

**Key Words:** Saltstone PA  
Concrete Degradation  
Concrete Properties  
Saltstone Properties

**Retention:** Permanent

**EVALUATION OF SULFATE ATTACK ON  
SALTSTONE VAULT CONCRETE AND SALTSTONE**

**SIMCO TECHNOLOGIES, INC.  
PART I: FINAL REPORT**

**SIMCO TECHNOLOGIES, INC.  
SUBCONTRACT SIMCORD08009 ORDER AC48992N**

**Christine A. Langton**

**AUGUST 19, 2008**

**Savannah River National Laboratory  
Savannah River Nuclear Solutions, LLC  
Aiken, SC 29808**

**Prepared for the U.S. Department of Energy  
Under Contract No. DE- AC09-08SR22470**



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SAVANNAH RIVER NATIONAL LABORATORY

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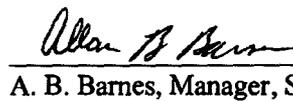
  
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## TABLE OF CONTENTS

<b>Reviews and Approvals.....</b>	<b>i</b>
<b>Table of Content.....</b>	<b>ii</b>
<b>List of Acronyms.....</b>	<b>iv</b>
<b>1.0 EXECUTIVE SUMMARY.....</b>	<b>1</b>
<b>2.0 INTRODUCTION .....</b>	<b>2</b>
2.1 Objective.....	2
2.2 Approach .....	2
2.3 Background.....	3
<b>3.0 STADIUM<sup>®</sup> MODEL and SIMULATION METHODOLOGY .....</b>	<b>4</b>
3.1 STADIUM <sup>®</sup> Model Description.....	4
3.2 STADIUM <sup>®</sup> Input Parameters.....	5
3.2.1 Selection of Surrogate Concrete Samples for Early Results.....	5
3.2.2 Compositions of Hypothetical Corrosive Solutions for Three Exposure Scenarios.....	6
3.2.3 Equilibrium Mineral Assemblages.....	9
3.3 Saltstone Vaults 1 / 4 and Disposal Unit 2 Service Life Simulations .....	9
<b>4.0 SALTSTONE VAULT CONCRETE SERVICE LIFE PREDICTIONS .....</b>	<b>11</b>
4.1 Simulation Results for Disposal Unit 2 Concrete Exposed to Case 2 Corrosive Solution.....	11
4.2 Simulations Over 10,000 Years.....	13
4.3 Discussion of Concrete Damage Mechanisms Based on Simulated Results.....	14
<b>5.0 VAULTS 1 / 4 and DISPOSAL UNIT 2 CONCRETE PROPERTIES.....</b>	<b>16</b>
<b>6.0 SALTSTONE PROPERTIES .....</b>	<b>19</b>
<b>7.0 CONCLUSIONS AND RECOMMENDATIONS.....</b>	<b>20</b>
<b>8.0 REFERENCES.....</b>	<b>23</b>
<b>9.0 ATTACHMENT 1. Summary of Subcontract No. AC 48992N Work Requirements .....</b>	<b>A1-1</b>
<b>10.0 ATTACHMENT 2. STADIUM<sup>®</sup> Code Predictions: Effect of High Sulfate Alkaline Solutions and SRS Soil Pore Water on Surrogate Saltstone Vaults 1 / 4 and Disposal Unit 2 Concrete (Task 1 Report) .....</b>	<b>A2-1</b>
<b>11.0 ATTACHMENT 3. Saltstone Vaults 1 / 4 and Disposal Unit 2 Concrete Sample Preparation and Fresh Property Characterization (Tasks 2 and 4 Status Report) .....</b>	<b>A3-1</b>
<b>12.0 ATTACHMENT 4. Saltstone Characterization Results (Task 6 Status Report) .....</b>	<b>A4-1</b>

## LIST OF TABLES

Table 3-1. Vault Concrete and Surrogate Concrete Mix Designs. ....	7
Table 3-2. Approximate Saltstone Pore Solution Compositions [Langton, 1987]. ....	8
Table 3-3. Saltstone Leachate Compositions Used for the STADIUM <sup>®</sup> Simulations. ....	8
Table 3-4. Mineral Phases Considered for the Calculations .....	9
Table 5-1. Compressive Strength of Saltstone Vault Concretes at 7 and 28 days. ....	16
Table 5-2. Compressive Strength for the Vault 1/4 Concrete (Cast 5/05/2008) <sup>1</sup> [Dixon, et al., 2008]. ....	16
Table 5-3. Compressive Strength for the Disposal Unit 2 Mix 1 Concrete (Cast 3/25/2008) <sup>1</sup> [Dixon, et al., 2008]. ....	17
Table 5-4. Transport properties for Saltstone Vault concretes at 28 days. ....	17
Table 5-5. Comparison of Transport Properties Measured by SIMCO and Others. ....	18
Table 6-1. Compressive strength for MCU Saltstone. ....	19
Table 6-2. Compressive Strength for the MCU Saltstone Grout (Cast 3/31/2008) <sup>1</sup> [Dixon, et al, 2008]. ....	19

## LIST OF FIGURES

Figure 3-1. Simulation Case for Surrogate Vault Concretes. ....	10
Figure 4-1. Ionic species in the pore solution for the surrogate Disposal Unit 2 concrete after exposure to Case 2 corrosive solution for 2000 years. ....	11
Figure 4-2. Solid phases in the hydrated cement paste for the surrogate Disposal Unit 2 concrete after exposure to Case 2 corrosive solution for 2000 years. ....	11
Figure 4-3. Simulated Progression of the Ettringite Front as a Function of Time. ....	13
Figure 4-4. Progression of the Decalcification Front from the Soil – Concrete Interface. ....	14

## List of Acronyms

ASR	Alkali Silica Reaction
ASTM	American Society for Testing & Materials
C3A	Tricalcium aluminate
cm	centimeters
C-S-H	Calcium silicate hydrate (non to poorly crystalline solid)
CV	coefficient of variance
d	Days of time
DCR	Document Control Register
E&CPT	Engineering and Chemical Process Technology
ICP	Inductively Coupled Plasma spectrometry
MCU	Modular Caustic Side Solvent Extraction Unit
Mol/L	Moles per liter
MPa	Mega Pascals
PA	Performance Assessment
pH	Measure of the hydrogen ion concentration in an aqueous solution (acidic solutions, pH from 0–6; basic solutions, pH > 7; and neutral solutions, pH = 7)
PS&E	Process Science and Engineering
Psig	Pound-force per square inch gauge (pressure relative to the surrounding atmosphere)
s	Seconds
SIMCO	SIMCO Technologies, Inc.
SQRT	Square Root of Time
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
SRS	Savannah River Site
STR	Subcontract Technical Representatives
TTR	Technical Task Request
WSRC	Washington Savannah River Company
yr	Year

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## 1.0 EXECUTIVE SUMMARY

This report summarizes the preliminary results of a durability analysis performed by SIMCO Technologies Inc. to assess the effects of contacting saltstone Vaults 1 / 4 and Disposal Unit 2 concretes with highly alkaline solutions containing high concentrations of dissolved sulfate. The STADIUM<sup>®</sup> code and data from two surrogate concretes which are similar to the Vaults 1 / 4 and Disposal Unit 2 concretes were used in the preliminary durability analysis. Simulation results for these surrogate concrete mixes are provided in this report. The STADIUM<sup>®</sup> code will be re-run using transport properties measured for the SRS Vaults 1 / 4 and Disposal Unit 2 concrete samples after SIMCO personnel complete characterization testing on samples of these materials. Simulation results which utilize properties measured for samples of Vaults 1 / 4 and Disposal Unit 2 concretes will be provided in Revision 1 of this report after property data become available.<sup>1</sup>

The modeling performed to date provided the following information on two concrete mixes that will be used to support the Saltstone PA:

- Relationship between the rate of advancement of the sulfate front (depth of sulfate ion penetration into the concrete) and the rate of change of the concrete permeability and diffusivity.
- Relationship between the sulfate ion concentration in the corrosive leachate and the rate of the sulfate front progression.
- Equation describing the change in hydraulic properties (hydraulic conductivity and diffusivity) as a function of sulfate ion concentration in the corrosive leachate.

These results have been incorporated into the current Saltstone PA analysis by G. Flach (Flach, 2008).

In addition, samples of the Saltstone Vaults 1 / 4 and Disposal Unit 2 concretes have been prepared by SIMCO Technologies, Inc. Transport and physical properties for these materials are currently being measured and sulfate exposure testing to three high alkaline, high sulfate leachates provided by SRNL is underway to validate the predicted results.

Samples of saltstone were also prepared and will be evaluated for durability using the STADIUM<sup>®</sup> code and SIMCO methodology. Results available as of August 15 are included in this draft report. A complete set of results for saltstone will be available by December 31, 2008.

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<sup>1</sup> Drying isotherms and other moisture data are taking longer to obtain than expected because the high quality saltstone vault concretes have very low moisture transmission properties.

## 2.0 INTRODUCTION

### 2.1 Objective

The objective of this report is to summarize preliminary results of a durability analysis performed by SIMCO Technologies Inc. to assess the effects of sulfate attack on saltstone Vaults 1 / 4 and Disposal Unit 2 concrete.

This work was requested by J. L. Newman, REG INTEGRATION & ENV SERVICES, and coordinated through H. H. Burns, PS&E / SRNL, and will support the 2008 Saltstone Performance Analysis [Burns, 2008]. Input on concrete vault degradation required for the Saltstone PA includes a:

- Relationship between the rate of advancement of the sulfate front (depth of sulfate ion penetration into the concrete) and the rate of change of the concrete permeability and diffusivity
- Relationship between the sulfate ion concentration in the corrosive leachate and the rate of the sulfate front progression.
- Equation describing the change in hydraulic properties (hydraulic conductivity and diffusivity) as a function of sulfate ion concentration in the corrosive leachate.

### 2.2 Approach

The STADIUM<sup>®</sup> code and data from two surrogate concretes which are similar to the Vaults 1 / 4 and Disposal Unit 2 concretes were used in the preliminary durability analysis. (These results are provided in this report.) The STADIUM<sup>®</sup> code will be re-run using transport properties measured for the SRS Vaults 1 / 4 and Disposal Unit 2 concrete samples after SIMCO personnel complete characterization testing on samples of these materials.

Validation of the predicted results for the surrogate concretes is complete for typical sulfate solutions encountered in typical concrete service environments. Exposure testing to validate the predicted results for SRS vault concretes involves: 1) exposing samples of the two concretes to the three highly alkaline, sulfate containing solutions (compositions provided by SRNL) for several months, and then 2) characterizing the samples with respect to chemistry, mineralogy, damage as a function of distance from the solution-concrete interface. The long exposure times are a consequence of the high quality of the concrete used in the SRS saltstone vaults.

Preliminary results for the saltstone Vaults 1 / 4 and Disposal Unit 2 concretes are provided. In addition, saltstone samples have been prepared and are being characterized. The STADIUM<sup>®</sup> code and test methodology will be used to evaluate the durability of the saltstone waste form. These efforts are currently in progress.

### 2.3 Background

The saltstone waste form contains high concentrations of more or less soluble sulfate and aluminate. The waste form is cast as a slurry into concrete vaults which isolate the cured waste form from the environment. The performance of the waste form over the long time (10,000 years) is required for disposal of long lived radionuclides in the near surface environment.

The ability of the concrete vault to serve as a barrier between the environment (water in the environment) and source of mobile, water soluble radionuclides depends on how aging and exposure changes the permeability and water, gas and contaminant diffusivities of the concrete vault. The vaults are part of a large landfill that will be covered by an engineered barrier that will limit infiltration of water during a portion of the performance time.

A subcontract was awarded to SIMCO Technologies, Inc., to use existing expertise and simulation codes (STADIUM<sup>®</sup>) and methodology to predict the effects of sulfate and aluminate exposure (from saltstone, a cement waste form) on reinforced concrete, specifically SRS saltstone Vaults 1 / 4 and 2 concrete, over 10,000 years. A summary of the requirements in the Statement of Work are provided in Attachment 1 [Contract SIMCORD08009, 2008].

Results of the study will be used as input to the Saltstone Performance Assessment, which predicts transport of radionuclides from the saltstone waste form into the surrounding environment and water table.

### 3.0 STADIUM<sup>®</sup> MODEL and SIMULATION METHODOLOGY

#### 3.1 STADIUM<sup>®</sup> Model Description

STADIUM<sup>®</sup> is a multi ionic one dimensional transport model based on a sequential split operator approach that separates ionic movement and chemical reactions. The ionic transport module in STADIUM<sup>®</sup> is based on the extended Nernst-Planck equation applied to unsaturated and non-isotherm materials. The equation accounts for electrical coupling as well as the chemical activity between ionic fluxes, transport due to water content gradient and temperature: See Equation 1.

#### Equation 1.

$$\frac{\partial(wc_i)}{\partial t} - \text{div} \left( D_i w \text{grad}(c_i) + \frac{D_i z_i F}{RT} w c_i \text{grad}(\psi) + D_i w c_i \text{grad}(\ln \gamma_i) + \frac{D_i c_i \ln(\gamma_i c_i)}{T} w \text{grad}(T) + c_i D_w \text{grad}(w) \right) = 0$$

Where:  $c_i$  = Ion concentration [mmol/L]  
 $w$  = Water content [ $\text{m}^3/\text{m}^3$ ]  
 $D_i$  = Diffusion coefficient [ $\text{m}^2/\text{s}$ ]  
 $z_i$  = Valence number of the ionic species  $i$   
 $F$  = Faraday constant [96488.46 C/mol]  
 $\psi$  = Electrodiffusion potential [V]  
 $R$  = Ideal gas constant [8.3143 J/mol/°K]  
 $T$  = Temperature [°K]  
 $\gamma_i$  = Activity coefficient  
 $D_w$  = Water diffusivity [ $\text{m}^2/\text{s}$ ].

For the evaluation of sulfate attack on the Saltstone vault concrete, eight ionic species were considered:  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}(\text{OH})_4^-$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$ . The activity coefficients used in the model were evaluated on the basis of the Harvie, Moller and Weare implementation of Pitzer's ion interaction model. Details are provided in Attachment 2 and in references supplied in Attachment 2.

