

SRR-CWDA-2020-00050

Revision 0

September 24, 2020

To: K. H. Rosenberger, 705-1C

From: G. P. Flach, 705-1C

Reviewed per SRR Procedure S4-ENG.51: S. P. Hommel, 705-1C

Update to Projected Degradation of Saltstone Disposal Facility Cementitious Materials to Evaluate SDU Concrete Mix 3B and Cement-Free Saltstone

The Saltstone Disposal Facility (SDF) Performance Assessment (PA) considers degradation of cementitious materials through sulfate attack, corrosion of embedded steel (reinforcing bars) that is controlled by carbonation, and/or decalcification. [SRR-CWDA-2019-00001] The SDF cementitious materials analyzed are:

- Saltstone composed of 45% slag, 45% fly ash, and 10% cement mixed with decontaminated salt solution (45/45/10 saltstone) and
- The various concrete mixes used in Saltstone Disposal Unit (SDU) design-types 1, 2, 4, 6, and 7. [SRNL-STI-2018-00077]

Since then two new cementitious materials have been proposed for use in future SDF liquid waste solidification and SDU construction:

- Cement-free saltstone with a dry mix composed of 60% slag and 40% fly ash as described in SRR-CWDA-2019-00003 (60/40/0 saltstone), and
- High-quality concrete with a binder composed of cement, slag, and metakaolin for future SDUs (e.g., SDU 8) and identified as “Mix 3B” in mix design and testing report SRR-SDU-2019-00026 (SDU 8/Mix 3B concrete).

Purpose

This study expands the SDF PA degradation analysis (SRNL-STI-2018-00077) to include 60/40/0 saltstone and SDU 8/Mix 3B concrete. The degradation analysis has also been updated to reanalyze 45/45/10 saltstone and SDU 2/6/7 design-type concrete using alternative estimates of chemical reaction capacity for sulfate attack, carbonation, and decalcification.

Normative Mineral Analysis

Chemical reaction capacities in the SDF PA degradation analysis are based on normative mineral compositions of hydrated saltstone and SDU 2/6/7 concrete estimated by SIMCO Technologies, Inc. (2010, 2012). In this study, reaction capacities are based on an updated normative mineral composition analysis, SRR-CWDA-2020-00066, recently conducted for all four materials of interest: 45/45/10 saltstone, 60/40/0 saltstone, SDU 2/6/7 concrete, and SDU 8 (Mix 3B) concrete. SRR-CWDA-2020-00066 generated four normative mineral compositions for each cementitious material by combining two methods with two assumptions on binder reactivity (degree of hydration). One method is a slight modification of the SRNL-STI-2018-00586 / SRNL-TR-2008-00283 approach and the other method is that of Herfort and Lothenbach



(2017). The two reactivity assumptions are 100% hydration of all binders and partial hydration: 100% of cement, 70% of slag, and 40% for the remaining binders.

The other needed material properties are taken from SRR-CWDA-2020-00036 and SRR-CWDA-2020-00040. The physical properties of 45/45/10 saltstone and SDU 2/6/7 concrete are unchanged from the SDF PA, and the recommended physical properties of 60/40/10 saltstone for modeling are the same as 45/45/10 saltstone. The saturated hydraulic conductivity (K_{sat}) and effective diffusion coefficient (D_e) of SDU 8/Mix 3B concrete are slightly higher than those for SDU 2/6/7 concrete.

A normative mineral analysis uses general knowledge of cement hydration reactions, equilibrium constants and kinetics, and degrees of reaction to virtually react the mix dry ingredients with water to form a plausible set of hydrated minerals constituting the cured material. Stoichiometry is used to preserve the collective mass of each chemical element through the process, based on the specified proportions and metal oxide analyses of the dry ingredients and the water-to-cementitious materials (w/c) ratio. Tables 1 and 2 list the hydrated minerals considered in each normative mineral analysis using cement chemist notation. The SRNL method was modified primarily by adding Portlandite and gypsum to the previously assumed set of potential minerals present in hydrated material; these two minerals were added to consume any excess calcium and sulfur, respectively. Minerals in common to both sets are highlighted. [SRR-CWDA-2020-00066]

Table 1. Mineral set assumed in modified SRNL normative mineral composition analysis.

