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Office of Nuclear Material Safety and Safeguards

CBarr Signed by Barr, Cynthia on 01/26/21

SUBJECT: SUMMARY OF DECEMBER 9, 2020, WEBINAR CALL RELATED TO EXPERIMENTS CONDUCTED BY THE SAVANNAH RIVER ECOLOGY LABORATORY AND THE CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES TO SUPPORT TANK FARM CLOSURE AT THE SAVANNAH RIVER SITE

On December 9, 2020, the U.S. Nuclear Regulatory Commission (NRC) and U.S. Department of Energy (DOE) held a webinar on research related to the closure of high-level waste tanks at the Savannah River Site (SRS) in Aiken, SC. The webinar included NRC contractors from the Center for Nuclear Waste Regulatory Analyses (CNWRA) and DOE contractors from Savannah River Remediation (SRR) and Savannah River Ecology Laboratory (SREL). The purpose of the webinar was for NRC and DOE contractors to discuss experimental details related to ongoing research conducted by the CNWRA and SREL related to aqueous and solid phase characterization of tank grout and in particular the ability of reducing tank grout to condition infiltrating groundwater to maintain low solubility of key radionuclides in the tank waste. Additional details regarding the webinar are provided below.

Docket No.: PROJ0734

Enclosure: Meeting Summary

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Meeting Summary

Meeting Background

Prior to the webinar, the U.S. Nuclear Regulatory Commission (NRC) and the U.S. Department of Energy (DOE) exchanged the following draft technical reports related to the experiments conducted by the Center for Nuclear Waste Regulatory Analyses (CNWRA) and Savannah River Ecology Laboratory (SREL).

1. SREL Doc.: R-21-0001, *Aqueous and Solid Phase Characterization of Potential Tank Fill Materials*, ML20303A339, Savanah River Ecology Laboratory, Aiken, SC, August 2020.
2. SRR-CWDA-2020-00061 *Application of Characterization of the Aqueous and Solid Phase Chemistry of Closure Grouts*, Savannah River Remediation, Aiken, SC, August 25, 2020.
3. Walter. G.R., C.L. Dinwidddie, *Tank Grout Water-Conditioning Tests—Fiscal Year 2019 Status Report*, ML20126G298, Center for Nuclear Waste Regulatory Analyses, San Antonio, Texas, April 2020.

Additionally, DOE provided two presentations

1. SRR-CWDA-2020-00085, Rev. 1, *Tank Grout Bulk Chemistry Experiments*, Savannah River Remediation, Aiken, SC, December 9, 2020.
2. SRR-CWDA-2020-00088, *Long Term Radiological Lysimeter Program*, Savannah River Remediation, Aiken, SC, December 9, 2020.

CNWRA also provided a presentation, which is attached to this meeting summary.

List of Participants:

NRC
Steve Dembek
Cynthia Barr
George Alexander
Mark Fuhrman

CNWRA/SwRI®
David Pickett
Cynthia Dinwiddie
Gary Walter

DOE-SR
Chuck Comeau

SREL
John Seaman
Christina Logan

SRR
Larry Romanowski
Steve Thomas
Kent Rosenberger
Mark Layton
Greg Flach
Jerry Mangold
Tim Coffield
Bre Cantrell

Larry Romanowski (SRR) opened the meeting. A roll call and brief introductions were conducted. Cynthia Barr (NRC) provided the welcome and discussed the purpose of the meeting, which was to share information on similar research performed by CNWRA and SREL. Research was related to conditioning of infiltrating groundwater by reducing tank grout. Free flowing discussion and questions were encouraged so that the research staffs could learn from each other and help inform future experiments in this area.

Discussions on SRS Grout Experiments
Cynthia Barr provided a summary of tank grout experiments conducted by CNWRA over the last several years including an intermediate-scale grout monolith experiment conducted to study flow through the system, as well as experiments to study the ability of SRS tank grout to condition infiltrating groundwater to favorable chemical conditions necessary to maintain low solubility of key radionuclides in the tank waste. The intermediate-scale (20 ft diameter) tank grout monolith test showed that water could flow through shrinkage gaps between the grout and tank wall, around in-tank components, and even between grout lifts. With regard to the groundwater conditioning experiments, column or flow through experiments were initially conducted to study the ability of the tank grout to condition the groundwater to high pH and low E_h. However, it was difficult to keep oxygen out of the system and achieve the low E_h conditions assumed in the performance assessments (PA) in these tests. Next, batch experiments were performed using tank grout of different particle sizes (i.e., both cubed and crushed grout). Additionally, individual cementitious grout components and simple mixtures of cementitious grout components were also tested in batch experiments to see if lower E_h conditions could be achieved.