The second module in STADIUM<sup>®</sup> consists of a chemical equilibrium code. Following the transport step, the chemical equilibrium module verifies equilibrium conditions between the ion concentrations in the pore solution and the solid phases of the hydrated cement paste, i.e., calcium hydroxide, calcium silicate hydrates, ettringite, and mono-sulfate phases.<sup>2</sup> This is done

<sup>2</sup> Mono-sulfate phases are calcium alumina ferrites that contain one mole of anhydrite,  $\text{CaSO}_4$ , in the chemical formula. The formation of Friedel's salt, a chloride-containing calcium alumina-sulfate solid phase that forms as the result of exposure of concrete to chloride is modeled as an ion-exchange mechanism with monosulfate.

at each node of the finite element mesh. Details of are provided in Attachment 2 and in references supplied in Attachment 2.

### 3.2 STADIUM<sup>®</sup> Input Parameters

The following concrete properties are required as input to the STADIUM<sup>®</sup> code:

- Porosity: Measured using ASTM C-642 standard method for concrete.
- Ionic Diffusivities: Determined by determining the tortuosity of the pore structure from data generated by a modified chloride ASTM C-1202 rapid chloride penetration test. The test method and calculations are described in SRNS-STI-2008-00052.
- Water Diffusivity: A and B coefficients in Equation 2 and the equilibrium water content are determined from a Sorption – Desorption Test described in SRNS-STI-2008-00052.

**Equation 2.**  $D_w = A \exp(Bw)$

Where:  $D_w$  = Water diffusivity (nonlinear)

$w$  = Volumetric water content

$A$  = Experimentally determined parameters

$B$  = Experimentally determined parameter (positive)

- Initial Pore Solution Composition: Determined by extraction of pore solution under 345 MPa (50,000 psi) pressure and analyzed by ICP techniques. The solution is typically analyzed for  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}(\text{OH})_4^-$ . However, for the saltstone materials it will also be analyzed for  $\text{NO}_2^-$ , and  $\text{NO}_3^-$ .
- Initial Mineralogy: The initial solid phases in the hydrated cement paste are estimated from the cement and admixture chemical compositions.

#### 3.2.1 Selection of Surrogate Concrete Samples for Early Results

Two concrete mix designs similar to the saltstone Vaults 1 / 4 and Disposal Unit 2 mixes were selected for the initial modeling effort in order to provide an early indication of the effect of sulfate exposure to the saltstone vault concrete. The surrogate concretes are similar to the actual Vaults 1 / 4 and Disposal Unit 2 concrete mixes. Consequently the surrogate data can be used in the initial SRNL Porflow runs required to meet the Saltstone PA schedule.<sup>3</sup>

<sup>3</sup> STADIUM<sup>®</sup> results using data for the saltstone Vaults 1 / 4 and Disposal Unit 2 concrete samples prepared at SIMCO Technologies, Inc., are expected to be available and will be provided in the final report due at the end of the calendar year. Due to the low porosities and permeabilities and high degree of sulfate resistance of the saltstone Vaults 1 / 4 and Disposal Unit 2 concretes, validation of the model results is not expected for several months after the final report is issued. Validation test results will be provided as revisions to the final report as they become available. Validation consists of exposing samples of the vault concretes to the corrosive solutions and characterizing the depth of penetration of the various chemical and mineralogical fronts in addition to other chemical and physical effects.

The mix designs for the Vaults 1 / 4 and Disposal Unit 2 concretes and the surrogate concretes are provided in Table 3-1. Oxide compositions and additional characterization data for the surrogate concrete mixes are provided in Attachment 2.

### 3.2.2 Compositions of Hypothetical Corrosive Solutions for Three Exposure Scenarios

Compositions for three corrosive solutions containing high concentrations of sulfate were constructed by G. Flach, M. Phifer, and M. Denham, SRNL, from potential scenarios related to leaching of the saltstone [Flach, et al., 2008.]. The bases for these high sulfate solutions are provided below:

**Case 1 - Saltstone pore water, undiluted**

This case is intended to be a surrogate for concrete in diffusional contact with saltstone at early times. Determine composition of saltstone pore water by analyzing water squeezed from a sufficiently cured saltstone sample. Exposure vault concrete to a simulant of this water (no dilution).

**Case 2 - Saltstone pore water, diluted 10:1**

This case is intended to be a surrogate for concrete in diffusional contact with saltstone at later times, after saltstone pore water near the saltstone/concrete interface has been diluted through diffusion. Same as Case 1, except that the Case 1 simulant is diluted 10:1 with a simulant of ground water that has equilibrated with vault concrete (defined below and used as a permeant in recent saltstone permeability testing, WSRC-STI-2007-00649).

**Case 3 - Leached saltstone pore water at 10:1 dilution**

This case is intended to be a surrogate for infiltrating soil moisture that flows through saltstone before contacting concrete.

Equilibrate ground water simulant in Case 2 with crushed saltstone at 10:1 dilution. That is, the volume of groundwater simulant should be 10x the volume of pore water in the saltstone sample assuming 60% porosity.

The pore solution extracted from a saltstone formulation cured for 28 days was used as the Case 1 (most aggressive) solution. The Case 2 and 3 solutions are 10:1 and 100:1 dilutions of the Case 1 solutions in equilibrium with  $\text{Ca}(\text{OH})_2$ . The composition of saltstone pores solutions at various curing times is provided in Table 3-2. The compositions of the three hypothetical saltstone leachates used in the STADIUM<sup>®</sup> simulation to evaluate the durability of the surrogate Vaults 1 / 4 and Disposal Unit 2 concretes are provided in Table 3-3.

Figure 3-1. Vault Concrete and Surrogate Concrete Mix Designs.

Ingredient	Vaults 1 / 4 Concrete (1)	Surrogate Binary Concrete	Disposal Unit 2 Concrete (2)	Surrogate Ternary Concrete
	(kg/m <sup>3</sup> ) <i>(lbs/cu yd)</i>		(kg/m <sup>3</sup> ) <i>(lbs/cu yd)</i>	
Cement Type I	0 <i>0</i>	276 <i>465</i>	0 <i>0</i>	0 <i>0</i>
Cement Type I/II	239 <i>419</i>	0 <i>0</i>	0 <i>0</i>	0 <i>0</i>
Cement Type V (Lehigh)	0 <i>0</i>	0 <i>0</i>	116 <i>201</i>	0 <i>0</i>
Ternary Blended Cement (3)	0 <i>0</i>	0 <i>0</i>	0 <i>0</i>	425 <i>716</i>
Slag	158 <i>278</i>	149 <i>251</i>	153 <i>268</i>	0 <i>0</i>
Silica Fume	0 <i>0</i>	0 <i>0</i>	25.5 <i>44.7</i>	Included in ternary blend
Fly Ash Class F	0 <i>0</i>	0 <i>0</i>	89 <i>156.3</i>	Included in ternary blend
Water	152 <i>268</i>	149 <i>251</i>	145 <i>255</i>	149 <i>251</i>
Coarse Aggregate <sup>3</sup> / <sub>4</sub> in.	1025 <i>1798</i>	925 <i>1559</i>	1055 <i>1850</i>	910 <i>1534</i>
Fine Aggregate (quartz sand)	646 <i>1133</i>	815 <i>1374</i>	519 <i>911</i>	800 <i>1348</i>
Unit Weight (kg/m <sup>3</sup> ) (lbs/yd <sup>3</sup> )	2220 3896	2314 <i>3900</i>	2103 3626	2284 <i>3850</i>
Density	2.31	2.31	2.19	2.29
Water to total cementitious material ratio	0.385	0.35	0.38	0.35

- (1) Vaults 1 / 4 concrete mix design is representative of the concrete mixes for the Vault 1 and Vault 4 floor and wall concrete shown in Tables 4-5 and 4-6 of Phifer et al., 2006.
- (2) Disposal Unit 2 concrete mix design is representative of the concrete mixes being proposed for the future disposal cells indicated in Table 4-7 of Phifer et al., 2006.
- (3) Ternary blended cement that included a Type I portland cement equivalent (CSA Type 10).

**Table 3-1 Approximate Saltstone Pore Solution Compositions [Langton, 1987].**

(mg/L)	7d	28d	56d	90d
AlO <sub>2</sub> <sup>-</sup>	17.7	6.3	26.9	1.33
Ca <sup>+2</sup>	9.0	29	94.6	92.05
Fe <sup>+3*</sup>	1.6	3.5	1.74	2.21
K <sup>+</sup>	6,000	7,000	7,400	6,500
Mg <sup>+2*</sup>	0.1	1.2	11.5	1.96
Na <sup>+</sup>	77,000	85,000	91,000	60,000
SiO <sub>3</sub> <sup>-2*</sup>	203.6	230.7	169.6	76.6
CO <sub>3</sub> <sup>-2</sup>	800	1,000	675	736.5
Cl <sup>-</sup>	1170	1380	661	739
NO <sub>2</sub> <sup>-</sup>	42,000	43,000	33,800	27,000
PO <sub>4</sub> <sup>-3</sup>	<150	<150	<150	<150
NO <sub>3</sub> <sup>-</sup>	175,000	205,000	177,000	122,700
SO <sub>4</sub> <sup>-2</sup>	26,000	25,000	25,500	24,000
OH <sup>-a</sup>	14,258	16,315	227	3,794
pH	13.8	13.98	12.13	13.3

a = Calculated values.

**Table 3-2. Saltstone Leachate Compositions Used for the STADIUM<sup>®</sup> Simulations.<sup>4</sup>  
(Boundary conditions at x=0)**

Ionic species	Concentrations (mmol/L)		
	High level	Mid level	Low level
OH <sup>-</sup>	769.0	76.9	7.69
Na <sup>+</sup>	4366.0	436.6	43.66
K <sup>+</sup>	215.0	21.5	2.15
SO <sub>4</sub> <sup>2-</sup>	208.0	20.8	2.08
Ca <sup>2+</sup>	1.0	0.1	0.01
NO <sub>3</sub> <sup>-</sup>	2649.0	264.9	26.49
NO <sub>2</sub> <sup>-</sup>	749.0	74.9	7.49

<sup>4</sup> The concentrations listed in Table 3-2 are about 20 % lower than the concentrations in the pore solution extracted from a cement - slag – fly ash samples cured for 28 days [Langton, 1987]. Since the concentrations decrease with curing time, this discrepancy is not expected to impact the overall conclusions.

### 3.2.3 Equilibrium Mineral Assemblages

The hydrated mineral assemblage considered in the durability analysis for the surrogate concretes exposed to the Case 1 corrosive solution (saltstone pore solution) is shown in Table 3-3. For the simulations it was assumed that the  $\text{NO}_3^-$  and  $\text{NO}_2^-$  did not react with other species to form additional phases or solid solutions. A more detailed discussion of the equilibrium mineral assemblage is provided in Attachment 2.

**Table 3-3. Mineral Phases Considered for the Calculations**

Minerals	Composition	$\log(K)$ @ 25°C
Portlandite	$\text{Ca}(\text{OH})_2$	-5.15
C-S-H (portlandite fraction)	$\text{Ca}(\text{OH})_2$	-6.2
Monosulfates	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$	-29.4
Ettringite	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 26\text{H}_2\text{O}$	-44.0
Glauberite	$\text{Na}_2\text{Ca}(\text{SO}_4)_2$	-5.18
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-4.58
Mirabilite	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	-1.4
Syngenite	$\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	-7.45
Glaserite	$\text{NaK}_3(\text{SO}_4)_2$	-3.8

### 3.3 Saltstone Vaults 1 / 4 and Disposal Unit 2 Service Life Simulations

Service life simulations were performed on a 1-D case illustrated in Figure 3-1 using the STADIUM<sup>®</sup> code. The simulations were performed using a 90 element finite element mesh for a 20 cm thick slab ( $L = 20$  cm, Disposal Unit 2 concrete was assumed to be 20 cm thick) and 154 elements for a 46 cm slab ( $L = 46$  cm, Vaults 1 / 4 concrete was assumed to be 46 cm thick) and were refined near the domain boundaries.

The time steps were increased progressively to reduce the calculation time. Details are provided in Attachment 2. The temperature was set at 15°C and the concrete was assumed to be saturated with the water content at  $x = 0$ . The volume of water in the concrete corresponded to the volume of pores (porosity) that transmits fluid. The concrete surface at the concrete-corrosive solution interface was assumed to always be saturated. The concrete surface in contact with the soil ( $x = L$  cm) was assumed to be at 100 % relative humidity. This boundary condition corresponds to saturated concrete with water content equal to the porosity of the concrete.