Potential Mineral	Cement Chemist Notation†	Molecular Formula
Portlandite	CH	$Ca(OH)_2$
Calcium Silicate Hydrate	CSH	$CaSiO_3 \cdot H_2O$
Hydrotalcite	M_4AH_{10}	$Mg_4Al_2O_7 \cdot 10H_2O$
Kaolinite	AS_2H_2	$Al_2Si_2O_5(OH)_4$
Gibbsite	$A_{0.5}H_{1.5}$	$Al(OH)_3$
Gypsum	CsH_2	$CaSO_4 \cdot 2H_2O$
Pyrrhotite	—	FeS
Unreacted Quartz	S	SiO_2
Unreacted Iron Oxide	F	Fe_2O_3
Unreacted H ₂ O	H	H_2O

† Shorthand notation: $A:Al_2O_3$, $c:CO_2$, $C:CaO$, $H:H_2O$, $M:MgO$, $s:SO_3$, $S:SiO_2$

Table 2. Mineral set assumed by Herfort-Lothenbach (2017).

Potential Mineral	Cement Chemist Notation†	Potential Mineral	Cement Chemist Notation
Portlandite	CH	Calcite	Cc
High-Ca C-S-H	$C_{1.75}SH_4$	Monocarbonate	C_4AcH_{11}
High-Ca C-A-S-H	$C_{1.75}SA_{0.05}H_4$	Hemicarbonate	$C_4Ac_{0.5}H_{12}$
C-A-S-H	$C_{1.3}SA_{0.1}H_3$	OH-AFm	C_4AH_{13}
Low-Ca C-A-S-H	$C_{0.67}SA_{0.05}H_2$	Friedel's salt	$C_4ACl_2H_{10}$
Low-Ca C-S-H	$C_{0.67}SH_2$	Kuzel's salt	$C_4As_{0.5}Cl_2H_{12}$
Hydrotalcite	M_4AH_{10}	Strätlingite	C_2ASH_8
Gypsum	CsH_2	Katoite	C_3AH_6
Ettringite	$C_6As_3H_{32}$	Ca-stilbite	$C_{0.17}SA_{0.17}H_{1.04}$
Thaumasite	C_3SscH_{15}	Amorphous silica	S
Monosulfate	C_4AsH_{12}	Aluminum hydroxide	AH_3
Hemisulfate	$C_4As_{0.5}H_{12.5}$	Unreacted H ₂ O	H

† Shorthand notation: $A:Al_2O_3$, $c:CO_2$, $C:CaO$, $H:H_2O$, $M:MgO$, $s:SO_3$, $S:SiO_2$

Although the two mineral sets are quite different, the impact on degradation predictions is much lower than might be expected because degradation reaction capacities are expressed in terms of total aluminum and calcium, regardless of the hydrated mineral(s) in which they appear. Total hydrated aluminum and calcium concentrations depend mostly on mix ingredients, ingredient proportions and compositions, assumed degree of hydration, and any calibration to measured properties (e.g., bulk density). The SRNL method calibrated the hydrated mineral set to measured bulk density and reduction capacity. No calibration was performed using the Herfort-Lothenbach method.

Reaction Capacities from the Normative Mineral Analysis

Table 3 presents reaction capacities from SRR-CWDA-2020-00066. Among the four normative mineral composition cases, the Herfort / Lothenbach method coupled with the partial hydration exhibits the lowest *Al* reaction capacity for concretes which controls sulfate attack, the dominant degradation phenomenon. For saltstone, the modified SRNL method coupled with partial hydration produces the lowest reaction capacity. The partial hydration assumption produces a lower reaction capacity and higher degradation rate than the complete hydration assumption for either material. As a conservatism, only the reaction capacities from the partial hydration cases are carried forward.

