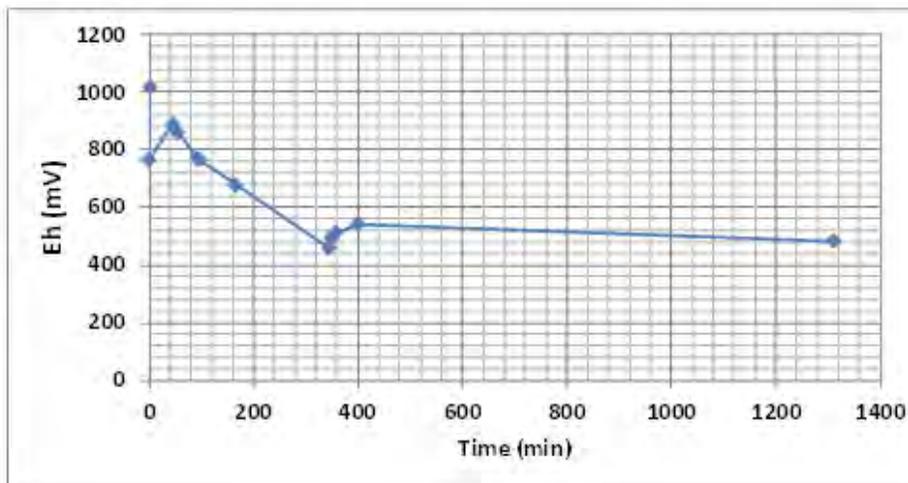
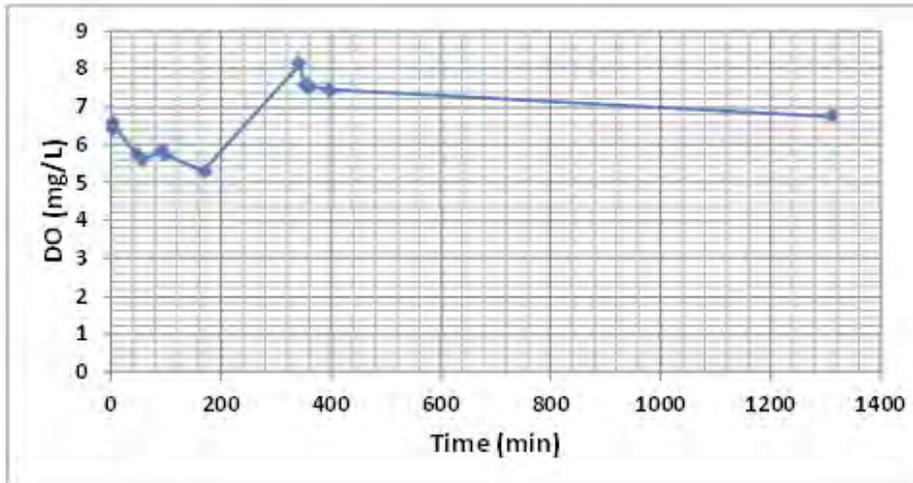
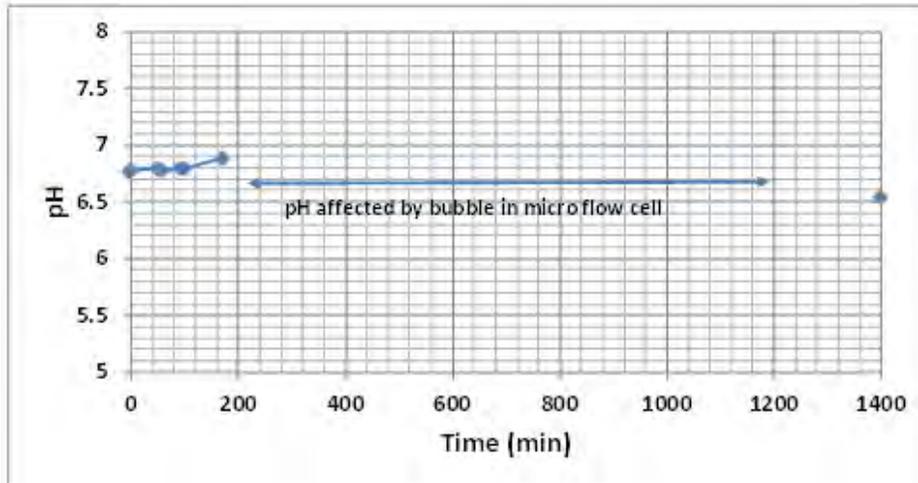
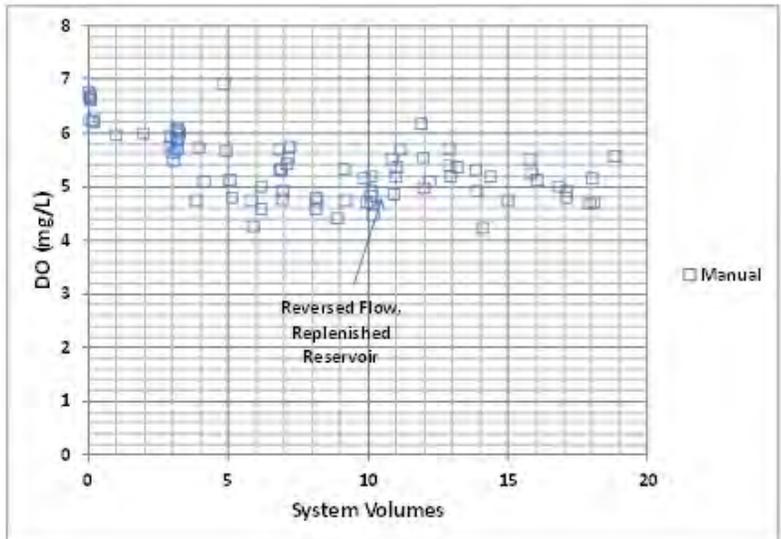
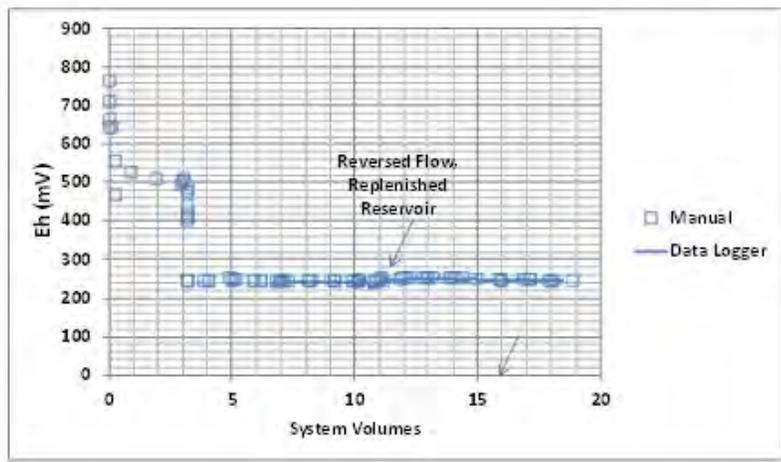
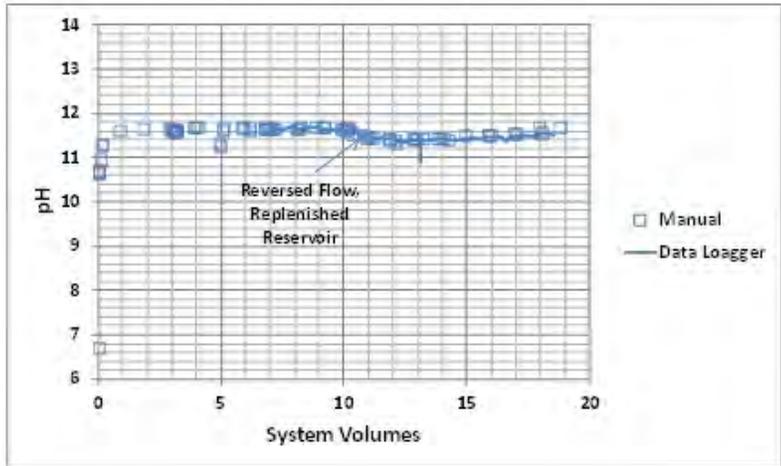


Figure 3-3. Core 11, Middle Section, Closed-Loop Pretest Measurements Prior to Placing Core in Flow Loop



D:\Gourt Work\Tank Grout Experiments\Core 11 Middle Section\Cell 1, Middle Section Manual Measurements Aerated Test

Figure 3-4. Core 11, Middle Section, Closed-Loop, Aerated Measurements Versus Flow Loop System Volumes (1 System Volume Approximately Equals 1 Day)

- Chloride and sulfate by EPA Method 300¹
- Ferrous iron by SM 3500Fe-B²
- Hexavalent chromium by EPA SW 846³ 7196A Sulfide by EPA 376.2⁴
- Sulfite and thiosulfate by EPA 300M⁵
- Metals by EPA SW-846, Method 6010B

Figure 3-5 shows the change in major ions between the water that contacted the core and the original sSRS water. The major ions, except magnesium, increased significantly after contact with the grout core, but magnesium was below the detection limit of 0.05 mg/L [0.05 ppm]. The charge balance for the major ions in the samples that contacted the grout shows a significant anion deficiency that is attributed to carbonate species not included in the analytical suite. Based on the high pH of the water contacting the grout, the carbonate species should be predominately carbonate (CO_3^{-2}). Back calculating from the charge imbalance, the CO_3^{-2} concentration would be approximately 140 mg/L [140 ppm].