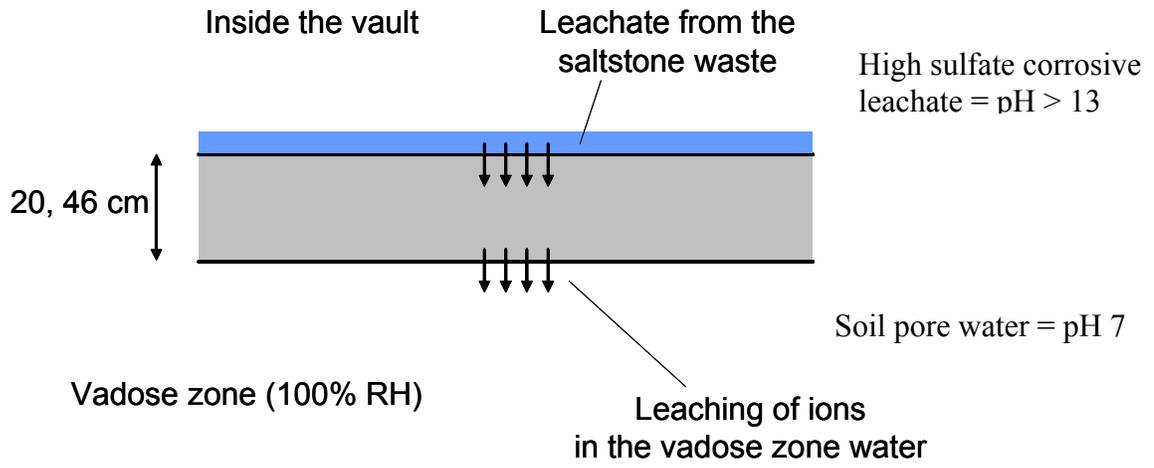
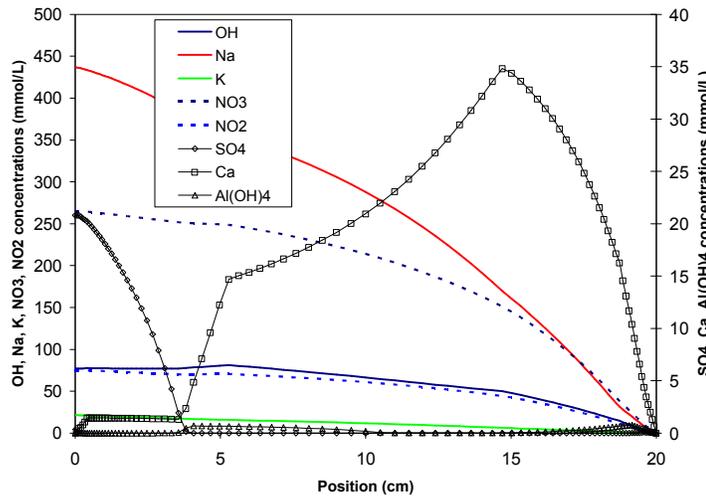


Figure 3-1. Simulation Case for Surrogate Vault Concretes.

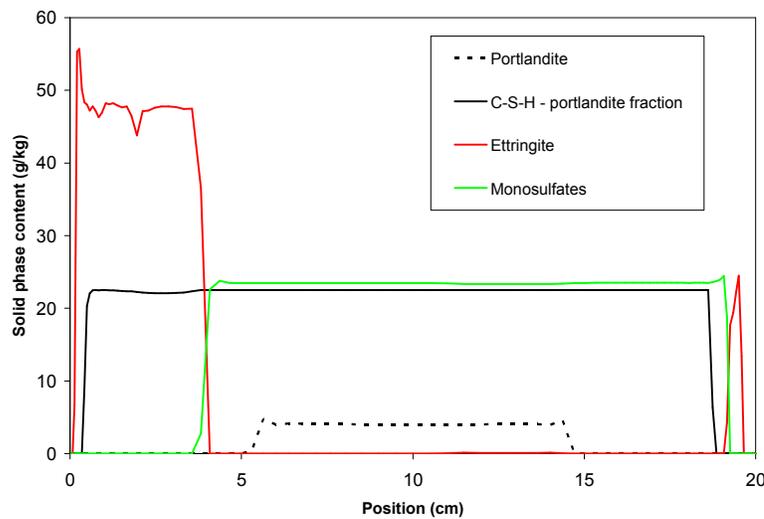
## 4.0 SALTSTONE VAULT CONCRETE SERVICE LIFE PREDICTIONS

### 4.1 Simulation Results for Disposal Unit 2 Concrete Exposed to Case 2 Corrosive Solution

The surrogate Disposal Unit 2 concrete (20 cm thick) exposed to the Case 2 corrosive solution (10:1 dilution of the saltstone pores solution) was used to illustrate the STADIUM<sup>®</sup> output for a 2000 year exposure simulation. The concentrations of eight ionic species in the pore solution as a function of position in the sample (penetration depth) are plotted after 2000 years exposure. See Figure 4-1. The corresponding solid phases in equilibrium with the calculated pore solutions were also calculated and plotted in Figure 4-2.



**Figure 4-1. Ionic species in the pore solution for the surrogate Disposal Unit 2 concrete after exposure to Case 2 corrosive solution for 2000 years.**



**Figure 4-2. Solid phases in the hydrated cement paste for the surrogate Disposal Unit 2 concrete after exposure to Case 2 corrosive solution for 2000 years.**

Simulation results presented in Figures 4-1 and 4-2 that pertain to the corrosive leachate – concrete interface can be summarized as follows:

- Ettringite formation begins at the surface exposed to the corrosive high sulfate leachate.
- Since ettringite formation also requires additional calcium, portlandite initially present in the concrete paste will dissolve as the ettringite is formed.
- However, the high pH, (high OH<sup>-</sup>) and high concentration of sulfate in the corrosive leachate at the leachate – concrete interface limits decalcification of the poorly crystalline calcium silicate hydrate phase, C-S-H. (This condition is outside the conditions encountered in typical sulfate attack.)
- Ettringite is the only sulfate containing phase predicted to form. Gypsum is not predicted as an equilibrium phase in the highly alkaline pore solution predicted for the exposed concrete.<sup>5</sup>
- The rate at which the ettringite front progresses depends on the transport properties of the material and on the initial amount of hydrated monosulfate phase (source of aluminate) in the cement paste since ettringite formation requires dissolution of monosulfate (assuming no other source of aluminate.)
- For concretes with comparable transport properties, the ettringite front will penetrate the concrete more rapidly for a cement paste with a lower tricalcium aluminate (C3A) content compared to a concrete with a paste with a higher C3A content.

Simulation results pertaining to the soil – concrete interface can be summarized as follows:

- A dissolution front progresses from the concrete surface in contact with the vadose zone soil inward toward the advancing ettringite front.
- The rate of decalcification is controlled primarily by the transport properties.
- A small ettringite peak is predicted in front of the C-S-H front due to the release of calcium and sulfate in the pore solution upon D-S-H decalcification and monosulfate dissolution.

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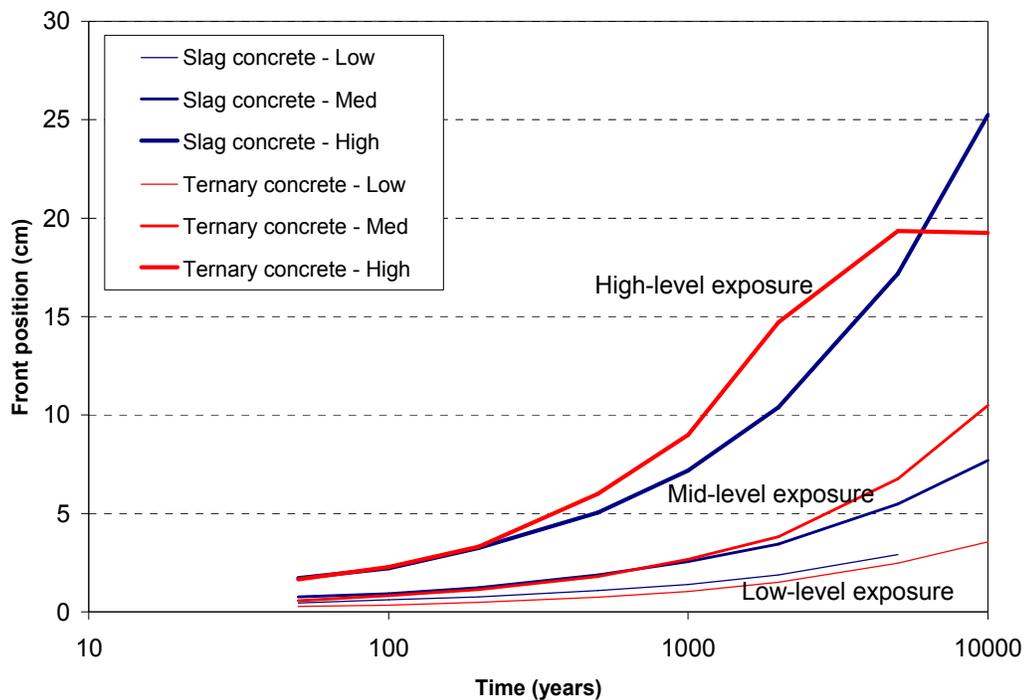
<sup>5</sup> The influence of gypsum formation on the damage caused by sulfate attack is controversial but important. Formation of gypsum as the result of incongruent dissolution of C-S-H is reported to weaken the matrix and contribute to the damaging effects of ettringite formation, i.e., expansion that leads to cracking.

A consequence of the absence of gypsum in the exposed material is that the amount of sulfur bound in the hydrated paste is independent of the external sulfate concentration because the amount of ettringite (g/kg of concrete) is limited by the amount of alumina present in the material. Consequently, the sulfate concentration in a corrosive leachate will only influence the rate of advancement of the ettringite front.

## 4.2 Simulations Over 10,000 Years

Plots of the progression of the ettringite fronts as a function of time are presented in Figure 4-3 for the two surrogate vault concretes and the three corrosive leachate solutions. The progression is from the corrosive leachate – concrete contact into the concrete. The results of these simulations can be summarized as follows:

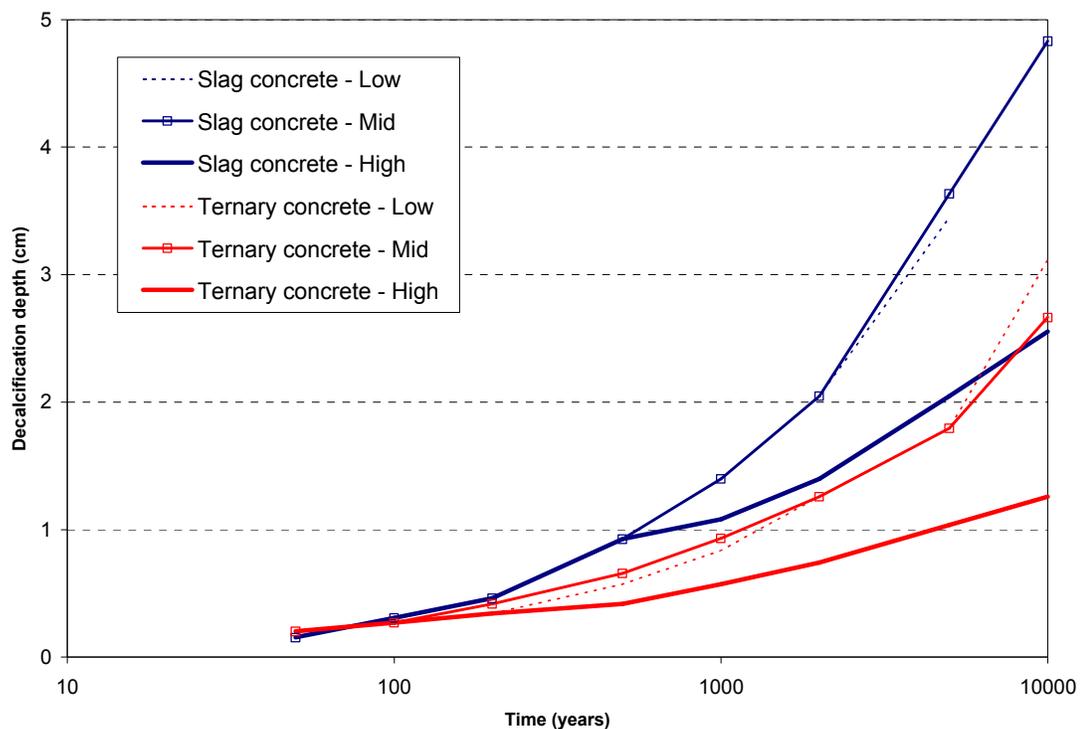
- The rate of advancement of the ettringite front depends on the concentration of sulfate in the corrosive solution in contact with the concrete.
- Small differences in material properties do not significantly affect the rate of the ettringite front advancement.
- If the exposure conditions are continuous over the service life of the Disposal Unit 2 (20 cm thick), the ettringite front will completely penetrate the walls in about 5000 years for the Case 1 corrosive solution. The reduction in advancement of the ettringite front after 5000 + years is due to the interaction of this front with the decalcification front advancing from the opposite direction (soil-concrete interface).
- If microcracks form as the ettringite front advances, the rate of ingress of the ettringite front will increase.



**Figure 4-3. Simulated Progression of the Ettringite Front as a Function of Time.**

Plots of the advancement of the decalcification fronts as a function of time are presented in Figure 4-4 for the two surrogate vault concretes and the three corrosive leachate solutions. The progression of the decalcification front is from the soil – concrete contact into the concrete). The results of these simulations can be summarized as follows:

- For the first 500 years, the rates of decalcification for the six cases are similar.
- After about 500 years, the penetration of  $\text{OH}^-$  from the advancing corrosive leachate front on the other side of the element tends to slow the decalcification process.
- Consequently the advancement of the decalcification front is lessened for the cases exposed to the most corrosive alkaline, sulfate leachates on the opposite side.
- The STADIUM<sup>®</sup> code predicts that the decalcified degraded zone should not exceed 4 cm after 10,000 years.



**Figure 4-4. Progression of the Decalcification Front from the Soil – Concrete Interface.**

### 4.3 Discussion of Concrete Damage Mechanisms Based on Simulated Results

For the concrete at the soil – concrete interface, decalcification of the C-S-H resulted in a calculated increase in porosity from 10 volume percent to 15 volume percent which results in doubling the rate of degradation of the material at this interface.

Ettringite is the only sulfate phase predicted to form at the concrete – corrosive solution interface. This is due to the high pH of the corrosive leachate solutions. Lack of a gypsum front between the ettringite front and the exposed surface is atypical. This finding is significant because the gypsum – decalcified C-S-H – calcium hydroxide absent zone is where the cracks, associated with sulfate attack, are formed. (Replacement of C-S-H by gypsum is known to weaken the matrix and make it more vulnerable to cracking parallel to the exposed surface caused by expansive reactions.)

The simulation results account for dissolution and precipitation of phases which locally modifies the porosity of the material and thereby affects the transport properties. In the absence of cracking, the formation of ettringite will reduce the porosity. However, if cracking does occur, the rate of advancement for the ettringite will increase.

Although considerable research has been done on damage associated with sulfate attack, little work has been performed under controlled conditions relevant to the cases analyzed. Related research work at SIMCO Technologies, Inc. has shown that micro cracks (less than about 100 $\mu$ m) have little effect (about a 50 % increase) on diffusion and drying rates (related to moisture diffusivity). Macro cracks (greater than about 100 $\mu$ m) in concrete result in saturated diffusion coefficients corresponding to those reported for free water which represents about a 50 times increase.