Table 3: Chemical reaction capacities from SRR-CWDA-2020-00066.

Parameter	45/45/10 Saltstone	60/40/0 Saltstone	SDU2/6/7 Concrete	Mix 3B Concrete
Modified SRNL method w/property adjustment, complete hydration				
Aluminum concentration, mol/g-solid	2.82E-03	3.04E-03	4.27E-04	4.90E-04
Calcium concentration, mol/g-solid	3.53E-03	4.60E-03	1.18E-03	1.59E-03
Calcium concentration, mol/cm ³	3.29E-03	4.29E-03	2.57E-03	3.58E-03
Modified SRNL method w/property adjustment, partial hydration				
Aluminum concentration, mol/g-solid	1.43E-03	1.73E-03	2.43E-04	3.11E-04
Calcium concentration, mol/g-solid	2.89E-03	3.21E-03	1.03E-03	1.44E-03
Calcium concentration, mol/cm ³	2.69E-03	2.99E-03	2.25E-03	3.23E-03
Herfort-Lothenbach method, complete hydration				
Aluminum concentration, mol/g-solid	2.59E-03	2.74E-03	4.26E-04	4.89E-04
Calcium concentration, mol/g-solid	3.27E-03	4.19E-03	1.19E-03	1.58E-03
Calcium concentration, mol/cm ³	4.11E-03	5.48E-03	2.69E-03	3.64E-03
Herfort-Lothenbach method, partial hydration				
Aluminum concentration, mol/g-solid	1.34E-03	1.64E-03	2.42E-04	3.08E-04
Calcium concentration, mol/g-solid	2.75E-03	3.05E-03	1.03E-03	1.41E-03
Calcium concentration, mol/cm ³	3.18E-03	3.51E-03	2.28E-03	3.20E-03

Degradation Rate Coefficients

Tables 4 and 5 summarize degradation rate coefficients calculated from the reaction capacities (Table 3) and using the same methods as described in SRNL-STI-2018-00077, for partial hydration and for each of the three analysis cases: Compliance Value (CV), Best Estimate (BE), and Conservative Estimate (CE). Figures 1 through 3 present the CV results in graphical form.

Cement-free 60/40/0 saltstone is projected to degrade slower than 45/45/10 saltstone (Figure 3). SDU 8/Mix 3B concrete is projected to degrade faster than SDU 2/6/7 concrete (Figures 1 and 2), primarily because of its higher effective diffusion coefficient rather than compositional differences. However, the rate coefficients used in the SDF PA are higher than those from this study, except for carbonation of SDU 8/Mix 3B concrete. Although SDU 8/Mix 3B concrete is projected to carbonate at a faster rate than assumed in

the SDF PA, sulfate attack dominates concrete degradation such that the net degradation rate of SDU 8/Mix 3B concrete is projected to be slower than the rate assumed in the SDF PA. Because concrete degradation rates are more impactful to the SDF PA than saltstone rates within the 1000-year Compliance Period, only the Herfort-Lothenbach partial hydration rate coefficients are carried forward.

Table 4: Degradation rate coefficients for concrete.

Rate Coefficient (cm/Vyr)	Sulfate Attack			Carbonation-Controlled Corrosion		
	PA Ref.	Mod. SRNL partial hydration	Herfort- Lothenbach partial hydration	PA Ref.	Mod. SRNL partial hydration	Herfort- Lothenbach partial hydration
<i>SDF PA Compliance Value (CV) case</i>						
SDU 2/6/7 Concrete	0.223	0.110	0.110	0.120	0.101	0.101
SDU 8 Concrete	N/A	0.157	0.159	N/A	0.144	0.144
<i>SDF PA Best Estimate (BE) case</i>						
SDU 2/6/7 Concrete	0.182	0.089	0.090	0.023	0.082	0.082
SDU 8 Concrete	N/A	0.123	0.124	N/A	0.113	0.113
<i>SDF PA Conservative Estimate (CE) case</i>						
SDU 2/6/7 Concrete	0.238	0.117	0.117	0.199	0.108	0.107
SDU 8 Concrete	N/A	0.195	0.197	N/A	0.178	0.179

Table 5: Degradation rate coefficients for saltstone.