Figure 3-6 shows the change in metals and secondary elements based on the laboratory analysis. Only those constituents present above detection limits are shown in the graph. Aluminum, barium, boron, chromium, silicon, strontium, and sulfate were detected in the water contacting the core, whereas only chromium and sulfate were present in the sSRS water. Interestingly, no iron was detected in the contact water despite the presence of iron minerals in the fly ash and slag cement incorporated into the grout (Walter et al., 2010).

Figure 3-7 shows the sulfur speciation in the grout contact water in mmol/L of sulfur in various oxidation states in comparison to the total sulfur from the Method 6010B analysis. Although the reported total sulfur slightly exceeds the sum of sulfur based on the individual species, the agreement between the analytical results is fairly good. The principal sulfur species was sulfate (sulfur oxidation state +6) which increased dramatically after contact with the core. The second most abundant sulfur species was thiosulfate (sulfur oxidation state +2). Sulfite (sulfur oxidation state +4) was present in low concentration and sulfide was below detection limits. The laboratory report, however, indicates that the sulfite may be under-reported due to low spike recovery.

The increased sulfate concentration in the water contacting the grout core could be due to oxidation of reduced sulfur species in the fly ash and slag cement in the grout formulation either during the water conditioning test or prior to the test. Based on the final sulfate concentrations, the flow loop contained approximately 0.18 mmol of sulfur. Assuming no oxygen infused into the flow loop during the test—an assumption that remains to be evaluated—the DO in the flow loop decreased by approximate 2 mg/L (Figure 3-4). The volume of water introduced into the flow loop was the initial volume of 1.6 L [54 fl oz] plus 1.2 L [40 fl oz] added when the reservoir was replenished after approximately 10 system volumes. Thus, approximately

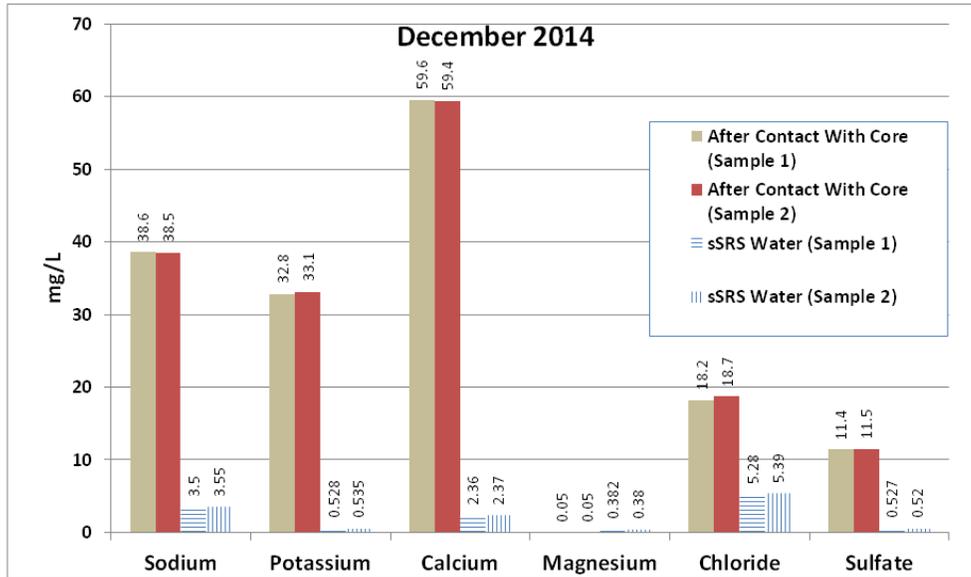
¹Determination of Inorganic Anions by Ion Chromatography

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

³Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), <http://www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm>

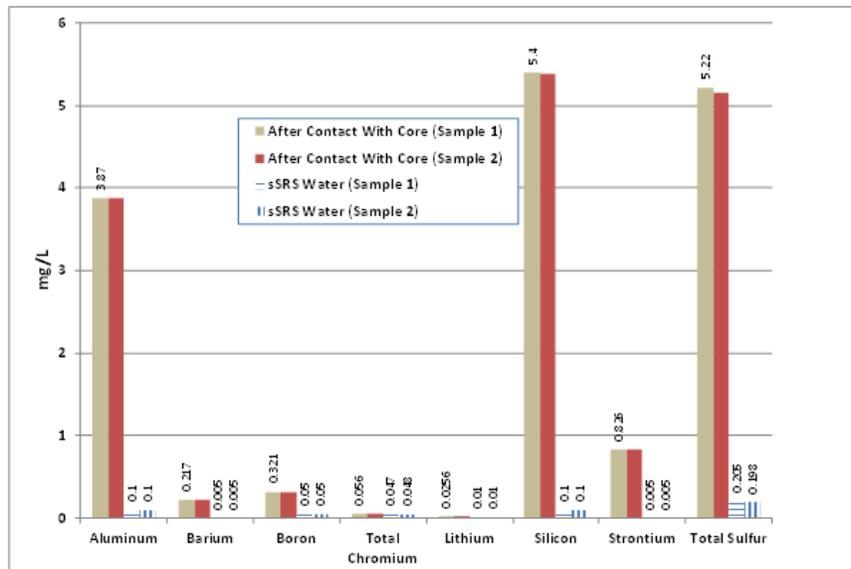
⁴Methods for the Chemical Analysis of Water and Wastes (MCAWW) EPA/600/4-79/020, https://www.nemi.gov/methods/method_summary/5318/

⁵Determination of Inorganic Anions by Ion Chromatography



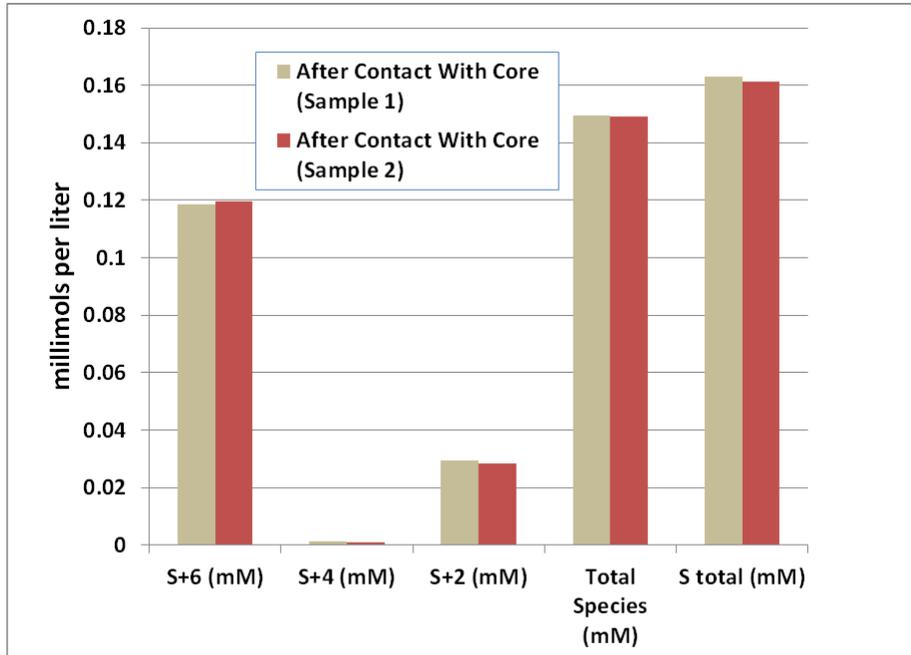
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Figure 3-5. Comparison of Major Ion Concentrations Before and After Contact With Grout Core, Core 11 Middle Section Closed-Loop Aerated Test



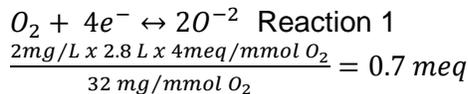
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Figure 3-6. Comparison of Metals in Water Samples Before and After Contact With Grout Core, Core 11 Middle Section Closed-Loop Aerated Test

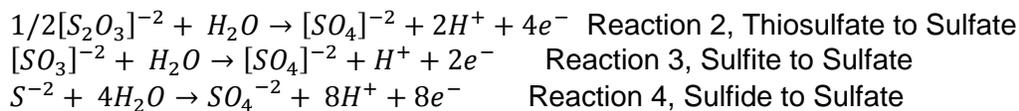


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Figure 3-7. Sulfur Molar Speciation in Contact Water, Core 11 Middle Section Closed-Loop Aerated Test. Total Species is the Total of the Analyzed Species. S Total is the Total Sulfur from the ICP Analyses.



With respect to sulfur oxidation, the following general reactions are possible:



0.7 milliequivalents (meq) of oxygen could have been reduced based on the following reaction and calculation:

Reaction 2 produces 4 meq of electrons per mmol of sulfate, whereas Reaction 3 produces 2 meq of electrons per mmol of sulfate produced and reaction 4 produces 8 meq of electrons per mmol of sulfate. The sulfate mass in the flow loop increased by approximately 0.31 mmol (11 mg/L \times 2.8 L/96 mg/mmol) during the test. If sulfide oxidation was the source of the sulfate, approximately 2.5 meq of oxygen would have been consumed. If the sulfate was produced solely from oxidation of thiosulfate, 1.2 meq of oxygen would have been consumed. If the sulfate was produced from sulfite oxidation, 0.62 meq of oxygen would have been consumed. The minimum milliequivalents of oxygen consumed falls between these bounds. However, oxidation of iron sulfide, most likely in the form of solid metal sulfides in the grout, is possible if a

substantial amount of oxygen infused into the flow loop during the test. Otherwise, oxidation of more soluble sulfite and thiosulfate salts is more likely the source of the sulfate.