Observations are required to determine how exposure to highly alkaline high sulfate solutions affects the saltstone vault concrete. The approach to more completely addressing damage under the conditions provided for this study is to perform exposure tests to validate the model and characterize the consequences of exposure with respect to cracking and porosity.

## 5.0 VAULTS 1 / 4 and DISPOSAL UNIT 2 CONCRETE PROPERTIES

Samples of saltstone Vaults 1 / 4 and Disposal Unit 2 concretes were prepared and characterized by SIMCO personnel. Details of the test methods and discussion of the results for fresh properties are provided in Attachment 3. Compressive strengths ( $f_c$ ) and densities for samples cured 7 and 28 days are listed in tables 5-1. Values for the SRS saltstone vault concretes and surrogate concretes used in the initial service life modeling simulations are provided for comparison.

These results are in reasonable agreement for 28 day results obtained for samples prepared and tested by another subcontractor which are provided in Tables 5-2 and 5-3.

**Table 5-1. Compressive Strength of Saltstone Vault Concretes at 7 and 28 days.**

Properties	Saltstone Vault 1/4			Saltstone Disposal Unit 2		
	Actual		Surrogate	Actual		Surrogate
	average	CV (%)		Average	CV (%)	
$f_c$ 7d (MPa) (psi)	32.1 4650	13	42.7 6190	20.1 <sup>(*)</sup> 2915	4.5	41.6 6030
Density at 7d (kg/m <sup>3</sup> ) (lb/ft <sup>3</sup> )	2380 148	0.5	-	2250 <sup>(1)</sup> 140	0.7	-
$f_c$ 28d (MPa) (psi)	59.8 8,670	3.8	54.0 7830	35.2 5,102	2.8	56.7 8220
Density at 28d (kg/m <sup>3</sup> ) (lb/ft <sup>3</sup> )	2,390 149	0.1	-	2,250 140	1.0	-

(\*) measured at 8 days

**Table 5-2. Compressive Strength for the Vault 1/4 Concrete (Cast 5/05/2008)\*  
[Dixon, et al., 2008].**

Days Aged	Date Tested	Compressive Strength (psig)		
		Measured		Average
14	5/19/2008	7440	6870	7155
28	6/02/2008	8690	8750	8720
56	6/30/2008	10160	10220	10190
90	8/03/2008	9560	9280	9420

\*Samples were 4 x 8 inch cylinders and were tested per ASTM C 39. Lab Batch ID 080025.

**Table 5-3. Compressive Strength for the Disposal Unit 2 Mix 1 Concrete (Cast 3/25/2008)\* [Dixon, et al., 2008].**

Days Aged	Date Tested	Compressive Strength (psig)		
		Measured		Average
14	4/08/2008	6380	6390	6385
28	4/22/2008	7550	7310	7430
56	5/20/2008	8040	8070	8055
90	6/23/2008	9450	9120	9285

\*Samples were 4 x 8 inch cylinders and were tested per ASTM C 39. Lab Batch ID 080010.

Transport properties for the saltstone vault concretes were also measured on samples cured for 28 days and are listed in Table 5-4. A comparison of these values with values used in the SRS PAs is provided in Table 5-5.

**Table 5-4. Transport properties for Saltstone Vault concretes at 28 days.**

	Saltstone Vaults 1 / 4		Saltstone Disposal Unit 2	
	Actual	Surrogate	Actual	Surrogate
Porosity (%)	10.0	10.0	10.3	10.2
Effective Diffusion Coefficients* ( $10^{-11}$ m <sup>2</sup> /s)				
OH <sup>-</sup>	5.5	13.0	1.3	4.0
Na <sup>+</sup>	1.4	3.3	0.3	1.0
K <sup>+</sup>	2.0	4.8	0.5	1.5
SO <sub>4</sub> <sup>2+</sup>	1.1	2.6	0.3	0.8
Ca <sup>2+</sup>	0.8	2.0	0.2	0.6
Al(OH) <sub>4</sub>	0.6	1.3	0.1	0.4
NO <sub>3</sub>	1.9	4.7	0.4	1.4
NO <sub>2</sub>	1.9	4.7	0.4	1.4
Water diffusivity				
A ( $10^{-13}$ m <sup>2</sup> /s)	N/A	4.3	N/A	1.0
B (-)	N/A	80	N/A	80
w @ 50%RH (m <sup>3</sup> /m <sup>3</sup> )	N/A	0.059	N/A	0.064

\*  $D_{\text{effective}} = D_{\text{molec in water}} \div \text{Tortuosity}$

$D_{\text{intrinsic}} = (D_{\text{effective}})(\text{Porosity})$

**Table 5-5. Comparison of Transport Properties Measured by SIMCO and Others.**

Parameter	Vaults 1 / 4 Concrete (SIMCO)	Vaults 1 / 4 Concrete [Dixon, et al., 2008]	Disposal Unit 2 concrete (SIMCO)	Disposal Unit 2 concrete [Dixon, et al., 2008]
Porosity	10.0		10.3	
$D_{\text{eff}}(\text{cm}^2/\text{s})$				
$\text{OH}^-$	5.5 E-07	5 E-08	1.3 E-07	5 E-08
$\text{Na}^+$	1.4 E-07		3 E-08	
$\text{K}^+$	2.0 E-07		5 E-08	
$\text{SO}_4^{2-}$	1.1 E-07		3 E-08	
$\text{Ca}^{2+}$	8 E-08		2 E-08	
$\text{Al}(\text{OH})_4$	6 E-08		1 E-08	
$\text{NO}_3$	1.9 E-07		4 E-08	
$\text{NO}_2$	1.9 E-07		4 E-08	

Once the complete data set is obtained for the saltstone vault concretes, the STADIUM<sup>®</sup> code will be re-run using the properties measured for the Vaults 1 / 4 and Disposal Unit 2 concretes.

**6.0 SALTSTONE PROPERTIES**

Samples of saltstone were prepared and cured for 28 days. The compressive strength results are provided in Table 6-1. The measured compressive strength ( $f_c$ ) values are relatively low. Transport properties are currently being measured. Sample preparation and testing are described in Attachment 4.

**Table 6-1. Compressive strength for MCU Saltstone**

	average	CV (%) <sup>*</sup>
$f_c$ 7d (MPa) (psi)	2.1 300	7.4
$f_c$ 28d (MPa) (psi)	3.2 460	6.3

<sup>\*</sup>for three cubic specimens

The average 28 day compressive strength of saltstone samples prepared by SIMCO personnel was only 460 psi which is lower than values measured for 2 inch MCU saltstone cubes measured by another subcontractor. See results in Table 6-2.

**Table 6-2. Compressive Strength for the MCU Saltstone Grout (Cast 3/31/2008)<sup>\*</sup> [Dixon, et al, 2008].**

Days Aged	Date Tested	Compressive Strength (psig)			
		Measured			Average
16	4/16/2008	970	1000	920	963
28	4/28/2008	1000	1000	1030	1010
56	5/26/2008	1130	1120	1170	1140
90	6/29/2008	1200	1230	1210	1213

<sup>\*</sup>Samples were 2-in cube mold samples and were tested per ASTM C 109. Lab Batch ID 080014.

## 7.0 CONCLUSIONS AND RECOMMENDATIONS

Preliminary results on the durability of saltstone Vault 1 / 4 and Disposal Unit 2 concretes exposed to three corrosive alkaline solutions containing high concentrations of sulfate are summarized in this report. The analyses were obtained from SIMCO Technologies, Inc. using the STADIUM<sup>®</sup> Service Life Prediction Code.

Additional simulations are scheduled to be performed by SIMCO Technologies in early November 2008 that incorporate property data obtained on samples of Vaults 1 / 4 and Disposal Unit 2 concrete samples. Validation test for these simulations are scheduled to begin in early November 2008 and continue for approximately one year. Longer than expected testing times were required for these concrete samples because they are high quality mix designs and required more time than expected to obtain equilibrium moisture property results.

For the initial analyses, surrogate concretes in the SIMCO data base which were similar to the SRS saltstone Vaults 1 / 4 and Disposal Unit 2 concretes were used. Compositions of the corrosive solutions (leachates) and boundary conditions were provided by G. Flach, SRNL. The Case 1 solution has a composition representative of saltstone pore solution. Cases 2 and 3 are 10:1 and 100:1 dilutions with saturated lime water which was considered to represent infiltrating water equilibrated with concrete. The source of the sulfate is the saltstone make-up water. A significant amount of sulfate (for example, 25,000 mg/L of pore solution) is concentrated and remains in the pore water after the saltstone is cured.

In addition, initial characterization of the two saltstone vault concretes and of saltstone is in progress and results will be used to update the initial durability assessments using data collected from the Vault 1 / 4 and Disposal Unit 2 compositions. A partial set of property data are also reported.

Results of the initial STADIUM<sup>®</sup> simulations indicated that sulfate diffusion into the concrete resulted in ettringite formation which is a low density hydrated phase. The interface between the concrete and solution was always saturated and the sulfate concentration in each solution was assumed to be constant. Interestingly, gypsum precipitation which typically occurs between the ettringite front and the concrete surface exposed to the sulfate source was not observed in the simulations. (Gypsum is not stable at the high pHs produced by the corrosive alkaline solution.)

The formation of ettringite is considered to be an expansive reaction. Sulfate attack occurs if sufficient ettringite is formed to exceed the tensile strength of the concrete. Gypsum is another phase that forms as the result of decalcification of calcium silicate hydrate phases in the matrix when concrete is exposed to environmental solutions containing sulfate. Weakening of the matrix as the result of gypsum formation may be very important in the damage mechanics of sulfate exposure. Sulfate attack is expressed as cracking parallel to the exposed surface for unrestrained concrete.

Given the unusual mineralogy (ettringite but no gypsum) and the role of gypsum formation in the damage resulting from ettringite formation, it was not possible to predict the effects of cracking from changes in porosity calculated by the STADIUM<sup>®</sup> code or from damage mechanic models in the literature. (The STADIUM<sup>®</sup> model can not simulate cracking or changes in hydraulic conductivity due to cracking at this time.)

From an examination of the Sulfate Penetration Depth (cm) versus Time (yr) predictions for the surrogate concretes using the STADIUM<sup>®</sup> code (Appendix 2 Figure 7), it is obvious that this relationship is not linear. Consequently, it is important to the PA modeling to derive a relationship between the Concentration of Sulfate in the Leachate affecting the vault concrete and the depth of sulfate penetration into the concrete. At this time the following recommendations are made to obtain this relationship. The result will be concrete specific and given the present state of knowledge, must be developed for each concrete based on output from the STADIUM<sup>®</sup> code.

1. Construct a simplified model of the system.
  - a. Assume that the source of sulfate is the saltstone and that it is the interior surfaces of the concrete vault that are exposed to (in contact with) the corrosive sulfate solution (leachate).
  - b. Ignore the decalcification front and resulting damage (increase in porosity) that occurs at the concrete – soil interface which occurs on the exterior of the saltstone vault because it is negligible compared to the potential damage associated with the sulfate front.
  - c. Assume that the source of sulfate is an aqueous solution with a constant sulfate concentration over the entire exposure period. This assumes that the system is saturated over the entire exposure period. (very conservative)
  - d. Ignore interactions between the decalcification front and the sulfate front
  - e. Assume that ettringite formation in the concrete results in cracking and that no other phases (reactions) are required for the damage to occur.
  - f. Assume the ettringite front delineates intact concrete from damaged concrete.
  - g. Assume the concrete ahead of the front is undamaged and has a permeability of that measured by SRNL for cured material.
  - h. Assume the concrete behind the front is cracked to the extent that the hydraulic conductivity is similar to soil surrounding the vaults.
  - i. Assume that transport through the damaged concrete does not accelerate transport of the sulfate ions to the interface and thereby accelerate advancement of the front and of the resulting damage.
2. The relationship between the Sulfate Penetration Depth (cm) versus Time (yr) data for both concrete mixes exposed to three levels of sulfate concentrations is non-linear (Appendix 2 Figure 7). Consequently, a relationship between the sulfate concentration in the leachate solution versus the depth of penetration of sulfate into the concrete will

be useful for the PA calculations. Assume the depth of penetration corresponds to depth of damaged concrete.

Derive a relationship between the Sulfate Concentration in the Solution (mol/L) and the Sulfate Penetration Depth in the Concrete (cm) as a function of time.

- a. Extract data sets from Figure 4-3: Sulfate Penetration Depth (cm) versus Time (yr) and/or request data sets from SIMCO personnel. 10 points for each concrete-solution data set across the range of times is probably sufficient.
- b. Re-plot the data as Sulfate Penetration Depth (cm) versus the SQRT Time (yr) to obtain a linear relationship between time and depth for each concrete.
- c. Fit a curve to each data set of the form  $y = mx$ . (The  $m$  value is referred to as the proportionality factor for the relationship expressed by the equation.)
- d. Plot the proportionality factors from the Sulfate Penetration Depth versus the SQRT for the three different sulfate exposure conditions for each mix.
- e. Combine the following equations and solve for penetration depth, i.e.,  $X$

$$\text{Proportionality factor} = \text{Constant} (\text{sulfate concentration})^B$$

(where:  $B$  is the exponent in the equation (power law function) obtained from previous step)

$$\text{Penetration depth} = (\text{Proportionality Factor})(\text{sqrt Time})$$

$$X = (\text{Constant})(\text{Sulfate concentration})^B(\text{sqrt Time})$$

This analysis has already been conducted by G. Flach to support calculations for the Saltstone PA (Flach, 2008). He also extended the analysis to develop expressions for the depth of sulfate penetration (position of the sulfate front) for varying sulfate concentration (which also results in varying diffusion coefficients) as a function of time (Flach, 2008).

## 8.0 REFERENCES

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**9.0 ATTACHMENT 1**

**Summary of Subcontract No. AC 48992N Work Requirements**

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**SUBCONTRACT No. AC 48992N WORK REQUIREMENTS****Task Descriptions****Task 1. Preliminary estimate of service life.**

Predict degradation using literature data for concrete properties using mixes similar to the WSRC mixes or actual data supplied by SRNL for exposure to up to three (3) different corrodent solutions as specified by the STR at a later date.