Cynthia Dinwiddie and Gary Walter of the CNWRA discussed the tank grout water conditioning test results in more detail including grout formulations, experimental setup, and a summary of the test results. CNWRA's presentation slides are provided in an attachment to this meeting summary. The lowest E_h observed for *tank grout* was significantly higher (−300 mV) using grade 120 slag and a pulverized grout sample. In general, the tank grout experiments showed E_h values significantly higher than assumed in the PA (i.e., around −470 mV in the PAs).
Gregory Flach (SRR) presented results of SREL research that showed that the E_h endpoints

assumed in PA modeling were not achieved (high and low E_h values). The impact of E_h on solubility of key radionuclides and thoughts on future work were also discussed. Gregory Flach mentioned that updated geochemical modeling would be pursued to better understand radionuclide solubility.

Finally, Jerry Mangold (SRR) provided an update on lysimeter testing. Jerry Mangold provided information about lysimeter tests including those with Pu and Ra. Estimated K_d*s* for Pu were significantly higher than previously assumed values. These values will be recommended to Dan Kaplan for the next update to the geochemical data package used to support the tank farm PAs. SRR indicated that lysimeter reports were transmitted to NRC via the Box site at the end of October 2020.

Detailed Technical Discussions
Discussion topics during the presentations included the following:

- CNWRA inquired about tap water SREL used to mix the grout for the experiments (CNWRA used water from Strom and Kaback). Municipal water was used to mix grout at the Argos batch plant, which was later found out to be groundwater[1]. Because SRS groundwater has low dissolved solids content, SREL determined that tap water should be okay. John Seaman indicated that the real difference is how groundwater was modeled versus what was actually being used as mix water (the groundwater should be equilibrated with kaolinite).
- CNWRA inquired about the contents of SRR-CWDA-2019-00038 (Table 2) cited in the SREL report, which was not available for review. DOE explained that it was just a 2-page document cited by SREL by which DOE provided paste and water formulations to SREL for testing.
- CNWRA discussed differences in how environmental conditions were controlled in the tests. CNWRA initially sparged reaction vessels with N_2/CO_2 gas to remove dissolved oxygen. This is in contrast to SREL using hydrogen gas or a Coy Chamber to control oxygen.
- CNWRA discussed potential problems with degradation of septa used to seal water sampling ports in each reaction vessel. Septa were occasionally replaced, but the impact on oxygen ingress was unclear.
- CNWRA recorded ORP, pH, and DO measurements at 2- to 5-minute intervals with automated data recorders, and also recorded these parameters by hand in a scientific notebook at least once per business day.
- NRC inquired about the results of the SREL testing, including increases in E_h over time that suggested potential oxidation as the experiments continued. CNWRA inquired about dilution due to loss of water and inclusion of makeup water. SREL indicated that this would be similar to what is expected in the field.
- NRC inquired about sulfide content and use of XANES or other methods to determine sulfide content. John Seaman indicated that they only looked at total sulfur in XRF and

[1] Following the webinar, CNWRA confirmed that municipal water in Jackson, SC is sourced by groundwater. CNWRA also confirmed that the batch plant had changed ownership from Argos to Smyrna Ready Mix.

did not look at speciation.

- XRD analysis results were similar between CNWRA and SREL. NRC noted amorphous hump in Grade 120 slag (80 percent was in an amorphous phase).
- CNWRA confirmed that Grades 100 or 120 slag from any manufacturer may be used to mix SRS tank grout, because the specification for tank grout is not highly prescriptive. CNWRA also inquired about SREL's use of Ottawa sand rather than the sand from DOE's vendor.
- Sand was not used in the grout formulation for SREL experiments because the quartz peak associated with sand would overwhelm XRF results (quartz peak interference), although sand was added to the columns in the experiments to homogenize flow.
- NRC inquired if there were any pressure anomalies that would suggest channeling or blockage. There was also discussion of residence time and its impact on grout water conditioning. SREL's 5 mL/day flow rate was discussed and characterized as very low (and potentially leading to longer residence times for reaction compared to higher flow rates).
- CNWRA inquired if DOE's remaining compressive-strength grout cylinders could be used for grout water-conditioning testing. DOE indicated that these were not available.
- NRC indicated that it would be important to update geochemical modeling for solubility, as well as for E_h evolution, because even if the E_h were known, the solubility-limiting phases in the pH/ E_h diagrams from PA modeling may not be correct based on high-level waste leaching experiments. For example, solubility of key radionuclides such as Pu, Tc, and U were orders of magnitude higher than assumed in PA modeling. DOE agreed it planned to update the geochemical modeling, including an update of minerology and potentially using a new thermodynamic database. DOE invited NRC to provide recommendations for additional research and updated PA modeling.
- With regard to SRR's calculations of K_d for Pu, NRC inquired if SRR thought about calculating the K_d based on the retardation factor and how far Pu had traveled. Earlier research showed that a small fraction of Pu could travel much further and a K_d of 3 L/kg would be appropriate for this fraction.