Figure 3-8 compares the hexavalent and total chromium concentrations in the water that contacted the grout core with the concentration in the sSRS water. Hexavalent chromium had been added to the sSRS influent water at a nominal concentration of 0.05 mg/L as a redox indicator. The analytical value in the sSRS influent water was 0.0498 mg/L, whereas the analytical concentrations of hexavalent chromium in the samples that contacted the grout were 0.0358 and 0.0361 mg/L. These lower values indicate a slight reduction in chromium after contact with the grout core even though the total chromium concentration in the contact water was higher than in the sSRS water.

3.1.3 Core 11 Middle Section Closed-Loop, Deaerated Test

Attempts were made to start a closed-loop deaerated test on the middle section of Core 11 starting on December 5, 2014. The sSRS water was deaerated by sparging a 2 L [68 fl oz] bottle with gas from a compressed gas cylinder containing a mix of nitrogen and 388 ppmv carbon dioxide until the DO probe in the sparging reservoir read 0.0 mg/L [0.0 ppm] DO. Initial attempts to start the test were plagued by problems with gas bubbles forming in the flow loop and persistent DO concentrations in the flow loop between 0.5 and 3.5 mg/L. A successful closed-loop test was finally started on December 11, 2014, by isolating the flow loop from the sparging reservoir. The closed-loop system volume was 358 mL [12 fl oz]. The flow was set at 2 mL/min [0.068 fl oz/min] or approximately 8 system volumes per day. Figure 3-9 shows the pH, DO, and Eh during the final closed-loop test. The DO increased during the test while the pH and Eh remained relatively stable. The sudden decrease in DO starting at 23 system volumes occurred when the flow cell containing the DO probe was rotated. This behavior suggests that the relatively large volume of the DO flow cell resulted in incomplete mixing within the cell. Although some of the apparent increase in DO could be due to drift in the performance of the DO probe over the 7-day test, oxygen was apparently infusing into the flow loop through the tubing and fittings, or diffusing out of the grout core, which was not fully saturated prior to the test and may also have contained some aerated water. Thus, the ability of the grout core material to affect DO concentrations could not be assessed. Additional tests to investigate the source of the DO in the flow loop are described in Section 3.3. With regard to the degree of initial saturation of the core, the core was weighed before and after the test, and the weight increased by only about 0.4 percent, indicating that very little water was imbibed by the core during the test.

3.2 Core 12 Middle Section Close-Loop, Aerated Test

The closed-loop, aerated test on the middle section of Core 12 was started on November 17, 2014. The test apparatus was similar to that used for the Core 11 tests. The test was started with sSRS water aerated with an aquarium pump. Flow through the core flow cell was from top to bottom. Gas bubbles were removed from the system after placing the core in the flow cell and starting the test. The closed-loop system volume was 358 mL [12 fl oz] and the flow rate was set at 1.1 mL/min [0.037 fl oz/min]. Measurements of pH, DO, and Eh before placing the grout core in the flow cell and while recirculating through the flow loop (closed-loop flow) are

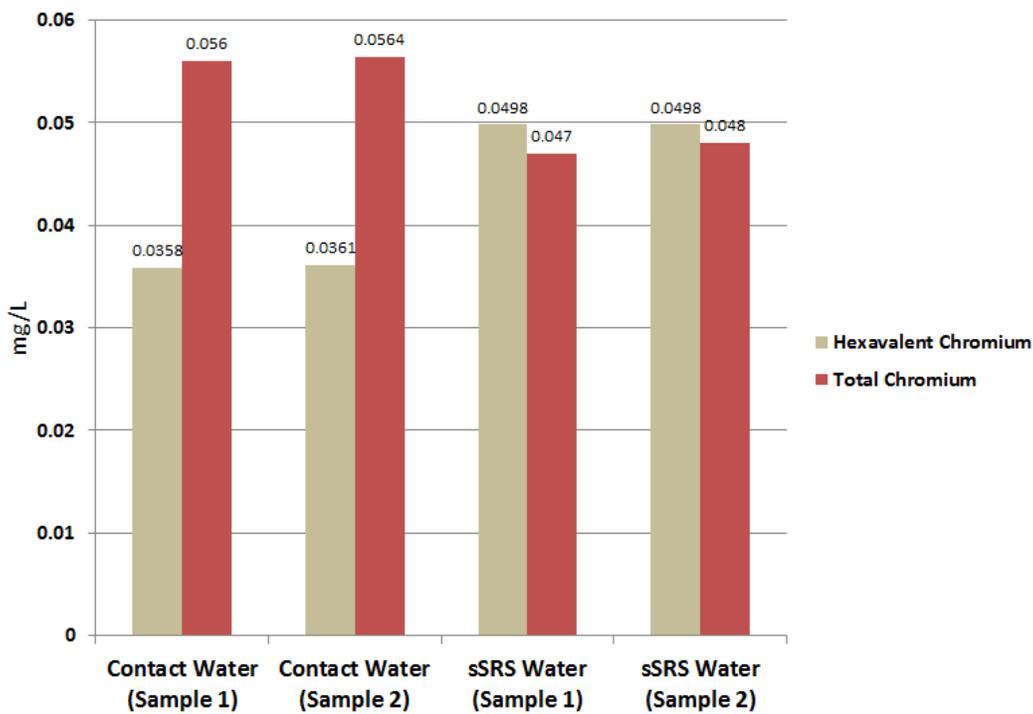


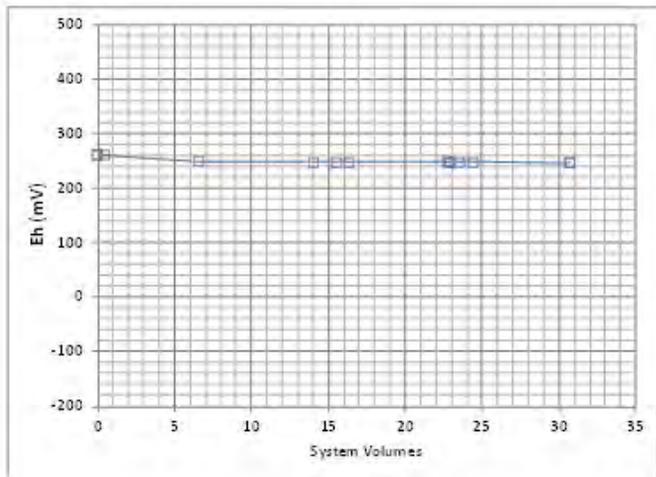
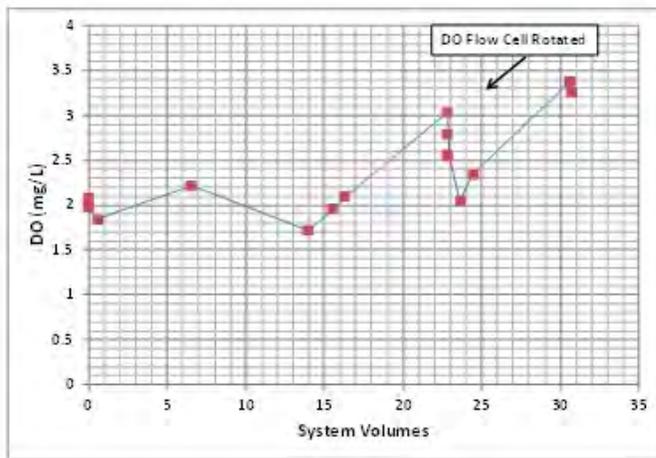
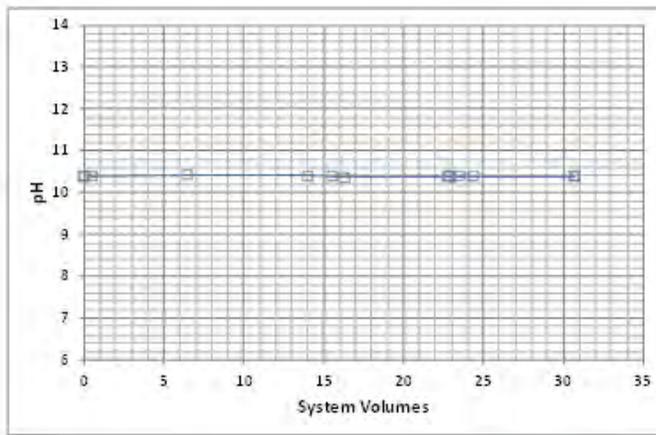
Figure 3-8. Comparison of Hexavalent and Total Chromium Concentration in sSRS Water and Water Contacted With Grout.

shown in Figure 3-10. The initially very high DO values {greater than 12 mg/L [12 ppm]} were due to a bubble trapped on the DO probe. DO and Eh stabilized prior to starting the core test, but pH was dropping slowly.

The test on Core 12 Middle Section lasted 9.7 days. Figure 3-11 shows the values of pH, DO, and Eh measured during the test on Core 12. As with Core 11, the pH increased immediately after the sSRS water contacted the core and then stabilized at approximately 11.87. DO stabilized at approximately 5 mg/L [5 ppm], although the final value of 4.81 gives the impression that DO was dropping toward the end of the test. However, any apparent decrease in DO was probably within the practical measurement accuracy of the DO probe. The Eh stabilized at approximately +215 mV, slightly lower than the final values for the test on Core 11 (+250 mV), and may have been decreasing slowly toward the end of the test. No water samples were collected for this test.