Use Stadium and/or other modeling capabilities to predict the depth of penetration (diffusion front) of corrodents, including sulfate, aluminate, chloride, sodium, etc., in 2 different concretes exposed to 3 different solutions for extended time (up to 10,000 years):

- a. Estimate values for the important parameters from data provided by SRNL and by analogy to similar materials previously tested by SIMCO, Inc.
- b. Run the Stadium code for a rough estimate of depth of penetration.
- c. Estimate service life taking into consideration penetration depth, formation of expansive phases, and consequence of formation of expansive phases including effect of reinforcement and post tensioning steel.
- d. Estimate the effective transport properties (effective permeability, effective diffusivity coefficient, effective porosity, etc.), according to in-house protocol in addition to providing an estimate assuming the concrete is fully degraded behind the advancing front and intact (not degraded) ahead of the front with respect to computing effective transport properties – if the two approaches are different.

**Task 2. Measure relevant properties for SRS mixes.**

Measure parameters for 2 concrete mix designs (on samples cured for 28 and/or 90 days) required to support Stadium and/or other service life prediction modeling. Up to two (2) different curing times may be requested by the STR.

**Task 3. Estimate for SRS mixes.**

Run Stadium using data on SRS mixes. Predict depth of penetration of the corrodent species using data generated in 3.1.2 for the 2 concrete mix designs.

Estimate the effective transport properties (effective permeability, effective diffusivity, effective porosity, etc.), according to in-house protocol in addition to providing an estimate assuming the concrete is fully degraded behind the advancing front and intact (not degraded) ahead of the front with respect to computing effective transport properties – if the two approaches are different.

**Task 4. Confirm short term predictions.**

Expose samples for 2 concrete mix designs to up to three (3) different corrodent solutions to support calculated depth of penetration and service life predictions. The exact number of

corrodent solutions and the compositions of those solutions will be specified by the STR at a later date.

Analyze samples for relevant data after exposure for 4 months to compare with model predictions. (A request may be made to continue testing to obtain additional data points.) Monitor volumetric changes due to sulfate reactions with the two different concretes. The corrodent solutions will contain at a minimum sulfate, aluminate, chloride, and sodium.

**Task 5. Provide approach and methodology.**

The SIMCO, Inc. proposal will document the approach and methodology, identify information and testing required, identify the number of samples and sample geometry required, recommend laboratory prepared samples or actual samples (Vault 4) or test samples (Disposal Unit 2), and include a cost for preparing samples from materials supplied by SRNL. In the event that certain test methods for quantifying advancing fronts of both sulfate (sulfur) and aluminate (aluminum) in concrete (which already contain significant concentrations of S and Al) are determined to involve the use of radio tracers, a joint work scope with SRNL should also be prepared for the proposal.

**Task 6. Characterize MCU Saltstone and predict durability.**

Prepare MCU saltstone samples and measure properties that are required to run the STADIUM code. Predict the durability of saltstone exposed to infiltrating water.

**Task 7. Final Report.**

A draft final report is due on August 15, 2008.

A final reviewed and accepted report is due on September 30, 2008.

Data and modeling runs performed after September 30, 2008 will be submitted in Revisions of the final report within one month after being generated.

**10.0 ATTACHMENT 2**

**STADIUM® Code Predictions: Effects of High Sulfate Alkaline Solutions  
and SRS Soil Pore Water on Surrogate Saltstone Vault 1/4 and Disposal Unit  
2 Concretes**

**Subcontract No. AC48992N Task 1 Report**

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**SIMCO**  
Technologies inc.

Washington Savannah River Company

Subcontract no. AC48992N

Report

Task 1

May 31, 2008

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THE STADIUM® MODEL IS A HELPFUL TOOL TO PREDICT THE FUTURE CONDITIONS OF CONCRETE MATERIALS. HOWEVER, ALL DURABILITY-MODELING PARAMETERS HAVE A STATISTICAL RANGE OF ACCEPTABLE RESULTS. THE MODELING USED IN THIS REPORT USES MEAN LABORATORY- OR FIELD-DETERMINED SINGLE VALUES AS INPUT PARAMETERS. THIS PROVIDES A SINGLE RESULT, WHICH PROVIDES A SIMPLE ANALYSIS EVALUATING CORROSION PROTECTION OPTIONS. PREVIOUS CONDITIONS ARE ASSUMED TO CARRY FORWARD IN THE PREDICTION MODEL; THERE ARE NO ASSURANCES THAT THE STRUCTURE WILL BE EXPOSED TO A SIMILAR ENVIRONMENT AS IN THE PAST.

## 1. OBJECTIVE

The objective of Task 1 was to predict the service life of two concrete mixtures similar to the concrete mixtures used at SRS for radioactive waste storage when exposed to an aggressive sulfate solution for an extended period of time. The composition of the aggressive solution was provided by SRNL. The surrogate concretes identified by SIMCO Technologies were previously tested by SIMCO Technologies as part of their own research activities for transport properties. The selected mixtures were:

- A. A concrete with a w/b ratio of 0.35 made with an ASTM Type I cement and 35% slag,
- B. A concrete made with a pre-blended ternary binder incorporating CSA Type 10 cement, fly ash and silica fume. Type 10 cement is general use cement and equivalent to ASTM Type 1 cement.

The first mixture (A) was selected as a surrogate for the concrete referred as “Saltstone Vault 1 and 4” concrete. The second mixture (B) was selected as a surrogate for the “Saltstone Disposal Unit 2” concrete.

The report is divided as follow. Section 2 describes the ionic transport model called STADIUM<sup>®</sup> that was used to perform the service life calculations. Section 3 describes the two concrete mixtures that were simulated, along with the tests that were performed to estimate their properties. Section 4 focuses on the simulation. The various hypotheses used for the calculations as well as the analysis of the results are outlined in this section.

## 2. MODEL DESCRIPTION

STADIUM<sup>®</sup> is a multiionic transport model based on a sequential split operator approach that separates ionic movement and chemical reactions. Details on the paper can be found in papers [1-3]. The present version of the model does not include any coupling with mechanical damages. It does not allow predicting the apparition of cracks resulting from the exposure to an aggressive environment (e.g. sulfate attacks) or internal chemical degradation such as alkali silica reaction (ASR). Given the high alkalinity of the aggressive solution composition provided by SRNL, the risk of ASR should be considered in a more global performance assessment study.

The ionic transport is described by the extended Nernst-Planck equation applied to unsaturated and non-isotherm materials. This equation accounts for the electrical coupling as well as the chemical activity between ionic fluxes, transport due to water content gradient and temperature effects:

$$\frac{\partial(wc_i)}{\partial t} - \operatorname{div} \left( D_i w \operatorname{grad}(c_i) + \frac{D_i z_i F}{RT} w c_i \operatorname{grad}(\psi) + D_i w c_i \operatorname{grad}(\ln \gamma_i) + \frac{D_i c_i \ln(\gamma_i c_i)}{T} w \operatorname{grad}(T) + c_i D_w \operatorname{grad}(w) \right) = 0 \quad (1)$$

where  $c_i$  is the concentration [mmol/L],  $w$  is the water content [ $\text{m}^3/\text{m}^3$ ],  $D_i$  is the diffusion coefficient [ $\text{m}^2/\text{s}$ ],  $z_i$  is the valence number of the ionic species  $i$ ,  $F$  is the Faraday constant [96488.46 C/mol],  $\psi$  is the electrodiffusion potential [V],  $R$  is the ideal gas constant [8.3143 J/mol/°K],  $T$  is the temperature [°K],  $\gamma_i$  is the activity coefficient, and  $D_w$  is the water diffusivity [ $\text{m}^2/\text{s}$ ]. Eight ionic species were considered for this task:  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}(\text{OH})_4^-$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$ . The activity coefficients in the model are evaluated on the basis of the Harvie, Moller and Weare (HMW) implementation of Pitzer's ion interaction model [4].

The electrodiffusion term in equation (1), involving the potential  $\psi$ , is mainly responsible for maintaining the electroneutrality of the pore solution. Its role is to balance each individual ionic mobilities so that there is no net accumulation of charge at any location in the pore solution. It is usually neglected in models dealing with ionic transport in groundwater where the concentration levels can be low. However, in cementitious materials, where pore solution concentrations are high (pH around 13.2), this term can have a significant influence on the ingress rate of contaminants in structures. This was emphasized for the case of sulfate attack in reference [3]. To solve the diffusion potential  $\psi$ , the ionic transport equation is coupled to Poisson's equation, which relates the electrodiffusion potential in the material to the ionic profile distributions:

$$\operatorname{div}(\tau w \operatorname{grad} \psi) + \frac{F}{\varepsilon} w \left( \sum_{i=1}^N z_i c_i \right) = 0 \quad (2)$$

where  $\varepsilon$  [C/V/m] is the medium permittivity and  $N$  is the number of ions in the pore solution.

To account for water flow in the presence of water content gradients in unsaturated materials, the previous equations are coupled to Richard's equation:

$$\frac{\partial w}{\partial t} - \operatorname{div}(D_w \operatorname{grad}(w)) = 0 \quad (3)$$

This diffusion-type equation gives the distribution of water content within the material. The water diffusivity parameter is nonlinear and follows an exponential function [5]:  $D_w = A e^{Bw}$ .<sup>6</sup> Finally, the temperature distribution in the material is calculated from the classical heat condition equation:

<sup>6</sup> Work is ongoing at SIMCO to model moisture flow based on a capillary pressure approach. The objective in that case is to use drying test results to estimate the permeability of cementitious materials.

$$\rho C_p \frac{\partial T}{\partial t} - \text{div}(\kappa \text{grad}(T)) = 0 \quad (4)$$

where  $\rho$  is the density of the material [ $\text{kg}/\text{m}^3$ ],  $C_p$  is the specific heat of the material [ $\text{J}/\text{kg}/^\circ\text{C}$ ], and  $k$  is the heat conductivity [ $\text{W}/\text{m}^2/^\circ\text{C}$ ].

The key material parameter that determines the rate of ingress of chloride and other contaminants in the structure is the diffusion coefficient  $D_i$  (see equation (1)). This parameter is influenced by multiple parameters:

$$D_i = D_i^{\text{ref}} \times S(w) \times G(T) \times H(t) \times M(\phi) \quad (5)$$

where  $D_i^{\text{ref}}$  is a reference value measured on sound material samples using the migration test procedure, described later in the report. It usually corresponds to the measurement at 28 days of curing. The various functions affecting the diffusion coefficient are given as:

$$\begin{aligned} S(w) &= \frac{w^{7/3}}{\phi_o^{7/3}} \\ G(T) &= e^{0.028(T-T^{\text{ref}})} \\ H(t) &= \frac{a}{1 + (a-1)e^{-\alpha(t-t^{\text{ref}})}} \\ M(\phi) &= \frac{e^{4.3\phi/V_p}}{e^{4.3\phi_o/V_p}} \end{aligned} \quad (6)$$

where  $\phi_o$  is the initial porosity of the material,  $\phi$  is the porosity at time  $t$  and  $V_p$  is the volumetric paste content of the cementitious material [ $\text{m}^3/\text{m}^3$ ]. The function  $S(w)$  models the influence of the water content on diffusion. It is based on the relationship derived by Millington and Quirk [6]. The function  $G(T)$  considers the effect of temperature [2,7] on transport properties, compared to a reference value evaluated at the temperature  $T^{\text{ref}}$ . The function  $H(t)$  takes into account the variation of transport properties as a result of the cement hydration process [2]. The transport properties of cementitious materials are generally high at young age but tend to decrease with time, especially when supplementary materials such as fly ash are used in the production of concrete. The reduction rate is determined by the factor  $\alpha$  while the ultimate value of  $H(t \rightarrow \infty)$ , when the hydration process is completed, is given by  $a$ .

Finally, the alteration to the material's microstructure caused by the chemical reactions between the external contaminants, such as sulfate, and the cement paste can induce local porosity variations that affect the diffusion coefficients. Alteration of the microstructure can result in one or more of the following consequences, increase or decrease in the porosity of the microstructure, fracturing of the microstructure, or macro fracturing of the structural element. This is taken into account using the function  $M(\phi)$ , which was established on the basis of porosity and diffusion coefficient measurements performed over a wide range of

cementitious materials [2]<sup>7</sup>. A similar approach has been widely used to predict the long-term effect of contaminant transport in soils (see for instance reference [8]).

The porosity variations are calculated by accounting at each node for changes in the solid phase distribution evaluated at the previous time step. The description of the chemical module is given below.

The water diffusivity, which governs the kinetic of the moisture movement in the materials, is affected by the same factors as the diffusion coefficient.

Since eight ionic species are considered in the model, there are 11 variables in the system of equations:  $8 \times c_i$ ,  $\psi$ ,  $w$  and  $T$ , which are solved using 8 ionic conservation equations (1), coupled with equations (2)-(4). This system of nonlinear equations is solved using the Newton-Raphson method with all equations solved simultaneously. The spatial discretization of this coupled system is based on the finite element approach using the standard Galerkin procedure. An Euler implicit scheme is used to discretize the time-dependent part of the model. The numerical details are given in reference [2].

The second module in STADIUM<sup>®</sup> consists in a chemical equilibrium code. Following the transport step, the chemical equilibrium module verifies, at each node of the mesh, the equilibrium between the concentrations and the solid phases of the hydrated cement paste: calcium hydroxide, calcium silicate hydrates, ettringite, and mono-sulfates. The equilibrium of each phase is modeled according to:

$$K_m = \prod_{i=1}^N c_i^{v_{mi}} \gamma_i^{v_{mi}} \quad \text{with } m = 1, \dots, M \quad (7)$$

where  $M$  is the number of solid phases,  $N$  is the number of ions,  $K_m$  is the equilibrium constant (or solubility constant) of the solid  $m$ ,  $c_i$  is the concentration of the ionic species  $i$ ,  $\gamma_i$  is its chemical activity coefficient, and  $v_{mi}$  is the stoichiometric coefficient of the  $i$ th ionic species in the  $m$ th mineral. If the solution is not in equilibrium with the paste, solid phases are either dissolved or precipitated to restore equilibrium. Solid phases can also be formed when aggressive species penetrate into the porous network of the material, e.g. ettringite, gypsum, hydrated sodium sulfate, and halite.