SRR indicated that a routine environmental monitoring report (Eastern and Western Groundwater Operable Unit scoping) was completed. The report was provided to NRC for review following the webinar.

Attachment
CNWRA Presentation Slides

CNWRA'S GROUT WATER-CONDITIONING EXPERIMENTS

by
Gary R. Walter &
Cynthia L. Dinwiddie

SRS REDUCING TANK GROUT, LP#8-16

SRS REDUCING TANK GROUT, LP#8-16

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

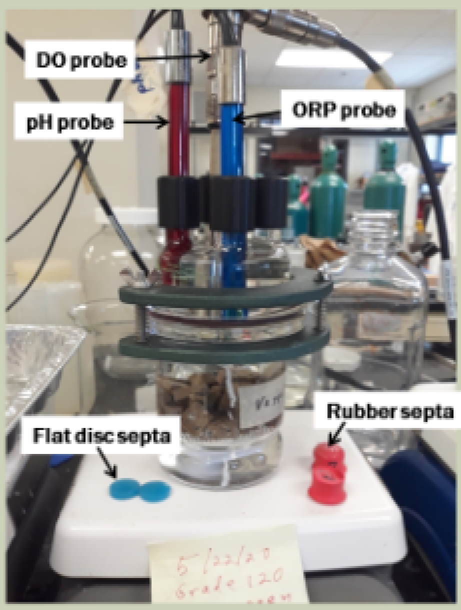
Table 1. Small-scale reducing tank grout LP#8-016[*] component quantities per batch

Formula	Cementitious Materials				DI Water	w:c	Aggregate		Admixtures[†]		
	Portland Cement Type I/II[‡]	Slag Grade 120[§]	Fly Ash Class F[‖]	Total Cementitious Mass			Quartz Sand[¶]	Gravel No. 8[#]	ADVA Cast 575	EXP-958	Recover Hydration Stabilizer
	grams								ml		
Nominal LP#8 Single Batch	100.0	168.0	290.4	558.4	323.2	0.58	1432.0	640.0	2.0	2.0	0.3
Actual LP#8 Double Batch	200.01	336.1	580.81	1116.92	627.1	0.56	2864.01	1279.96	4.0	4.0	0.6

[*]Final formula based upon Argos batch tickets (SRR-CWDA-2013-00026)
[†]W.R. Grace and Company, Columbia, Maryland
[‡]Holcim US, Inc., Birmingham, Alabama
[§]Lehigh Cement Co., LLC, Fort Lauderdale, Florida
[‖]SEFA Group, Inc., Lexington, South Carolina
[¶]South Carolina Minerals, Inc., North Augusta, South Carolina
[#]Aggregates USA, Grovetown, Georgia

Question: What is the source of water used at the Argos Batch Plant to mix their tank grout?

GROUT WATER-CONDITIONING 4-PORT REACTION VESSEL & PROBES



- Synthetic SRS groundwater prepared per WSRC-RP-92-450 (Strom & Kaback 1992)
- Previous tests performed by sparging reaction vessels with a N_2/CO_2 gas mixture to remove DO (Walter & Dinwiddie 2017)
- DO consumption test performed without sparging confirmed that reducing tank grout can consume DO under closed conditions (Walter & Dinwiddie 2019)
- Probes:
  - Hamilton VisiFerm™ D120 optical DO probe
  - Weiss Research gel-filled double-junction ORP & pH probes
- Conditioned solution chemistry sampled once at the end of each test

DYNAMIC TESTS (FY2015)

ML#/FY	Specimen (Slag Grade/Source/ Date Prepared	Physical Form/ Test Type	Storage Time (months)	Flow Rate (ml/min)/ H_2O-grout mass ratio/ test duration (days)	Final pH/DO(%sat)/Eh(mV)	Other parameters/ Experimental artifacts
ML15302A08/FY15	Unknown/Intermediate Scale Monolith/9-2014	Annular flow around core/ closed-loop	2	1.1/0.84/23	11.6/≈60/+254	Aerated sSRS water, Core 11 middle
	Unknown/Intermediate Scale Monolith/9-2014	Annular flow around core/ closed-loop	2	2.0/0.19/3.8	10.5/≈40/+250	deaerated sSRS water, Core 11 middle/ DO increased during test
	Unknown/Intermediate Scale Monolith/9-2014	Annular flow around core/ closed-loop	2	1.1/≈0.2/9.7	11.9/≈60/+215	Aerated sSRS water, Core 12 middle
	Unknown/Intermediate Scale Monolith/9-2014	Annular flow around core/ open-loop	6	2.0/not measured/1	10.5/≈20/≈+250	Deaerated sSRS water, Core 11 middle

Difficulties in preventing oxygen ingress led to pursuit of static tests in later years.