Rate Coefficient (cm/yr)	Decalcification		
	PA Ref.	Mod. SRNL partial hydration	Herfort- Lothenbach partial hydration
<i>SDF PA Compliance Value (CV) case</i>			
45/45/10 Saltstone	7.6E-05	3.5E-05	3.0E-05
60/40/0 Saltstone	N/A	3.2E-05	2.7E-05
<i>SDF PA Best Estimate (BE) case</i>			
45/45/10 Saltstone	5.1E-06	2.3E-06	2.0E-06
60/40/0 Saltstone	N/A	2.1E-06	1.8E-06
<i>SDF PA Conservative Estimate (CE) case</i>			
45/45/10 Saltstone	5.1E-04	2.3E-04	2.0E-04
60/40/0 Saltstone	N/A	2.1E-04	1.8E-04

Figure 1: Degradation rate coefficients for sulfate attack on concrete.

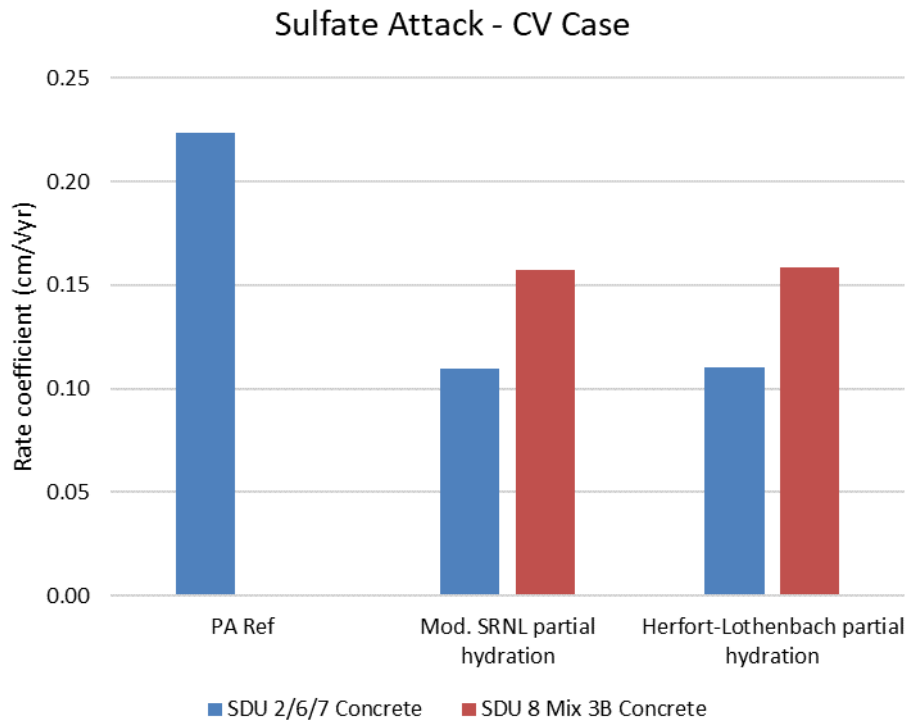


Figure 2: Degradation rate coefficients for carbonation of concrete.