The penetration of chloride in concrete structures leads to the formation of a chloride-AFm solid compound called the Friedel's salt [9],  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ . The formation of Friedel's salt upon chloride penetration is modeled following an ion-exchange mechanism with monosulfates:

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<sup>7</sup> At this time, the STADIUM<sup>®</sup> code does not predict fracturing caused by exposure to external contaminants. In addition to exposure to external contaminants, fracture patterns are a function of element geometry, initial conditions (cracking incurred during construction and curing), and specific loading conditions. Methodology to address fracture damage and consequences of microfracturing caused by exposure to chemical contaminants is included in the SIMCO scope for the CBP CRADA.



This reaction obeys the following equilibrium relationship [1]:

$$K_{Cl/so_4} = \frac{\{\text{Cl}\}^2 [\text{AFm}_{SO_4}]}{\{\text{SO}_4\} [\text{AFm}_{Cl}]} \quad (9)$$

where  $[\text{AF}_m]$  and  $[\text{FS}]$  are the solid content [mmol/g] in monosulfate and Friedel's salt respectively. The curly brackets  $\{\dots\}$  correspond to the chemical activity of the ionic species.

Papers describing laboratory validation of the model for different type of exposures can be found in references [1, 3, 10]. Field validation test cases were also performed [11, 12].

### 3. CONCRETE MIXTURE CHARACTERISTICS

The properties of the concrete mixtures that were used to emulate the Vault 1/4 and Disposal Unit 2 concretes are summarized in Tables 1 and 2. They had a water to binder (total cementitious materials ratio) ratio of 0.35. The Vaults 1 / 4 surrogate concrete was made with ASTM Type I cement and slag cement. The Disposal Unit 2 surrogate concrete was made with a ternary binder (CSA Type 10 cement, Class F fly ash, and silica fume). In both cases, the mixtures were cast in plastic cylinders (10 cm diameter, 20 cm length) and demolded 24 hours later. The cylinders were then placed in a fog room (100% RH) for curing. After selected curing periods (28 days, 90 days, 1 year, and 2 years) cylinders were taken from the chamber and tested for the different transport properties. The tests are described in the following paragraphs.

**Porosity:** The porosity was evaluated on the basis of the ASTM C642 procedure. This procedure consists in oven-drying a concrete sample and then re-saturating it with water. The mass difference provides the porosity value. Laboratory measurements at different curing age showed no significant effect of the curing age of concrete on the porosity. Accordingly, the porosity is not affected by the hydration in the model.

**Diffusivity:** The diffusion coefficients were evaluated using the migration test procedure. The migration test is a modified version of the ASTM C1202 standard procedure. It consists in accelerating the transport of ions in a saturated concrete sample by applying an external electrical potential. The experimental set-up is shown in Figure 1. To perform the test, 50-mm thick discs were first cut from the cores and vacuum saturated in a 300 mmol/L NaOH solution for 24 hours.

The lateral surface of the discs was coated with a silicon gel. The discs were then mounted on the migration cells. The cell/disc interface was also coated with silicon to ensure a watertight joint. Both compartments of the cells were filled with approximately 2.5 litres of solution. The test solution on the upstream side of the cell was made of 300 mmol/L of sodium hydroxide (NaOH) and 500 mmol/L of sodium chloride (NaCl). The downstream compartment of the cell was filled with a 300 mmol/L sodium hydroxide solution. During the

test, an external 20 V potential was applied to the cell, and the current passing through the samples was regularly measured over a 200-hour period. Current values were then analyzed following the procedure described in Samson et al. [13] in order to evaluate the diffusion coefficients.

The hydration of cementitious materials leads to a reduction of the diffusion coefficients with time. To account for this, migration tests were performed at different curing age and fitted to the time dependent function  $H(t)$  reported in equation (6). The hydration function for each material is plotted on Figure 2A and 2B. The hydration parameters are given in Tables 1 and 2.

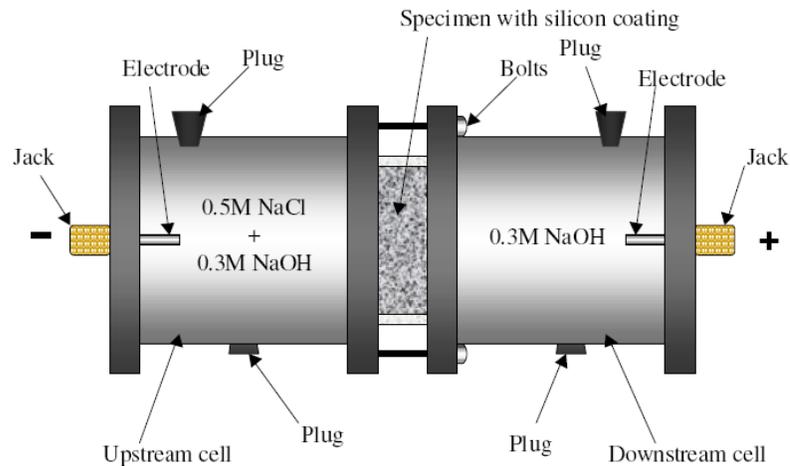


Figure 1 – Migration test setup

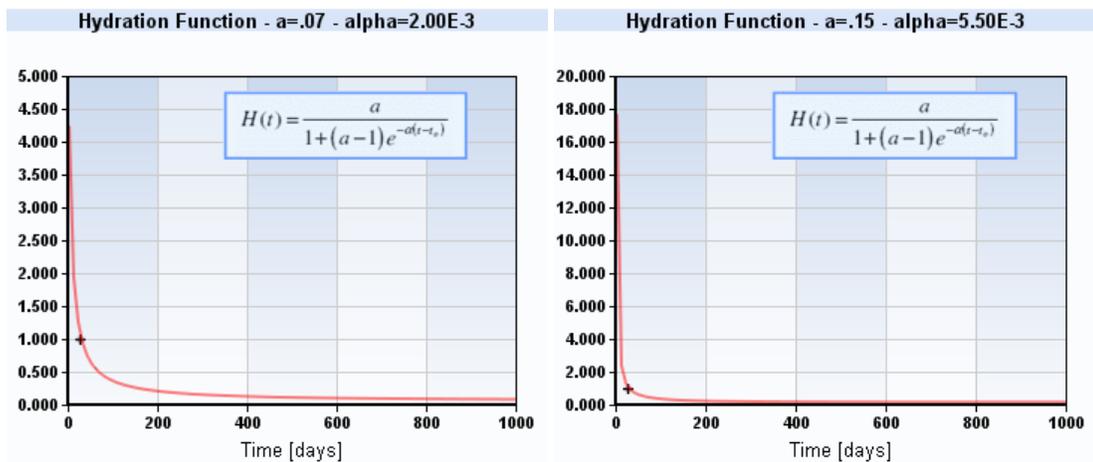
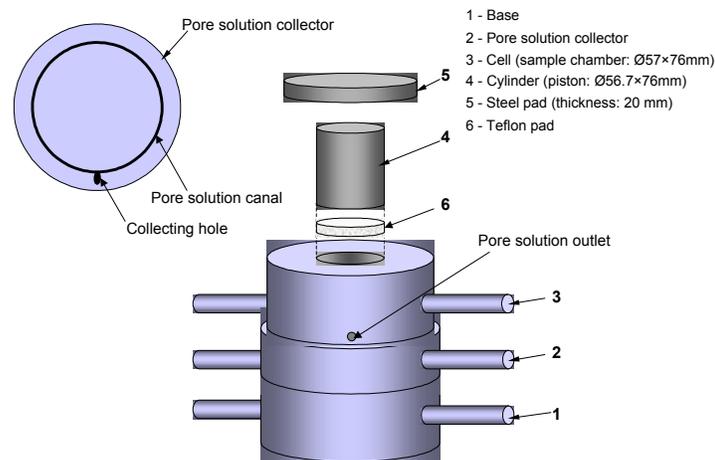


Figure 2 – Hydration functions for the two surrogate concretes. Figure A: slag concrete, Figure B: ternary concrete

**Pore Solution Extraction and Analysis:** The initial composition of the pore solution was obtained by extracting the solution under an applied external pressure [14]. Prior testing, a concrete sample was broken into pieces and placed in the extraction cell (Figure 3). The pressure was then applied. The solution was collected in a syringe to limit contact with air. It was stored in a refrigerator until the analysis was performed. Before the analysis, the solution was diluted approximately 10 times to get sufficient solution for all the measurements. The

concentrations in  $\text{OH}^-$  was evaluated by potentiometric titration, and the cation concentrations ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) were analyzed using ICP. The sulfate concentration was measured using ionic chromatography.

The initial  $\text{Al}(\text{OH})_4^-$  content was estimated at 0.1 mmol/L since it was too weak to be measured after the solution dilution. Also, due to experimental errors, the extracted solution was not strictly neutral. The solution was balanced to respect the electroneutrality requirement. One set of pore solution extractions was performed on samples directly from the curing room after 28 days for future service life simulations. Those values are reported in Tables 1 and 2. Another series of extraction was performed on samples saturated for 24 hours under vacuum in a 300 mmol/L NaOH solution. These results were used in interpretation of the migration tests.



**Figure 3 – Pore solution extraction cell**

**Water Diffusivity Characterization:** The water diffusivity is estimated from drying test results. The test procedure consists in drying two series of samples in a 50% RH room. In the first series, the samples were 50 mm thick while they had a 10 mm thickness in the second series. The samples were coated with epoxy on their circular face, which left two flat surfaces open for drying. The saturated samples were placed in a 50% RH room and their weight loss was monitored periodically. When the thin samples reached equilibrium, the test was analyzed by fitting the mass loss curves with Richards' model (equation 3). It is assumed that the water diffusivity is nonlinear and can be expressed as:  $D_w = Ae^{Bw}$  [5]. Parameters  $A$  and  $B$  were adjusted to fit the model prediction with the experimental mass loss curves. Details on the analysis are provided in reference [15]. Values for  $A$  and  $B$  for the surrogate concretes and are listed in Tables 1 and 2.

**Initial Mineralogy Characterization:** Finally, the initial solid phases of the hydrated cement paste are estimated from the cement and admixtures chemical composition. The calculations are based on a simple mass balance, assuming that the initial paste is made of portlandite, C-S-H, monosulfates, and ettringite. Details on the calculation are provided in reference [2]. It should be noted that only a small amount of portlandite is present initially in

both materials, due to the presence of supplementary cementitious admixtures which favor the formation of C-S-H.

**Table 1 – Properties of the slag concrete mixture (Vault 1/4 surrogate)**

Properties	Values	Properties	Values
Cement type	ASTM Type I	Porosity	10.0%
w/b	0.35	Diffusion coefficients	(E-11 m <sup>2</sup> /s)
Mixture proportions	(kg/m <sup>3</sup> )	OH <sup>-</sup>	13.0
Cement	276	Na <sup>+</sup>	3.3
Slag	149	K <sup>+</sup>	4.8
Water	149	SO <sub>4</sub> <sup>2-</sup>	2.6
Coarse aggregates	925	Ca <sup>2+</sup>	2.0
Fine aggregates	815	Al(OH) <sub>4</sub> <sup>-</sup>	1.3
Density	2314	NO <sub>3</sub> <sup>-</sup>	4.7
		NO <sub>2</sub> <sup>-</sup>	4.7
Cement composition	(% mass)	Water diffusivity	
CaO	64.5	A (E-13 m <sup>2</sup> /s)	4.3
SiO <sub>2</sub>	20.8	B (-)	80
Al <sub>2</sub> O <sub>3</sub>	5.3	w @ 50%RH (m <sup>3</sup> /m <sup>3</sup> )	0.059
SO <sub>3</sub>	2.8	Hydration parameters	
Fe <sub>2</sub> O <sub>3</sub>	2.1	a (-)	0.07
Slag composition	(% mass)	α (1/s)	2.0E-03
CaO	40.1	Initial pore solution	(mmol/L)
SiO <sub>2</sub>	36.8	OH <sup>-</sup>	217.2
Al <sub>2</sub> O <sub>3</sub>	8.7	Na <sup>+</sup>	108.7
SO <sub>3</sub>	2.3	K <sup>+</sup>	110.4
Fe <sub>2</sub> O <sub>3</sub>	0.7	SO <sub>4</sub> <sup>2-</sup>	1.9
Bogue cement analysis	(% mass)	Ca <sup>2+</sup>	1.0
C <sub>3</sub> S	57.9	Al(OH) <sub>4</sub> <sup>-</sup>	0.1
C <sub>2</sub> S	16.0	Initial solid phases	(g/kg)
C <sub>3</sub> A	10.5	Portlandite	3.3
C <sub>4</sub> AF	6.4	C-S-H	81.3
Compressive strength	(Mpa)	Monosulfate	29.3
7 days	42.7	Ettringite	2.0
28 days	54.0		
91 days	65.3		
1 year	56.7		
2 years	69.7		

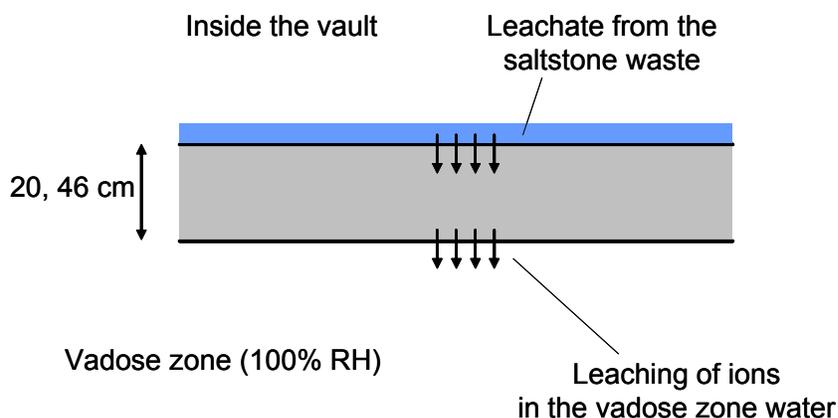
**Table 2 – Properties of the ternary concrete mixture (Disposal Unit 2 surrogate)**