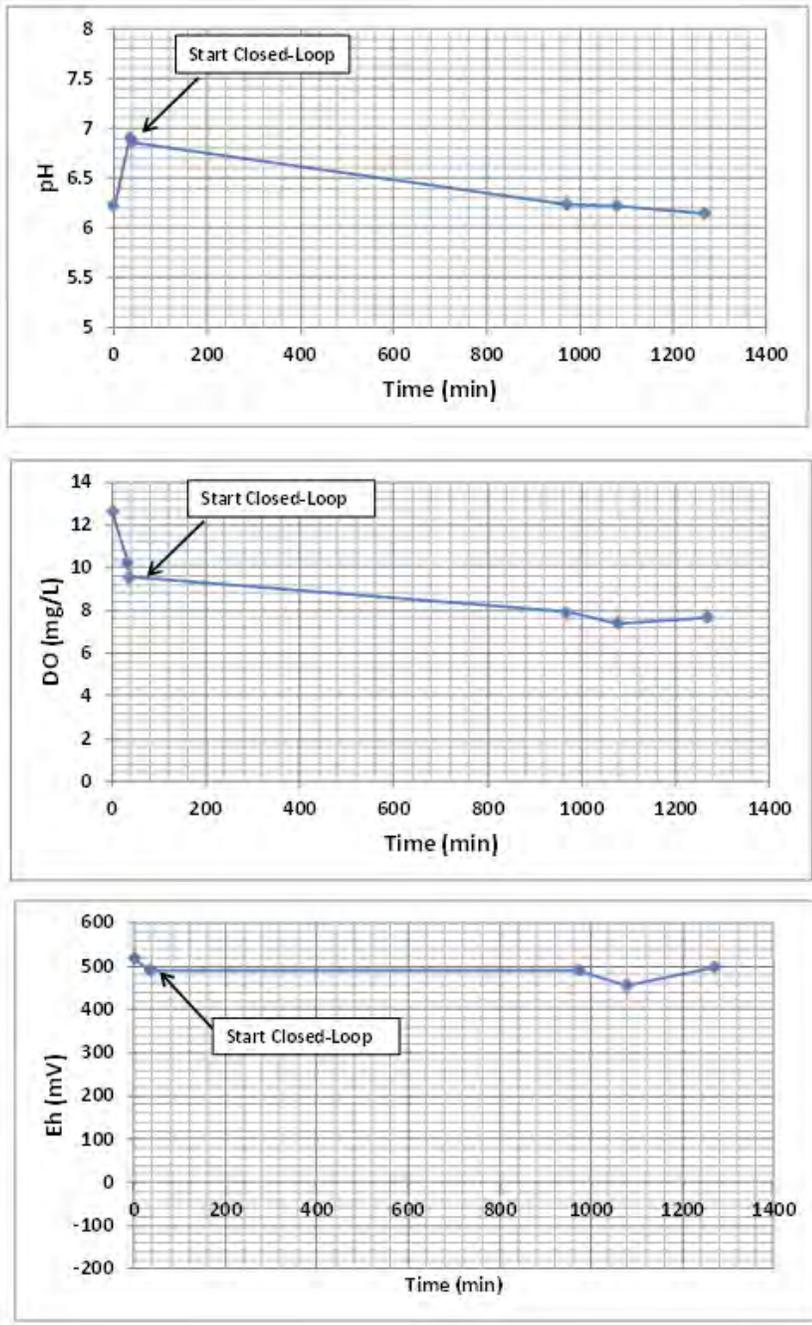
3.3 Investigation of Source of Dissolved Oxygen

The persistently elevated DO concentrations in the tests described in Section 3.2 led to investigation of the source of the DO. Potential sources of DO in the test apparatus included air bubbles trapped in various fittings and fluid reservoirs in the flow loop and diffusion of oxygen through the PVC tubing used to connect the components of the flow loop and used in the peristaltic pump. The galvanic membrane DO probes used to monitor DO in the flow loop may have also been subject to drift and spurious readings. Various efforts and tests were undertaken to reduce sources of DO in the flow loop. The galvanic membrane DO probes were replaced with solid state optical DO probes (Hamilton VisiFerm D120) that could be placed in the micro flow cells, thus replacing the relatively large flasks that were required for the galvanic



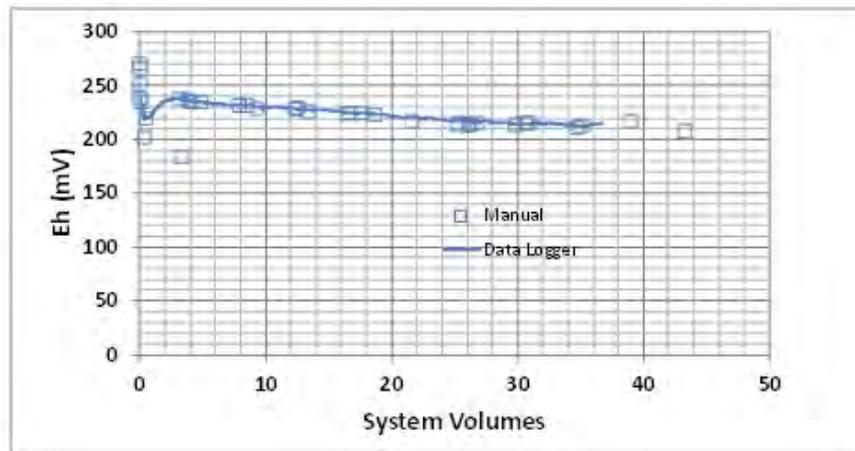
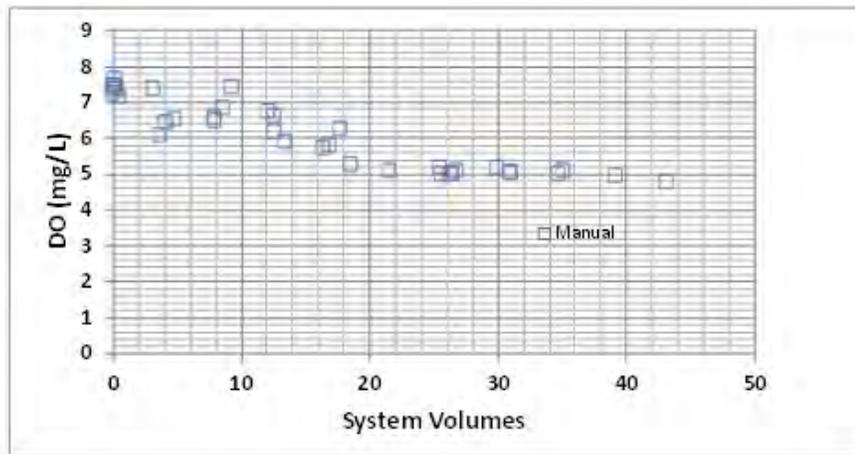
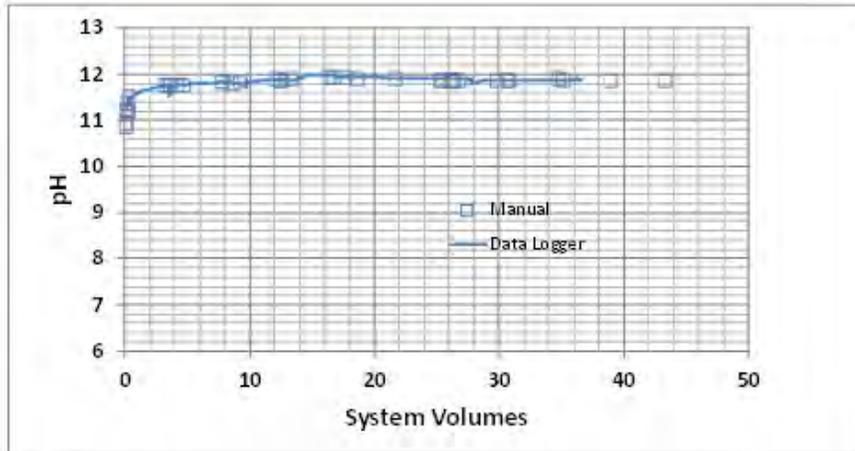
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Figure 3-9. pH, DO, and Eh Measured During Core 11 Middle Section Closed-Loop, Deaerated Test



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Figure 3-10. Pretest Measurements of pH, DO, and Eh for Core 12 Middle Section Closed-Loop, Aerated Test



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Figure 3-11. pH, DO, and Eh Measured During Core 12 Middle Section Closed-Loop, Aerated Test

membrane DO probes. Long sections of PVC tubing were replaced with 1/8-in [3.2-mm] OD by 1/16-in [1.6-mm] ID stainless steel tubing, and the micro-flow cells used to measure DO, as well as pH and ORP, were placed as close as possible to the core cell. However, the PVC tubing was still used in the peristaltic pump and short sections, typically a few inches long, were used to connect the cells holding the probes and to connect the probe flow cells to the core cell.

Several tests using the middle section of Core 11 were performed during June and early July 2015 to refine the test apparatus. Figure 3-12 is a schematic of the refined flow loop and Figure 3-13 shows the results of the last test using the refined apparatus started on July 6, 2015. DO was measured in terms of percent saturation and converted to DO in mg/L using DO tables from U.S. Geological Survey (2015) based on a temperature of 24 °C, an elevation of 244 m [800 ft] above sea level, and a nominal atmospheric pressure of 738 mm Hg. The resulting conversion from percent saturation to mg/L was 8.17 mg/L at 100 percent saturation. The redox potential measured with the ORP probe was converted to Eh by adding 200 mV to the ORP measurement referenced to the Ag|AgCl electrode. The test was performed at a constant flow rate of 2 mL/min.