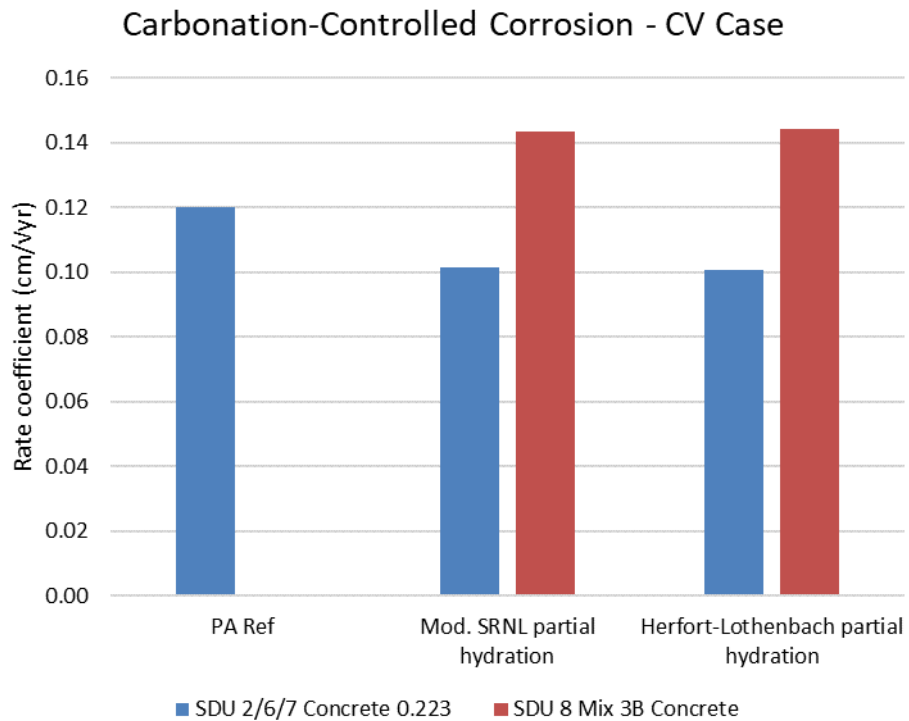
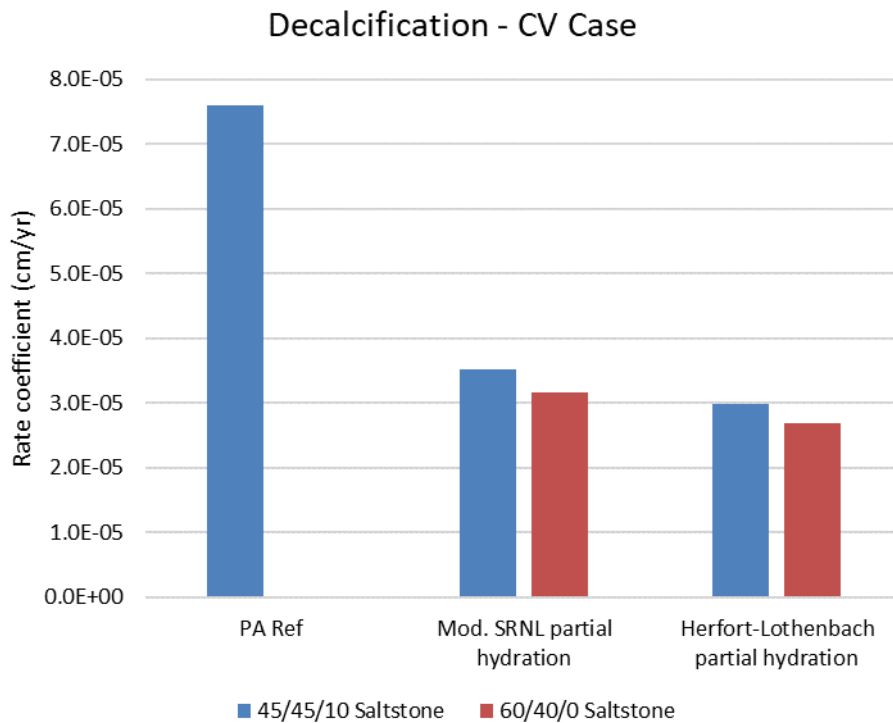


Figure 3: Degradation rate coefficients for advective decalcification of saltstone.