Properties	Values	Properties	Values
Cement type	CSA Type 10	Diffusion coefficients	(E-11 m <sup>2</sup> /s)
w/b	0.35	OH <sup>-</sup>	4.0
Mixture proportions	(kg/m <sup>3</sup> )	Na <sup>+</sup>	1.0
Blended Cement	425	K <sup>+</sup>	1.5
Water	149	SO <sub>4</sub> <sup>2-</sup>	0.8
Coarse aggregates	910	Ca <sup>2+</sup>	0.6
Fine aggregates	800	Al(OH) <sub>4</sub> <sup>-</sup>	0.4
Density	2284	NO <sub>3</sub> <sup>-</sup>	1.4
		NO <sub>2</sub> <sup>-</sup>	1.4
Blended cement composition	(% mass)	Water diffusivity	
CaO	47.1	A (E-13 m <sup>2</sup> /s)	1.0
SiO <sub>2</sub>	30.2	B ( - )	80
Al <sub>2</sub> O <sub>3</sub>	5.0	w @ 50%RH (m <sup>3</sup> /m <sup>3</sup> )	0.064
SO <sub>3</sub>	3.2	Hydration parameters	
Fe <sub>2</sub> O <sub>3</sub>	3.8	a ( - )	0.15
Bogue cement analysis*	(% mass)	α (1/s)	5.5E-03
C <sub>3</sub> S	N/A	Initial pore solution	(mmol/L)
C <sub>2</sub> S	N/A	OH <sup>-</sup>	204.0
C <sub>3</sub> A	N/A	Na <sup>+</sup>	58.8
C <sub>4</sub> AF	N/A	K <sup>+</sup>	149.9
Compressive strength	(Mpa)	SO <sub>4</sub> <sup>2-</sup>	3.3
7 days	41.6	Ca <sup>2+</sup>	1.0
28 days	56.7	Al(OH) <sub>4</sub> <sup>-</sup>	0.1
91 days	62.1	Initial solid phases	(g/kg)
1 year	66.5	Portlandite	3.0
2 years	72.8	C-S-H	85.2
Porosity	10.2%	Monosulfate	23.4
		Ettringite	2.0

\*Bogue analysis is not suited for blended cements

#### 4. SIMULATIONS AND ANALYSIS

**Model:** The service life simulations were performed on the case illustrated on Figure 4. The 1D simulations were performed on a 20-cm (8 in.) slab<sup>8</sup> for Disposal Unit 2 and 46-cm (18 in.) slab for Vault 1/4. The slabs were exposed on one side ( $x=0$ ) to the leachate from the saltstone waste and on the other side to groundwater ( $x=L$ ). It is assumed that the groundwater composition corresponds to pure water at a pH of 7<sup>9</sup>.



**Figure 4 – Test case for the simulations**

**Composition of Aggressive Solutions:** Compositions of three hypothetical saltstone leachates were provided by SNRL. The main species of the leachates are  $\text{OH}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{SO}_4^{2-}$ . For the purpose of the simulations, the minor species such as  $\text{AlO}_2^-$ ,  $\text{Fe}^{3+}$ ,  $\text{SiO}_3^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{PO}_4^{3-}$  were neglected. This is partly due to a lack of data concerning the mineral phases associated with these ions. Also, neglecting these species allow reducing calculation time. If it is estimated that these species cannot be neglected, additional simulations incorporating the associated chemical reactions would be performed.

Following these simplifications, the provided leachate compositions were adjusted to enforce the electroneutrality requirement. The concentrations previously discussed are provided in Table 3 and correspond to the “High level” “worst case” case. Other sets of simulations were performed with the “high (worst) case” solution diluted 10 (“Mid-level” case) and 100 times (“Low-level” case). All solutions are reported in Table 3. The concentrations for all ionic species at  $x=L$  cm, corresponding to the material in contact with the vadose water, are set to zero.

<sup>8</sup> The orientation of the slab is irrelevant for the calculations since gravity is a negligible factor for ionic and mass transport. The same results would be obtained with a vertical buried wall.

<sup>9</sup> Actual vadose water pH value is around 6. The present version of STADIUM<sup>®</sup> does not allow considering acid exposure. The slightly acid water would likely increase the degradation rate at  $x=L$ . However, the thick slab, combined to the high pH solution inside the vault would likely buffer the acid attack and limit its effect.

**Table 3 – Saltstone leachate composition used for the simulations  
(Boundary conditions at  $x=0$ )**

Ionic species	Concentrations (mmol/L)		
	High level	Mid level	Low level
OH <sup>-</sup>	769.0	76.9	7.69
Na <sup>+</sup>	4366.0	436.6	43.66
K <sup>+</sup>	215.0	21.5	2.15
SO <sub>4</sub> <sup>2-</sup>	208.0	20.8	2.08
Ca <sup>2+</sup>	1.0	0.1	0.01
NO <sub>3</sub> <sup>-</sup>	2649.0	264.9	26.49
NO <sub>2</sub> <sup>-</sup>	749.0	74.9	7.49

**Corrosion:** Chloride present in the saltstone leachate was also neglected. As discussed in reference [16], chloride does not have a major impact on the microstructure of the material but is a major concern for structure durability due to its role in the initiation of reinforcement corrosion. However, the amount of Cl<sup>-</sup> in the most concentrated leachate (<1500 ppm, or < 44 mmol/L) is too low to trigger the corrosion process [17].

The presence of CO<sub>2</sub> is also a concern for corrosion. This is especially the case for environmental carbonation, where CO<sub>2</sub> enter the material and reacts to form CaCO<sub>3</sub>. The various steps leading to the formation of calcite requires hydroxide ions, which lowers the pH of the pore solution. When carbonation reaches the rebars, the steel is depassivated due to the drop of pH and will corrode if oxygen and water are available. In the present case, the risks for carbonation-induce corrosion are minimal. The high pH of the leachate will likely prevent the depassivation of steel. For the concrete face exposed to the vadose zone water, poor oxygen availability would in this case prevent the corrosion process, even if CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> are dissolved in solution.

**Equilibrium Mineral Assemblages:** The minerals that were considered for the durability analysis are listed in Table 4. The portlandite, C-S-H, monosulfates, and ettringite were present initially in the hydrated cement paste. The other minerals were considered as possible precipitates due to the presence of SO<sub>4</sub><sup>2-</sup>. For these simulations, it was assumed that NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> did not react with other species. However, their strong concentration likely affected the precipitation of other phases due to their impact on the chemical activity calculations (equation (7)).

The chemical equilibrium of C-S-H is modeled on the basis of Berner's approach [17] that assigns separate C/S-dependent equilibrium relationships to the Ca(OH)<sub>2</sub> and CaH<sub>2</sub>SiO<sub>4</sub> fractions of this hydration product. For the present calculations, this approach is further simplified by considering solely the Ca(OH)<sub>2</sub> fraction and an equilibrium constant corresponding to a C/S ratio of approximately 1. This approach has been successfully validated previously for sulfate attack cases [3, 10]. Using this approach allows neglecting the H<sub>2</sub>SiO<sub>4</sub><sup>2-</sup> ion and the CaH<sub>2</sub>SiO<sub>4</sub> mineral, which saves calculation time.

**Table 4 – Mineral phases considered for the calculations**

Minerals	Composition	log(K) @ 25°C
Portlandite	Ca(OH) <sub>2</sub>	-5.15
C-S-H (portlandite fraction)	Ca(OH) <sub>2</sub>	-6.2
Monosulfates	3CaO.Al <sub>2</sub> O <sub>3</sub> .CaSO <sub>4</sub> .12H <sub>2</sub> O	-29.4
Ettringite	3CaO.Al <sub>2</sub> O <sub>3</sub> .3CaSO <sub>4</sub> .26H <sub>2</sub> O	-44.0
Glauberite	Na <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub>	-5.18
Gypsum	CaSO <sub>4</sub> .2H <sub>2</sub> O	-4.58
Mirabilite	Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O	-1.4
Syngenite	K <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub> .H <sub>2</sub> O	-7.45
Glaserite	NaK <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub>	-3.8

**Temperature and Moisture Boundary Conditions:** The temperature was set at a constant temperature of 15°C. The boundary condition for the water content at  $x=0$  corresponds to the porosity of the material, assuming that the concrete is always saturated at this interface. For the surface in contact with the soil ( $x=L$  cm), simulations were made at 100% relative humidity. This boundary condition corresponds to a water content set at the porosity value.

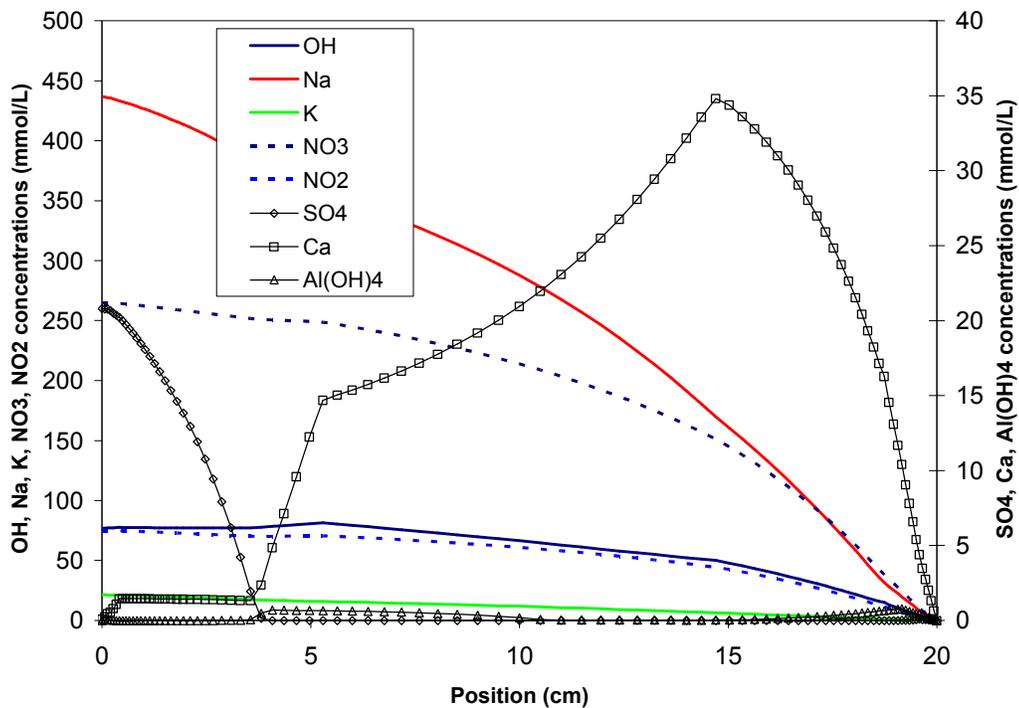
**Finite Element Mesh:** The simulations were performed with finite element meshes of 90 elements for  $L=20$  cm and 154 elements for  $L=46$  cm that are refined near the domain boundaries. The time steps were increased progressively to reduce the calculation time:  $\Delta t=1$  day for  $t<100$  years,  $\Delta t=2$  days for  $t<500$  years,  $\Delta t=5$  days for  $t<2000$  years, and  $\Delta t=8$  days for  $t=2000+$  years.

**Simulation Results:** Results are shown in Figures 5 and 6 for the ternary concrete (surrogate for Saltstone Disposal Unit 2 concrete) exposed to the mid-level conditions after 2000 years. One of the main features of all simulation results is the formation of ettringite, which was the only SO<sub>4</sub>-related mineral predicted by the model for all three exposure conditions. In all cases, an ettringite front begins at the surface exposed to the aggressive leachate,  $x=0$ , and penetrates deeper into the slab with time. As will be discussed later, the kinetic of the front progression depends on the transport properties of the materials and on the exposure conditions. It also depends on the initial amount of hydrated monosulfate in the cement paste, since the formation of ettringite requires monosulfate to dissolve. This dissolution provides calcium and alumina and part of the sulfur needed in the formation of ettringite. For comparable transport properties, cement with lower C<sub>3</sub>A content will exhibit an ettringite front that penetrates more rapidly in the material.

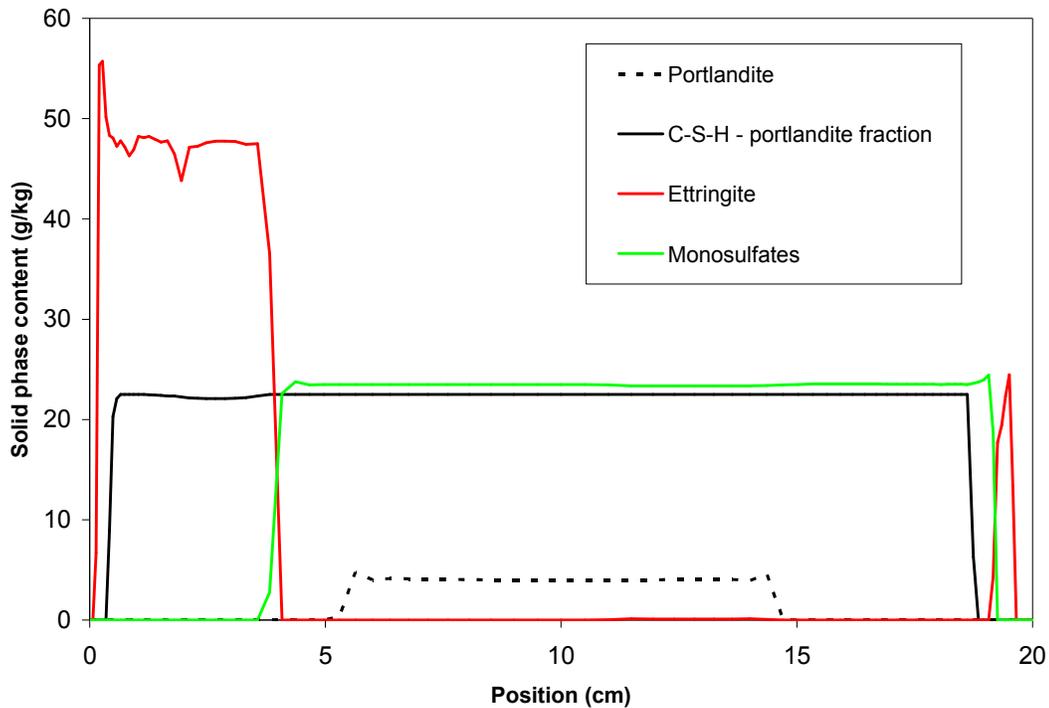
Since the formation of ettringite not only requires SO<sub>4</sub><sup>2-</sup> in the solution but also an additional amount of calcium, the small amount of portlandite initially present in the material is

dissolved upon ettringite formation. Similar observations were made on simulations of ordinary concrete mixtures exposed to sodium sulfate [3].