STATIC TESTS (FY2015–2020)

ML#/FY	Specimen (Slag Grade/ Date Prepared	Physical Form	Laboratory Storage Time (days)	Minimum Eh (mV)/Min DO% sat/Reaction Duration (days)	Solids Mass (g)/ Water Vol (mL)	Other parameters/ Experimental artifacts
TBD/FY20	Grade 100 slag grout/ 8/17/2015	Cubed Grout (~1cm³ scale)	1606	+171/96.7/1.11	99.0 (31 cubes)/ 538	4-neck vessel 3; grout sample on Pt-coated niobium screen
	Grade 120 slag grout/ 4/11/2016		700	−31/0.4/93	106 (24 cubes)/ 517	4-neck vessel 2, test 1; grout sample on Pt-coated niobium screen
			141	−129/0.4/40 −65/04/88	104/505	4-neck vessel 2, test 2; grout sample on SS screen
			48	+203/−63/19	98.2 (31 cubes)/ 560	4-neck vessel 1, test 1; grout sample on Pt-coated niobium screen, DO>60%
				+232/−65/7		4-neck vessel 1, test 2; grout sample on Pt-coated niobium screen, DO>60%
ML20126G298/FY19	Grade 120 GGBFS/NA	Neat	NA	−414/~3/36	100/546	4-neck vessel; bagged sample on Pt-coated niobium screen
	Grade 120 GGBFS/ Portland cement/NA	50/50 Mix	NA	−310/~2/10 −212/~2/15	100/538	4-neck vessel; bagged sample on Pt-coated niobium screen
	Grade 120 slag grout/ 4/11/2016	Pulverized Grout	318	−299/0/153	94/548	4-neck vessel; bagged sample on Pt-coated niobium screen
ML19105B156/ FY17 & FY18	Grade 120 slag grout/ 4/11/2016	Cubed Grout (~1cm³ scale)	2	−254/0/130	74/552	4-neck vessel; grout sample on SS screen
ML18285A834/FY16	Grade 100 slag grout/ 8/17/2015	Cubed Grout (~1cm³ scale)	≈1	−76/6	140/200	4-neck flask sparged w/ N_2/388 ppmv CO_2, Tests 1–3
	Grade 100 slag grout/ 8/17/2015	Cubed Grout (~1cm³ scale)	≈30	−100/3.5	180/200	4-neck flask sparged w/ N_2/388 ppmv CO_2, Tests 4–6
ML15302A081/FY15	Slag grade unknown/core sample from Intermediate Scale Grout Specimen	Various sized chips	1	−180/4	176/256	4-neck flask sparged w/ N_2/388 ppmv CO_2

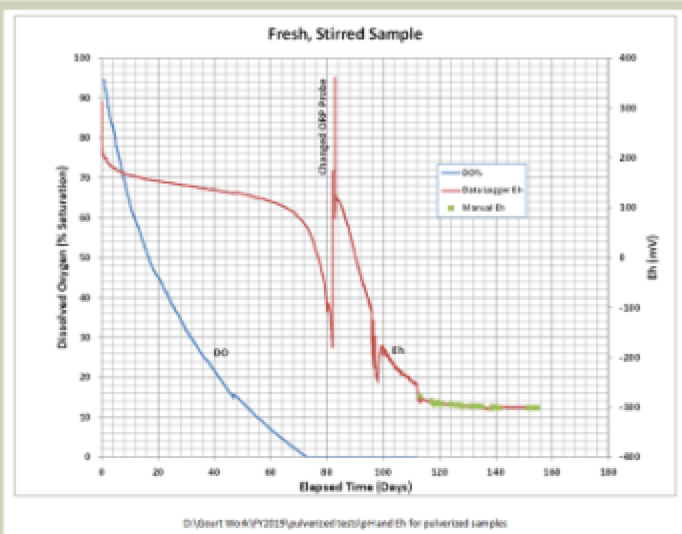
GROUT COMPONENT & MIXTURE TESTS

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

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

*Minimum value during test

PULVERIZED DO/EH



CUBED SAMPLE WITH STAINLESS STEEL AND PLATINUM SUPPORT SCREENS