Updated Degradation Analysis Results

Table 6 summarizes the start and end times of physical degradation and associated saturated hydraulic conductivity end members for various cementitious materials and analyses. “SDU 7 Design” columns present degradation times and K_{sat} values for SDU 7 from the SDF PA for reference (SRNL-STI-2018-00077). “SDU 7 + 45/45/10” denotes degradation times from this study for SDU 7, that is, the SDU 7 geometry, SDU 2/6/7 concrete mix, and 45/45/10 saltstone. Hydraulic conductivities are not affected by reaction capacity assumptions, so “SDU 7 + 45/45/10” K_{sat} values are the same as the SDF PA (“SDU 7 Design”) and not explicitly shown. “SDU 8 + 60/40/0” denotes the SDU 8 geometry (assumed same as SDU 7), Mix 3B concrete mix, and 60/40/0 saltstone. Further detail on degradation timing is provided in Tables 7 and 8.

Consistent with the earlier discussion of rate coefficients, degradation times from this study for all four cementitious materials (SDU 2/6/7 concrete, SDU 8/Mix 3B concrete, 45/45/10 saltstone, 60/40/0 saltstone) exceed those from the SDF PA, indicating relative conservatism in the PA. SDU 8/Mix 3B concrete has a higher initial K_{sat} than SDU 2/6/7 concrete per SRR-CWDA-2020-00036 (1.0E-09 cm/s versus 7.8E-10 cm/s), but the SDF PA determined that values as high as 1.0E-7 cm/s have minimal impact on SDF performance (Section 5.8.3.3 of SRR-CWDA-2019-00001). The initial K_{sat} is the same for 45/45/10 and 60/40/0 saltstone per SRR-CWDA-2020-00040.

Table 6: Summary of degradation times and saturated hydraulic conductivities.

Degradation start and end times

SDU 7 Design				SDU 7 + 45/45/10				SDU 8 + 60/40/0			
CE (yr)	CV (yr)	BE (yr)		CE (yr)	CV (yr)	BE (yr)		CE (yr)	CV (yr)	BE (yr)	
0	0	0		0	0	0		0	0	0	
Roof	12 in			Roof	12 in			Roof	12 in		
1371	1552	2306		3889	4294	6035		1933	2545	3597	
0	0	0		0	0	0		0	0	0	
Floor	24 in			Floor	24 in			Floor	24 in		
2312	2800	4603		6912	7745	11251		3004	4160	6288	
0	0	0		0	0	0		0	0	0	
Wall ⑤	10.72 in			Wall ⑤	11.02 in			Wall ⑤	11.02 in		
720	1075	2020		2818	3190	4831		1005	1547	2514	
0	0	0		0	0	0		0	0	0	
Wall ④	12.26 in			Wall ④	12.61 in			Wall ④	12.62 in		
824	1229	2316		3225	3651	5529		1151	1770	2877	
0	0	0		0	0	0		0	0	0	
Wall ③	14.92 in			Wall ③	15.37 in			Wall ③	15.38 in		
1002	1496	2829		3931	4451	6740		1403	2158	3507	
0	0	0		0	0	0		0	0	0	
Wall ②	17.62 in			Wall ②	18.17 in			Wall ②	18.18 in		
1184	1767	3349		4648	5262	7968		1658	2552	4146	
0	0	0		0	0	0		0	0	0	
Wall ①	20.22 in			Wall ①	20.88 in			Wall ①	20.89 in		
1358	2028	3851		5340	6046	9155		1906	2932	4764	
1371	1552	2306		3889	4294	6035		1933	2545	3597	
Grout	516 in			Grout	516 in			Grout	516 in		
2.6E+06	1.7E+07	2.6E+08		6.6E+06	4.4E+07	6.6E+08		7.3E+06	4.9E+07	7.3E+08	
0	0	0		0	0	0		0	0	0	
Column	10.63 in			Column	10.63 in			Column	10.63 in		
72	92	299		72	92	299		72	92	299	