Despite the improvements, the DO in the flow loop entering the core cell remained between 1.5 and 2 mg/L, although the DO measured between the sparging reservoir and the peristaltic pump was reduced to approximately 1 mg/L. The DO concentrations were similar between the core influent and core effluent, indicating no measureable decrease in DO by reaction with the core sample. Eh decreased by approximately 200 mV across the core cell but the core cell effluent remained oxidizing (Eh +250 to +300 mV) and was in the same range as that measured during the previous aerated and deaerated tests on cores 11 and 12. The pH measured in the sparging reservoir was 6.3 and the pH in the effluent from the core cell was relative steady at approximately 10.5.

Water samples were collected at the end of the test from the sparging reservoir and the core cell. The core cell sample was collected by pumping directly into a Tedlar bag without exposing the sample to the atmosphere, while the reservoir sample was collected in a 500-mL [17-fl oz] Nalgene bottle. The samples were analyzed by the Southwest Research Institute Chemistry and Chemical Engineering Division for the following constituents, as described in Section 3.1.2.

- Chloride and sulfate by EPA Method 300
- Ferrous iron by SM 3500Fe-B
- Hexavalent chromium by EPA SW 846 7196A
- Sulfide by EPA 376.2
- Sulfite and thiosulfate by EPA 300M
- Metals by EPA SW-846, Method 6010B

Figure 3-14 shows the major constituent composition of the sSRS water and the water that had contacted the core. Calcium and potassium were the only major constituents that increased after contact with the core. Figure 3-15 compares the major constituents in the contact water between the December 2014 samples and the July 2015 samples. All the major constituent concentrations were much lower in the July 2015 contact water sample than in the December 2014 samples, indicating that these constituents had been leached from the surface of the core as a result of the intervening tests.

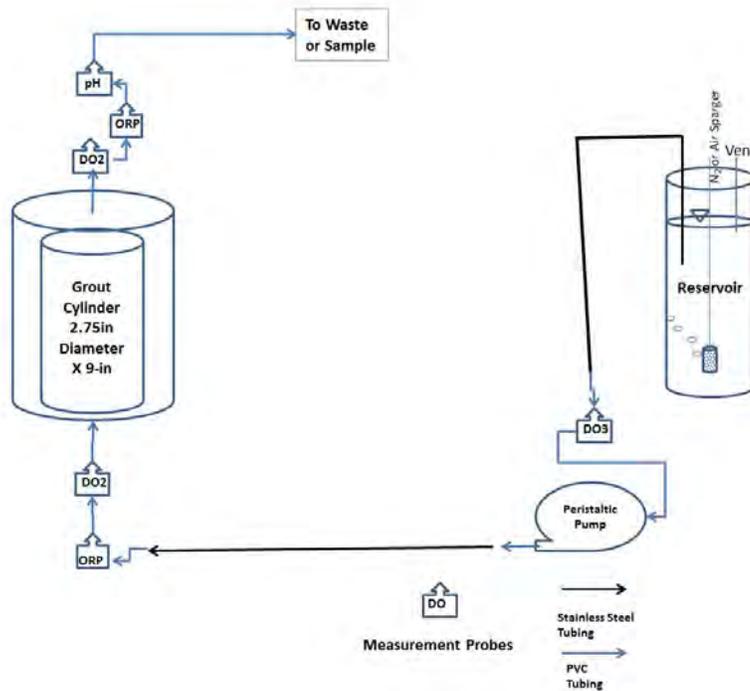
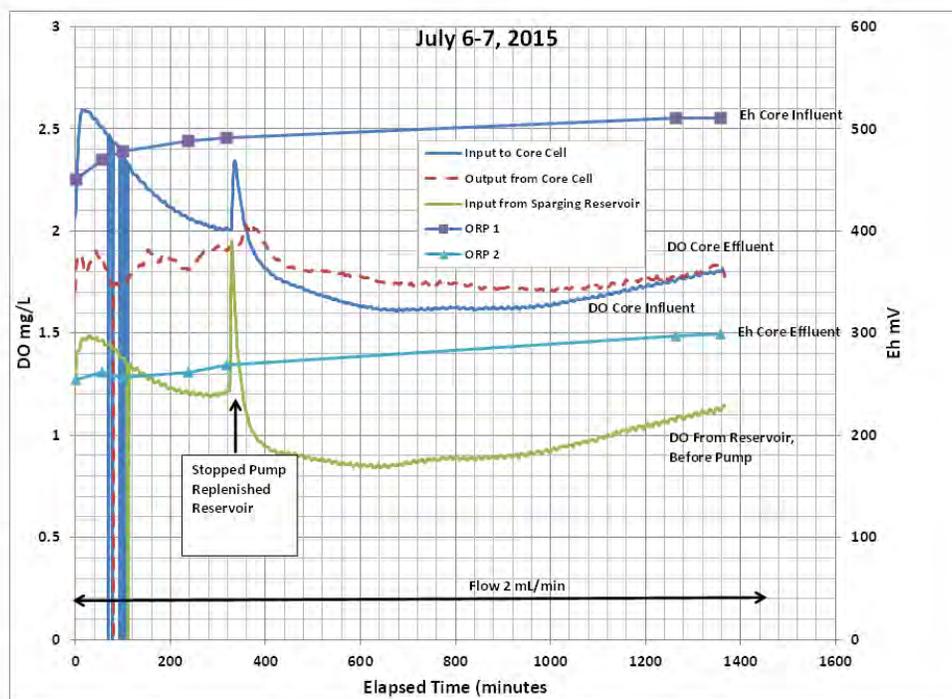
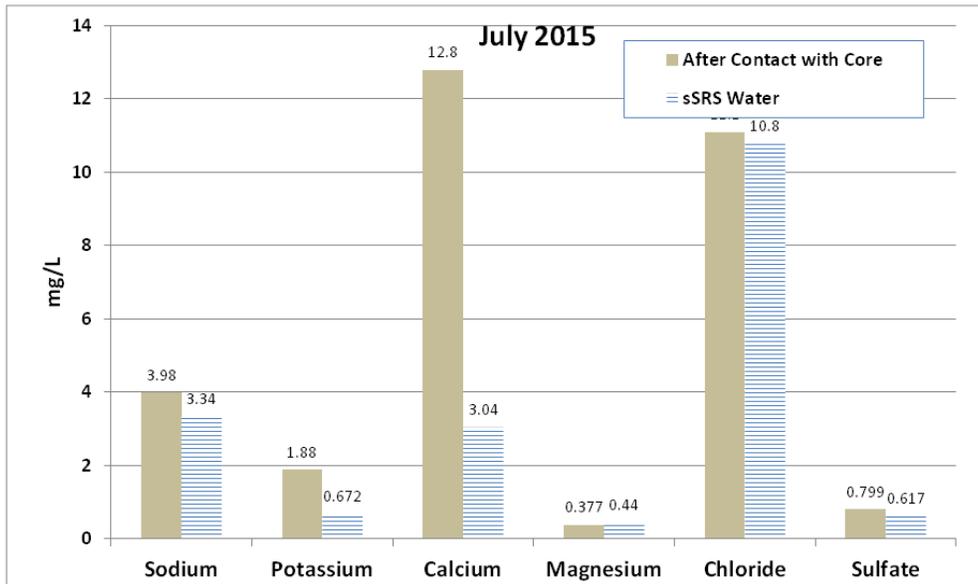


Figure 3-12. Revised Flow Loop Configuration Used in June–July Deaerated Dynamic Flow Tests



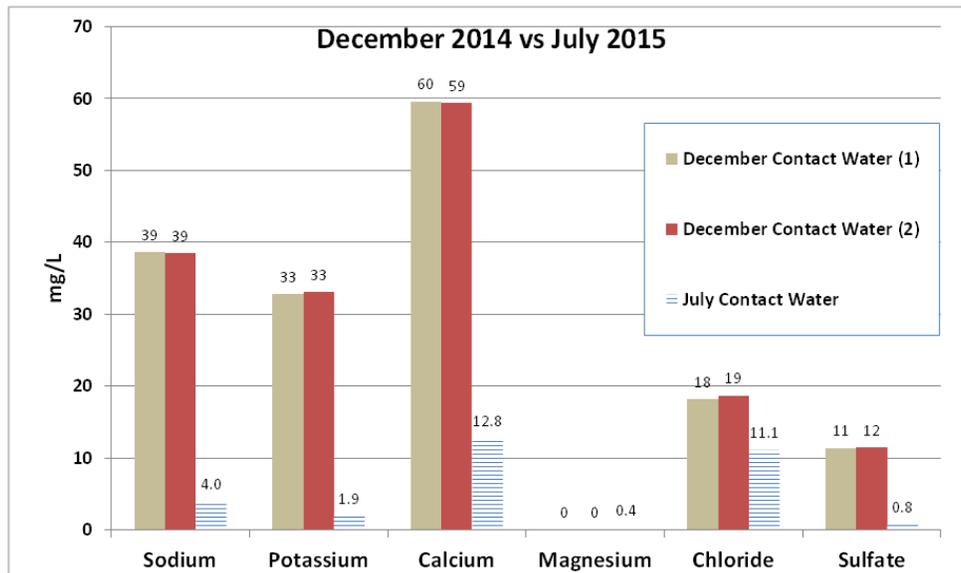
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Figure 3-13. Results of July 6–7, 2015, Deaerated Dynamic Flow Test Showing Changes in Dissolved Oxygen (DO) and Eh Before and After the Core Cell.



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Figure 3-14. Comparison of Major Constituents in Water Samples Before and After Contact With the Core for July 2015 Core 11 Deaerated Test



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Figure 3-15. Comparison of Major Constituents in Contact Water Samples Between December 2014 and July 2015 for Core 11 Tests

Figure 3-16 shows the metals detected in the water samples from the July 2015 test and Figure 3-17 compares the metals detected in the contact water samples between the December 2014 and July 2015 tests. Aluminum and silicon were the only metals that increased significantly after contact with the core in the July 2015 tests and, as shown in Figure 3-17, the metal concentrations in the contact water sample from the July 2015 test were much lower than those detected in the December 2014 contact water samples. Although the December 2014 test was performed under aerated conditions and the July 2015 under deaerated conditions, the pH and Eh values measured during both tests were similar. This suggests that the difference in dissolved metals between the tests was due to leaching of the surface of the core rather than differences in geochemical conditions.