Hydraulic conductivity end-members

SDU 7 Design				SDU 8 + 60/40/0			
CE (cm/s)	CV (cm/s)	BE (cm/s)		CE (cm/s)	CV (cm/s)	BE (cm/s)	
9.1E-10	7.8E-10	6.4E-10		2.0E-09	1.0E-09	7.0E-10	
Roof	12 in			Roof	12 in		
4.1E-05	4.1E-05	4.1E-05		4.1E-05	4.1E-05	4.1E-05	
9.1E-10	7.8E-10	6.4E-10		2.0E-09	1.0E-09	7.0E-10	
Floor	24 in			Floor	24 in		
9.1E-05	9.1E-05	9.1E-05		9.1E-05	9.1E-05	9.1E-05	
9.10E-10	7.80E-10	6.40E-10		2.00E-09	1.00E-09	7.00E-10	
Wall ⑤	10.72 in			Wall ⑤	10.98 in		
4.1E-05	4.1E-05	4.1E-05		4.1E-05	4.1E-05	4.1E-05	
9.10E-10	7.80E-10	6.40E-10		2.00E-09	1.00E-09	7.00E-10	
Wall ④	12.26 in			Wall ④	12.56 in		
4.1E-05	4.1E-05	4.1E-05		4.1E-05	4.1E-05	4.1E-05	
9.10E-10	7.80E-10	6.40E-10		2.00E-09	1.00E-09	7.00E-10	
Wall ③	14.92 in			Wall ③	15.31 in		
4.1E-05	4.1E-05	4.1E-05		4.1E-05	4.1E-05	4.1E-05	
9.10E-10	7.80E-10	6.40E-10		2.00E-09	1.00E-09	7.00E-10	
Wall ②	17.62 in			Wall ②	18.09 in		
4.1E-05	4.1E-05	4.1E-05		4.1E-05	4.1E-05	4.1E-05	
9.10E-10	7.80E-10	6.40E-10		2.00E-09	1.00E-09	7.00E-10	
Wall ①	20.22 in			Wall ①	20.79 in		
4.1E-05	4.1E-05	4.1E-05		4.1E-05	4.1E-05	4.1E-05	
2.0E-09	5.0E-10	1.0E-10		2.0E-09	5.0E-10	1.0E-10	
Grout	516 in			Grout	516 in		
4.1E-05	4.1E-05	4.1E-05		4.1E-05	4.1E-05	4.1E-05	
1.0E-08	5.0E-09	5.0E-09		1.0E-08	5.0E-09	5.0E-09	
Column	10.63 in			Column	10.63 in		
4.1E-05	4.1E-05	4.1E-05		4.1E-05	4.1E-05	4.1E-05	

Table 7: Degradation timing detail for SDU 7 and 45/45/10 saltstone (continued).