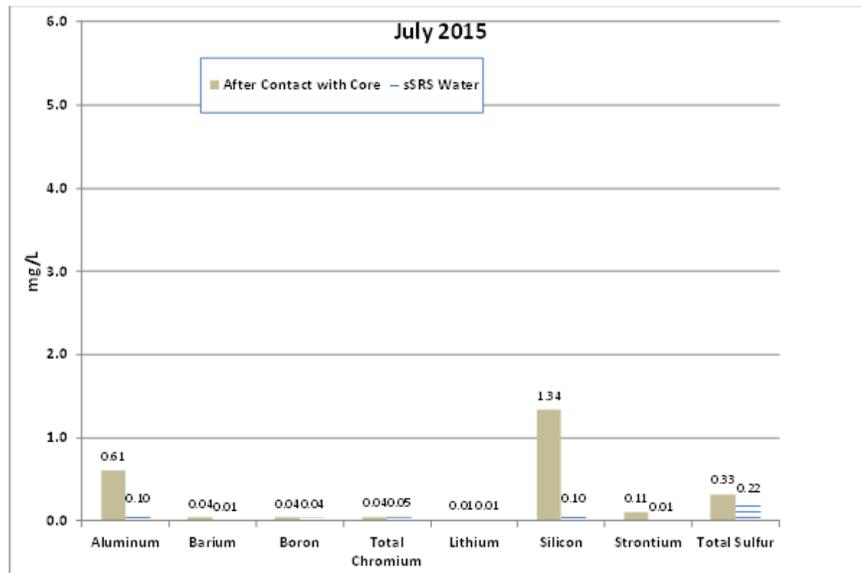
Figure 3-18 shows the distribution of sulfur species measured in the water samples from the July 2015 test and Figure 3-19 compares the contact water sulfur speciation in the

December 2014 and July 2015 tests. Sulfate was the major sulfur species detected in samples from both tests, but the sulfate concentration in the contact water from the July 2015 test was much lower than that detected in the samples from the December 2014 test. Thiosulfate, the major reduced sulfur species detected in the December 2014 samples, was not detected in the July 2015 test even though the July 2015 test was performed using deaerated sSRS water. However, this difference could be due to the overall lower total sulfur concentration in the July 2015 contact water rather than a difference in reducing conditions. As with the other constituents, soluble sulfur species had apparently been leached from the surface of the core during the various tests performed on this core between December 2014 and July 2015.

3.4 Reconfigured Dynamic Flow Apparatus

Based on the tests described in Section 3.3, oxygen was infusing into the flow loop between the sparging reservoir and the core cell, despite the reduced length of PVC tubing. The longest length of PVC tubing in the flow loop was that in the peristaltic pump. To further reduce the potential for oxygen entering the flow loop, the peristaltic pump was replaced with an Agilent 1100 high-performance liquid chromatography (HPLC) pump and the flexible PVC tubing was replaced with 1/8-in OD by 1/16-in ID Fluran[®] F-5500-A tubing (Saint Gobain), which is reported to have a lower permeability with respect to oxygen and other atmospheric gases than most PVC (Tygon) tubing (Saint-Gobain Performance Plastics, 2015). 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). Even lower DO concentrations may be achievable with additional refinements to the flow loop.

The initial dynamic flow tests performed using aerated and deaerated sSRS water indicated that contact with the tank grout raised the pH to values of 10.5 to 11 almost instantaneously but that contact with the tank grout had little effect on the Eh of the water. The lack of a reduction in Eh could have been due to the fact that initial tests using deaerated water still had DO concentrations in the range of 1 to 2 mg/L (1 to 2 ppm). Based on chemical analyses of water used in the November 2014 aerated test on Core 11, contact with the grout significantly increased the concentrations of major constituents and select trace metals. In particular, total dissolved sulfur increase approximately a factor of 10 in the effluent from the core cell relative to the sulfur concentration in the sSRS water. Speciation of dissolved sulfur indicated that sulfate and thiosulfate were the dominant sulfur species in the core cell effluent, suggesting that reduced sulfur compounds in the grout, such as metal sulfides, may have been oxidized by contact with the sSRS water. Some reduction of dissolved hexavalent chromium also occurred during the initial aerated test on Core 11. Subsequent analyses of the effluent from the core cell



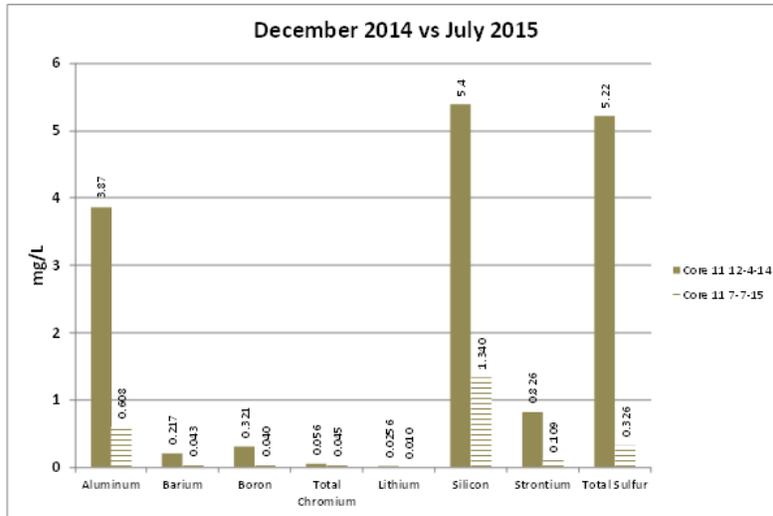
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Figure 3-16. Metals Detected in Water Samples Before and After Contact With Core for July 2015 Core 11 Test

after a test on Core 11 in July 2015 demonstrated that the reactivity of the core surface was significantly reduced by continued contact with sSRS water under oxidizing conditions.

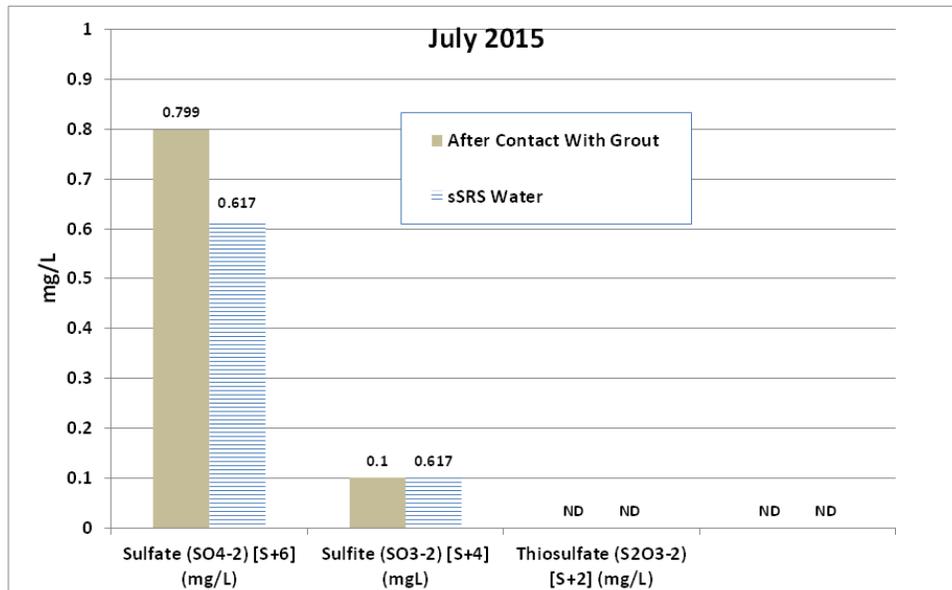
3.5 Summary of Dynamic Flow Tests

The dynamic test results were likely affected by diffusion of oxygen through the flexible tubing used in the flow loop and in the peristaltic pump. A preliminary test using an isocratic pump (Agilent 1100 high-performance liquid chromatography pump) and Fluran tubing indicated that dissolved oxygen concentrations in the flow loop can be reduced to 0.2 mg/L (0.2 ppm) or lower.