Component	Degradation mechanism:		Decalcification						Limiting						
	Thickness (in)	Thickness (cm)	CE	CV	BE	Time (yr)	max δ (cm)	CE (yr)	CV (yr)	BE (yr)	Initial thickness (in)	t=0 thickness (cm)	CE (yr)	CV (yr)	BE (yr)
Roof delay					HDPE-GCL:	1800	1800	1700	0	0	0				
Roof degradation	12	30.48	0.019	0.018	0.015	212368	240417	364060	214168	242217	365760	2.54			
Roof delay+degradation													3889	4294	6035
Floor/UMM delay					HDPE-GCL:	1700	1750	1600	0	0	0				
Floor/UMM degradation	24	60.96	0.019	0.018	0.015	424737	480834	728120	426437	482584	729720	2.54			
Floor/UMM delay+degradation													6912	7745	11251
Wall delay					no liner:	0	0	0	0	0	0				
Wall degradation	11.02	27.99	0.019	0.018	0.015	195003	220758	334291	195003	220758	334291	2.54			
Wall delay+degradation													2818	3190	4831
Wall delay					no liner:	0	0	0	0	0	0				
Wall degradation	12.61	32.03	0.019	0.018	0.015	223186	252664	382605	223186	252664	382605	2.54			
Wall delay+degradation													3225	3651	5529
Wall delay					no liner:	0	0	0	0	0	0				
Wall degradation	15.37	39.05	0.019	0.018	0.015	272049	307980	466369	272049	307980	466369	2.54			
Wall delay+degradation													3931	4451	6740
Wall delay					no liner:	0	0	0	0	0	0				
Wall degradation	18.17	46.16	0.019	0.018	0.015	321631	364110	551367	321631	364110	551367	2.54			
Wall delay+degradation													4648	5262	7968
Wall delay					no liner:	0	0	0	0	0	0				
Wall degradation	20.88	53.04	0.019	0.018	0.015	369539	418346	633496	369539	418346	633496	2.54			
Wall delay+degradation													5340	6046	9155
GROUT delay					A_0 (cm/yr)	3889	4294	6035	3889	4294	6035				
GROUT degradation	516	1311	2.0E-04	3.0E-05	2.0E-06	6598918	4.4E+07	6.6E+08	6.6E+06	4.4E+07	6.6E+08				
GROUT delay+degradation													6.6E+06	4.4E+07	6.6E+08
Column delay															
Column degradation	10.63	27.0											0	0	0
Column delay+degradation													72	92	299

References

Herfort, D., and B. Lothenbach, *Ternary Phase Diagrams Applied to Hydrated Cement*, chapter in Scrivener, K., R. Snellings, and B. Lothenbach, *A Practical Guide to Microstructural Analysis of Cementitious Materials*, CRC Press, July 2017.

SIMCO Technologies Inc., *Washington Savannah River Company Subcontract no. AC48992N Report; Task 6 – Characterization of a Wasteform Mixture*, June 2010.

SIMCO Technologies Inc., *Washington Savannah River Company Subcontract AC81850N Report – Vault Concrete Characterization*, March 2012.

SRNL-STI-2018-00077, Flach, G.P., *Degradation of Saltstone Disposal Unit Cementitious Materials*, Savannah River Site, Aiken, SC, Rev. 1, August 2018.

SRNL-STI-2018-00586, Dyer, J.A., *Geochemical Model of Eh and pH Transitions in Pore Fluids during Saltstone and SDU Concrete Aging; Saltstone Disposal Facility PA Revision*, Savannah River Site, Aiken, SC, Rev. 0, October 2018.

SRNL-TR-2008-00283, Denham, M., *Estimation of Eh and pH Transitions in Pore Fluids During Aging of Saltstone and Disposal Unit Concrete*, Savannah River Site, Aiken, SC, Rev. 0, December 2008.

SRR-CWDA-2019-00001, *Performance Assessment for the Saltstone Disposal Facility at the Savannah River Site*, Savannah River Site, Aiken, SC, Rev. 0, March 2020.

SRR-CWDA-2019-00003, Simner, S., *Cement-Free Formulation Down-Select Report*, Savannah River Site, Aiken, SC, Rev. 0, February 2019.

SRR-CWDA-2020-00036, Hommel, S.P., *Recommended Modeling Inputs for Evaluating SDU Concrete Mix 3B, Based on the Reports from Vendors*, Savannah River Site, Aiken, SC, Rev. 0, April 2020.

SRR-CWDA-2020-00040, Hommel, S.P., *Recommended Modeling Inputs for Evaluating Cement Free Saltstone, Based on Down Selection Report and Other Literature*, Savannah River Site, Aiken, SC, Rev. 0, June 2020.

SRR-CWDA-2020-00066, Flach, G.P., *Normative Mineral Compositions of Saltstone Disposal Facility Cementitious Materials*, Savannah River Site, Aiken, SC, Rev. 0, September 2020.

SRR-SDU-2019-00026, Thompson, J.P., *Evaluation of Future SDU Type II & V Concrete Mixtures*, Savannah River Site, Aiken, SC, Rev. 0, December 2019.