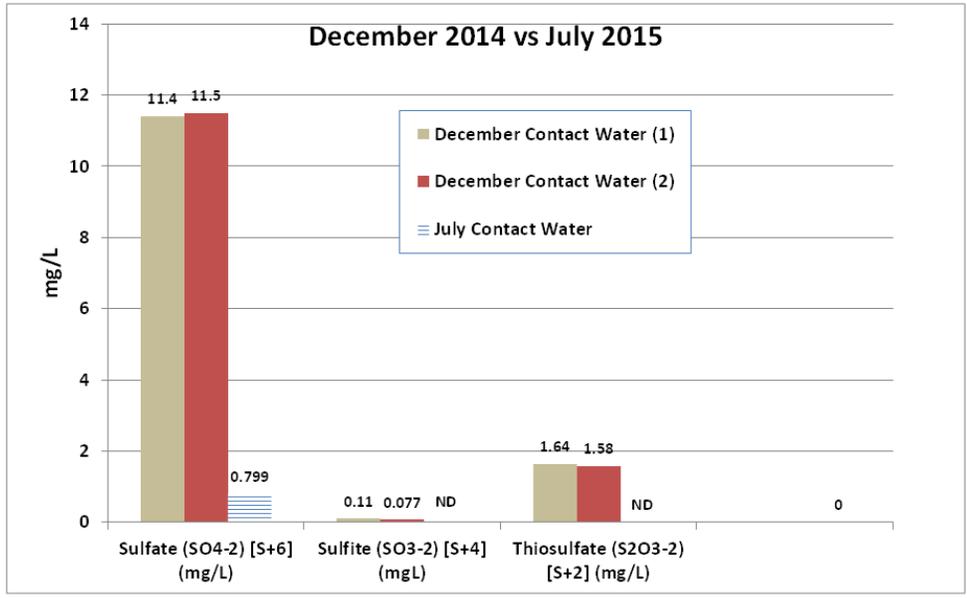
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Figure 3-17. Comparison of Metals Detected in December 2014 Contact Water Samples With Metals Detected in July 2015 Contact Water Samples for Core 11 Tests



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Figure 3-18. Sulfur Speciation in sSRS Water and Core Contact Water for the July 2015 Core 11 Test



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Figure 3-19. Comparison of Sulfur Speciation Between Contact Water for the December 2014 Core 11 Test With Contact Water for the July 2015 Test

4 STATIC TEST DESIGN

The static tests were designed to further investigate the potential reducing capacity of the tank grout by increasing the contact time of the Simulated Savannah River Site (sSRS) water with the grout, increasing the surface area of the grout in contact with the sSRS water, and reducing the dissolved oxygen (DO) concentration in the sSRS water. A preliminary test was performed on samples from Core 11, Middle Section, to test the procedure and a second test was performed on a sample from Core 10, Bottom Section.

4.1 Preliminary Static Test

A preliminary test was performed on a subsample of the middle section of Core 11 using the apparatus shown in Figure 4-1. The core was selected to test the preliminary static test apparatus, although it had been used in previous dynamic flow tests and had been subject to oxidizing conditions, to avoid sacrificing a pristine core if the static test design did not work. The subsample was collected by cutting the core into nominally 1.27-cm [0.5-in]-thick discs using a water-wet diamond saw and then cutting the discs into nominally 1-cm [0.4-in] cubes using the pattern shown in Figure 4-2. The volume of the grout cubes was approximately 26.2 cm³ [1.6 in³] and their surface area was approximately 122 cm² [18.9 in²] based on measurements of the dimensions of each cube.

The preliminary test was performed by placing the grout cubes in a 3-neck flask, adding 155 mL [5.2 fl oz] of sSRS water, and sparging with a gas mixture of nitrogen and 386 ppmv carbon dioxide to remove DO. Oxidation-reduction potential (ORP) was monitored with a Weiss Research gel-filled double junction ORP probe connected to a Hanna Instruments ORP Mini-Controller. ORP was measured in millivolts with respect to the silver/silver chloride (Ag|AgCl) electrode and converted to Eh by adding 200 mV. A prior test had been performed that demonstrated that the sparging process could reduce the dissolved oxygen concentration to less than 0.01 mg/L. Figure 4-3 shows the change in Eh over the course of the approximately 2,500 minute test. The Eh decreased from approximately +300 mV at the start of the test to approximately -100 mV after 1 day, and ended at -109 mV. This result contrasts with the Eh values of +200 to +300 mV measured in the dynamic flow tests reported in Section 3.

4.2 July 30-August 3 2015 Static Test

Based on the results of the preliminary static test, the 3-neck flask was replaced with a 250-mL [8.5-fl oz], 4-neck flask so that both DO and ORP could be measured during the test. The revised test apparatus is shown in Figure 4-4. The static test started on July 30, 2015, was performed using the lower section of Core 10 that had been kept in a heat-sealed mylar bag with an oxygen absorber packet since it was collected in September, 2014. The core was sliced into three nominally 1.27-cm [0.5-in]-thick discs using a water-cooled diamond saw. Each disc was then broken into chips using a hammer to avoid further wetting of the core samples. 176 grams of the chips were placed in the 4-neck flask with 255 mL [8.6 fl oz] of sSRS water. The sizes and shapes of the chips used in the test are shown in Figure 4-5. The Weiss ORP probe and Hamilton DO sensor used in the preliminary static test were then placed in the 4-neck flask (Figure 4-4) and the flask was sparged with the N₂/CO₂ gas described previously. The DO and ORP measurements were recorded manually and the DO percent saturation was recorded using the Hamilton Data Management software.

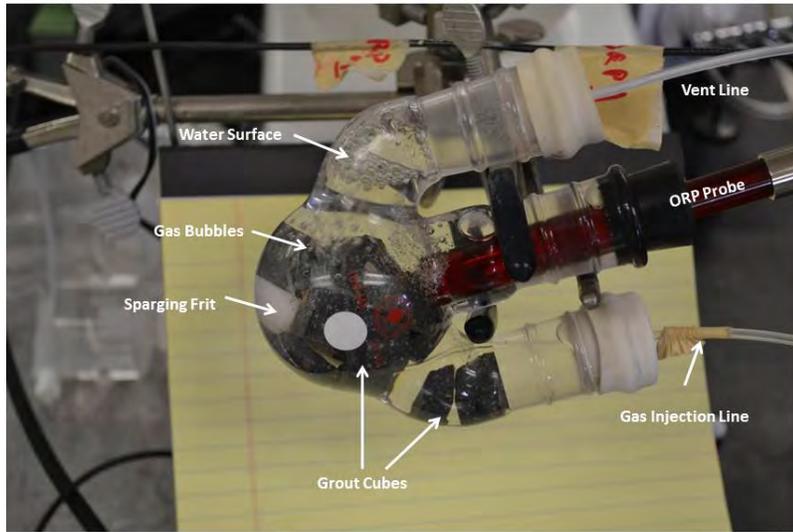
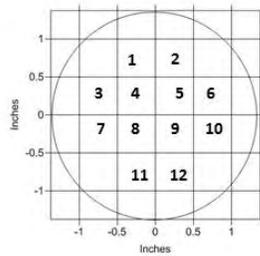


Figure 4-1. Preliminary Static Test Apparatus



Cutting Pattern



Core 11, Middle Section Test Cubes

Figure 4-2. Pattern Used to Cut Core Cubes and Cubes From Core 11, Middle Section, Used in Preliminary Static Test

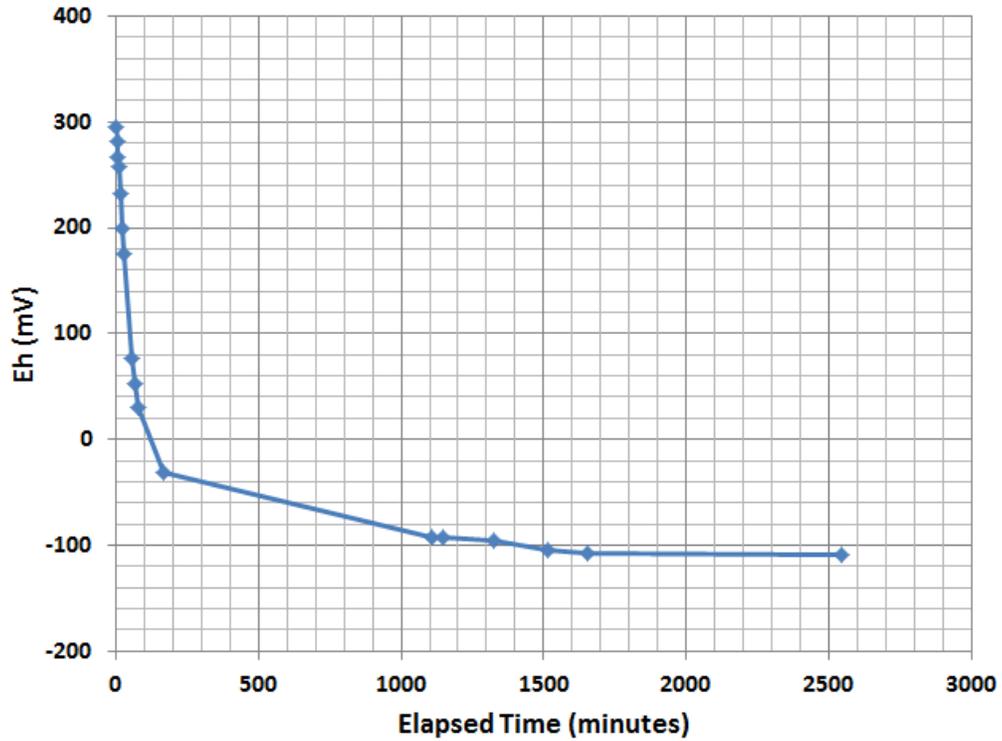


Figure 4-3. Eh Based on ORP Measurements for Preliminary Static Test July 21–23, 2015

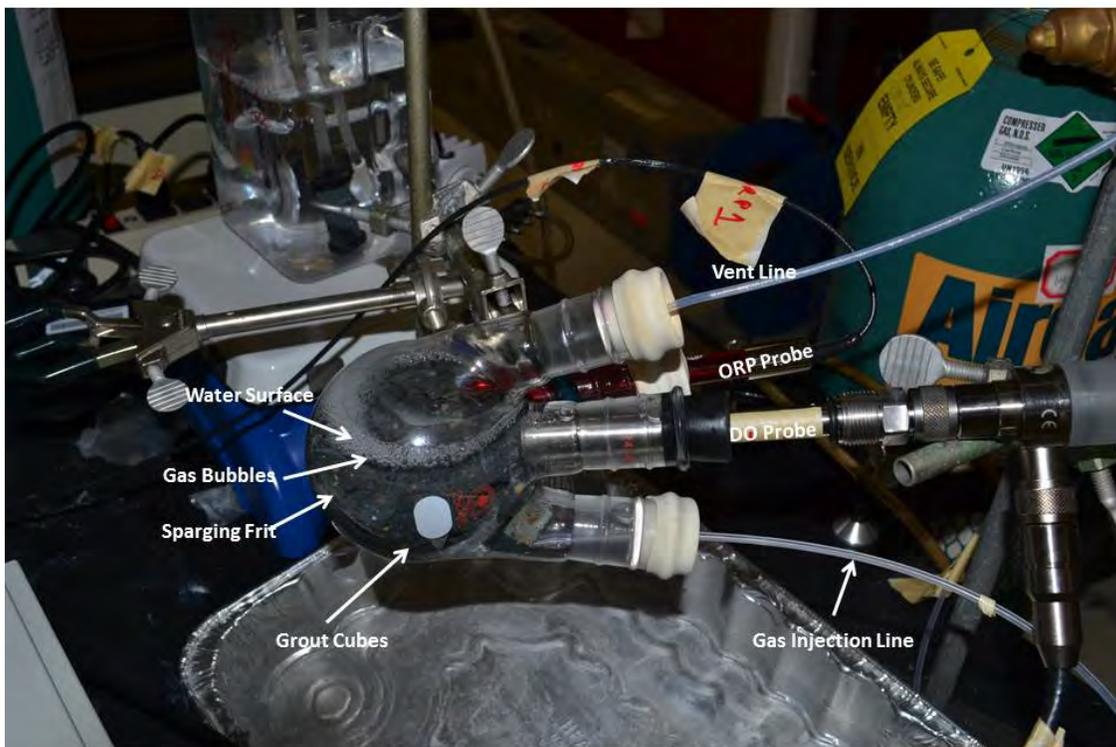


Figure 4-4. Apparatus Used in July 30–August 3, 2015 Static Test on Core 10



Figure 4-5. Chips of Core 10 Used in July 30–August 3, 2015 Static Test

Figure 4-6 shows the changes in DO (as mg/L) and Eh (ORP Ag|AgCl plus 200 mV) measured during the test. The DO concentration was converted from percent saturation using the conversion factor described in Section 3.2. Figure 4-6 shows that the DO in the 4-neck flask decreased rapidly during the first 10 minutes of the test and reached the detection limit of the DO probe (nominally 0.004 mg/L [0.004 ppm]) after 30 minutes. The Eh decreased from an initial value of approximately +320 mV to -180 mV after 5,640 minutes (i.e., almost 4 days). The final Eh was approximately 70 mV lower than the final Eh measured for the test on Core 11. The lower Eh for Core 10 could have been due to Core 10 not having been exposed to oxygenated conditions for as long as Core 11. The difference could also be due to the higher surface area of the Core 10 chips, but the surface area of the Core 10 chips could not be directly estimated because of their highly irregular shapes.

4.3 Summary of Static Tests

The static tests of core fragments from Core 11 Middle Section and Core 10 Bottom Section showed a significantly stronger reducing effect on the sSRS water than was observed during the dynamic flow tests. This increase in reducing effect is attributed to the greatly reduced dissolved oxygen content in the static tests, increased contact time between the water and the grout, and, possibly, the increased surface area and freshness of the surfaces of the grout fragments used in the static tests.

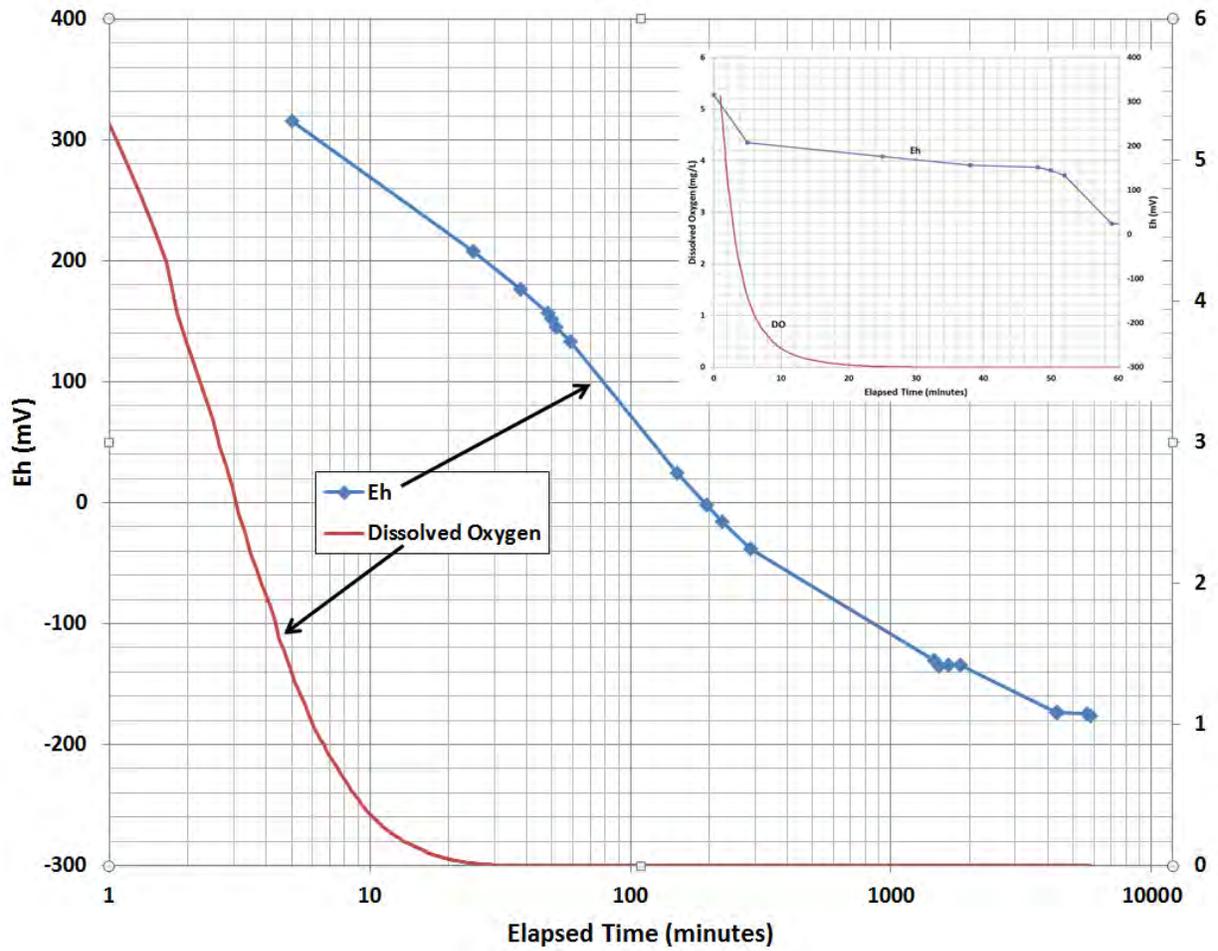


Figure 4-6. DO and Eh Measured During Static Test on Core 10, Bottom Section July 30–August 3, 2015. The Insert Shows the Changes During the First 60 Minutes of the Test on a Linear Time Scale.

5 SUMMARY AND RECOMMENDATIONS

The dynamic flow tests on tank grout core specimens indicated that the tank grout rapidly increased the pH of the sSRS water on contact with the core, but that the grout had little effect on the dissolved oxygen concentration and only slightly lowered the Eh. However, these tests were affected by oxygen diffusion through the flexible tubing used in the peristaltic pump and the flow loop, resulting in relatively high dissolved oxygen concentrations in the flow loop.

Chemical analyses of effluent from the core flow cell indicated that contact with the core significantly increased the concentration of major cations and sulfate, and added mg/L (ppm) concentrations of aluminum, barium, boron, silicon, and strontium. Analysis of sulfur species indicated that oxidation of reduced sulfur species (presumably metal sulfides) in the grout were the sources of the increased sulfate. Slight reduction of hexavalent chromium, added to the sSRS water as a redox indicator, was also observed. Modification of the sSRS water chemistry decreased with increased contact time between the sSRS water and the grout core.

Static tests on sub-samples from the grout cores, in which the dissolved oxygen concentration was reduced to the detection limit of the DO probe (nominally 0.004 mg/L [0.004 ppm]), indicated that the grout could produce strongly reducing conditions in the sSRS water. The difference in results between the dynamic and static tests with respect to the reducing capacity of the grout may be due to increased water-grout contact area and time in the static test apparatus, as well as the significantly reduced dissolved oxygen concentrations in the static tests.

To further investigate the reducing capacity of the grout under dynamic flow conditions, additional tests on intact core specimens using the revised dynamic flow loop apparatus are proposed. These tests will be performed with much lower dissolved oxygen concentrations in the flow loop. Chemical analyses of the effluent from the core flow cell will be performed after one flow loop volume has contacted the core and at the end of the test to further investigate how the grout core modifies the water chemistry with time. New static tests will be designed to investigate the effects of grout surface area and grout-mass-to-water ratios on Eh. The residual reductive capacity of the cores will be determined by slicing the cores into cross-sectional discs and subsampling based on distance from the perimeter. The subsamples will be used to measure the residual reductive capacity using the iron-cerium method described in Kaplan et al. (2008). The process of sectioning the core will inevitably result in exposure of the interior of the core to water and oxygen. To minimize the potential oxidation of the reductive constituents in the grout, the slices and cross-sections will be surface dried and placed in Mylar bags with an oxygen absorbing packet as soon as possible after they are cut.

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