Due to the strong concentration in  $\text{OH}^-$  at  $x=0$ , limited decalcification of C-S-H is predicted at this location. However, the simulation results indicate that the decalcification process is more important at the soil/concrete interface ( $x = 20$  cm for Disposal Unit 2 and  $x = 46$  cm for Vault 1/4 surrogates), where the material is exposed to pure water. On this side of the concrete, a dissolution front moves inward toward the surface in contact with the aggressive leachate and the advancing ettringite front. The kinetic of the decalcification front is mostly controlled by the transport properties. A small ettringite peak (shown in Figure 6) is predicted in front of the C-S-H front. It is caused by the release of calcium and sulfate in the pore solution upon C-S-H decalcification and monosulfate dissolution.



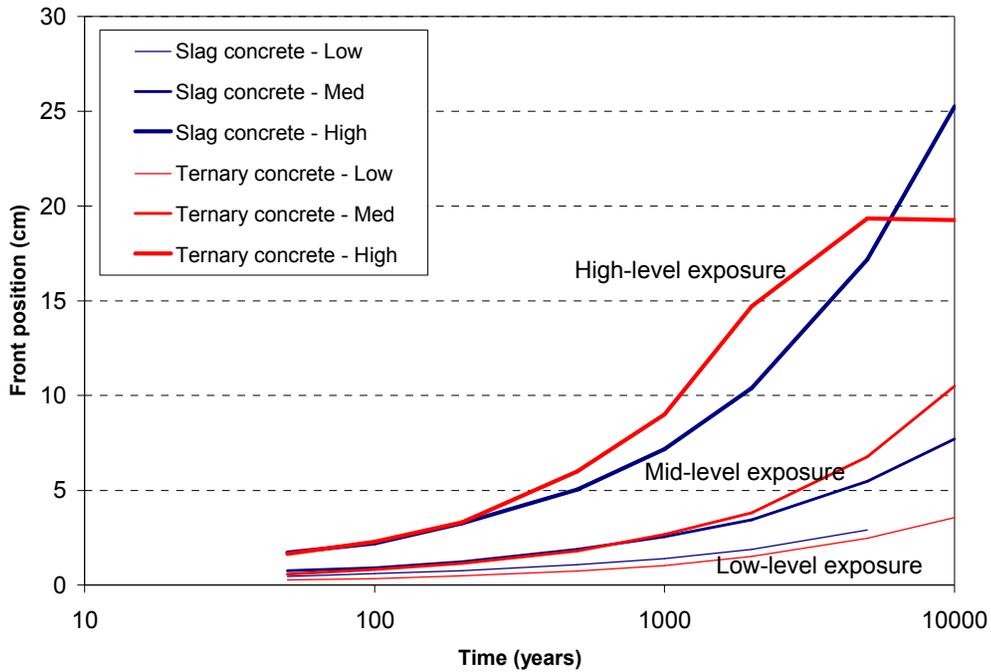
**Figure 5 – Ionic species in the pore solution for the ternary concrete exposed to the mid-level conditions after 2000 years**



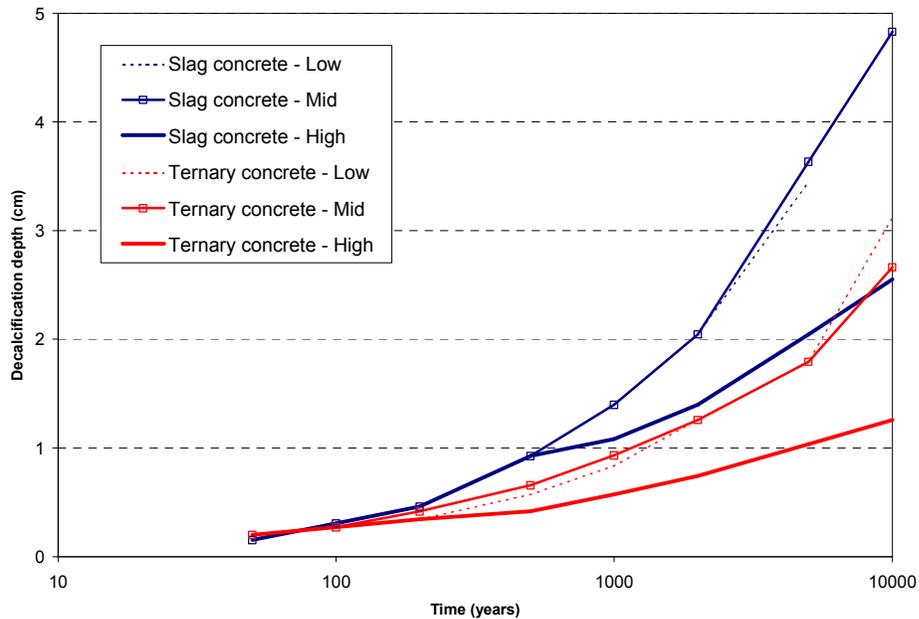
**Figure 6 – Solid phases in the hydrated cement paste for the ternary concrete exposed to the mid-level conditions after 2000 years**

The results of the six simulations (2 surrogate concretes and 3 sulfate solutions) are summarized in the following figures. Figure 7 shows the progression of the ettringite front from the leachate/concrete interface. The simulation results clearly emphasize that the main driving parameter of the front kinetic is the exposure level in sulfate. The small differences in the material transport properties do not translate into significant differences in the position of the ettringite front.

The simulations show that if the exposure conditions are maintained over the structure service-life, the ettringite is likely to go through the slab after approximately 5000 years for the high-concentration case. The reduction in the penetration rate after 5000+ years is due to the interaction with the decalcification ongoing at the soil/concrete interface. As mentioned previously, it should be remembered that these calculations do not consider the possible formation of microcracks associated with the formation of ettringite. In that case, the rate of ingress of the ettringite front would be increased.



**Figure 7 – Progression of the ettringite front from the saltstone leachate / concrete interface.**



**Figure 8 – Progression of the decalcification front from the soil/ concrete interface**

The situation for the decalcification front starting at the soil/concrete interface is different (Figure 8). For the first 500 years, the degradation kinetic is very similar for all the simulations cases. After that, the penetration of  $\text{OH}^-$  present in the leachate on the other side of the slab tends to slow down the decalcification process. Consequently, the decalcification

process is less important (has a lesser impact) for the high-concentration case while the low concentration case exhibits the higher rate of decalcification. In any case, the model predicts that the degraded zone should not exceed 4 cm, which means that if the rebars are deeper than that and the slab is thick enough, the decalcification process is not likely to affect the service life of the structure over its intended period of use.

**Discussion of Material Damage:** The mechanisms and conditions that cause damage to concrete as the result of exposure to sulfate solutions are topics of hundreds of research papers. Although ettringite formation is associated with expansion and consequent cracking, other conditions (chemical and mineralogical) are characteristic of the sulfate attack process and contribute at least in part to the damage (expansion and cracking) typically related to this type of concrete degradation.

As reported in reference [19], sulfate attacks in natural conditions usually occur most of the time at a pH around 7. In these conditions, ettringite is formed following the dissolution of monosulfate. The low pH also favors the dissolution of portlandite and C-S-H, which provide calcium to the pore solution and triggers the formation of gypsum. The degraded cement paste can be divided in the following zones, starting from the sound material toward the external surface [19]:

- The original paste not involved in the corrosion process,
- A zone in which ettringite had been formed in a reaction with monosulfate; the amount of calcium hydroxide is reduced,
- A zone containing gypsum; calcium hydroxide is absent, the C-S-H phase is partially decalcified (formation of horizontal cracks<sup>10</sup> preferentially in this region),
- A zone containing the C-S-H phase with a significantly reduced C/S ratio as its main constituent. Limited amounts of sulfates in adsorbed form may also be present.

In these conditions, many papers report losses in mechanical resistance [20] and expansions (see for instance reference [21]).

In the present case, the pH of the aggressive solution is around 13. As mentioned previously, the precipitation of gypsum was not observed in any simulations. The absence of gypsum from the results can be explained in part by the strong concentration in sodium, which tends to increase the solubility of this mineral [22], therefore limiting the precipitation process. Also, the strong OH<sup>-</sup> concentration in the saltstone leachate limits the decalcification process. As reported in reference [3], the formation of gypsum is associated with the dissolution of portlandite, or C-S-H in the present case, which provides the necessary calcium for the precipitation. Limiting the amount of calcium in the pore solution thus hinders the formation of gypsum.

Very little research work was done to investigate the effect of sulfate attack at such pH values. Brown [20] and Cao [21] exposed cementitious materials to sulfate solutions without controlling the pH in solution containers. This resulted in a pH increasing to around 12.5 due

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<sup>10</sup> For the geometry corresponding to Figure 4.

to the dissolution of portlandite. Cao [21] measured expansions that were more important for the high pH case (see Figure 9), where expansion is only caused by the formation of ettringite. Brown [20], on the contrary, measured more important expansions for low pH conditions, associated with more important drops in compressive strengths (Figure 10). It thus seems that the effect of a high pH on the damage sustained by concrete exposed to sulfate is not clear and will need additional research before it is settled.

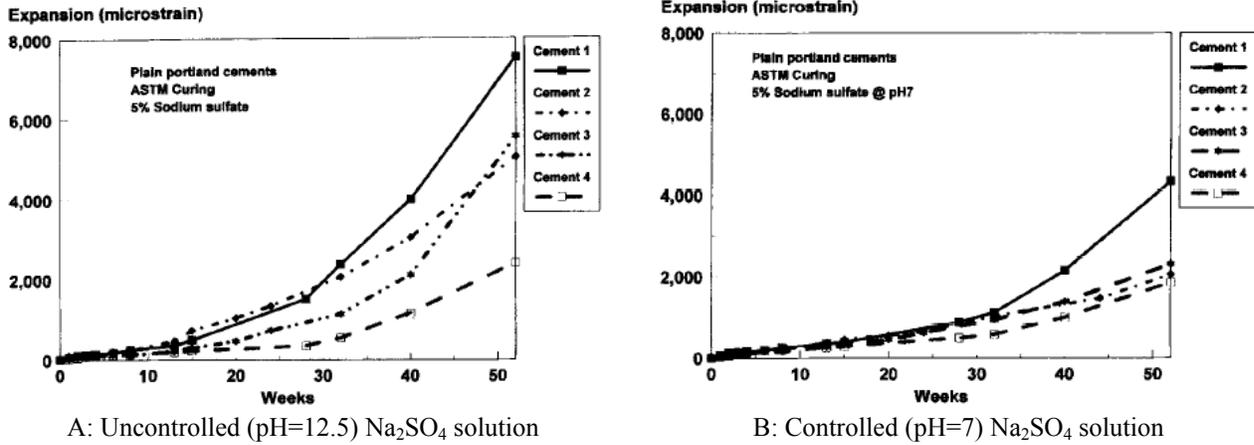


Figure 9 – Expansions of mortar bars made with different cements and immersed in 5% Na<sub>2</sub>SO<sub>4</sub> solutions (taken from reference [21])

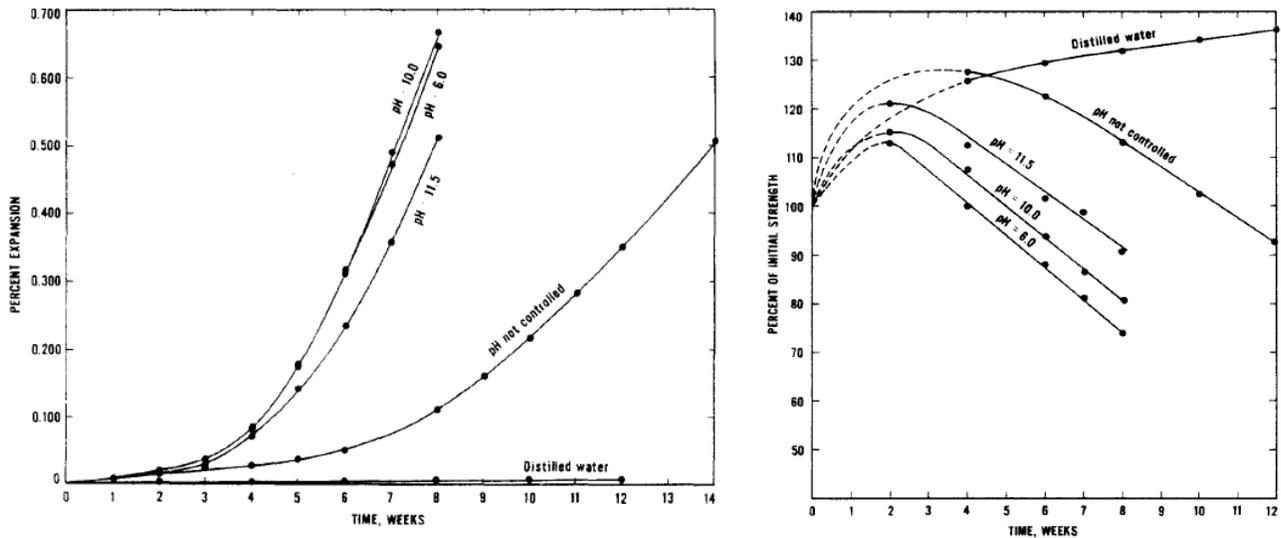
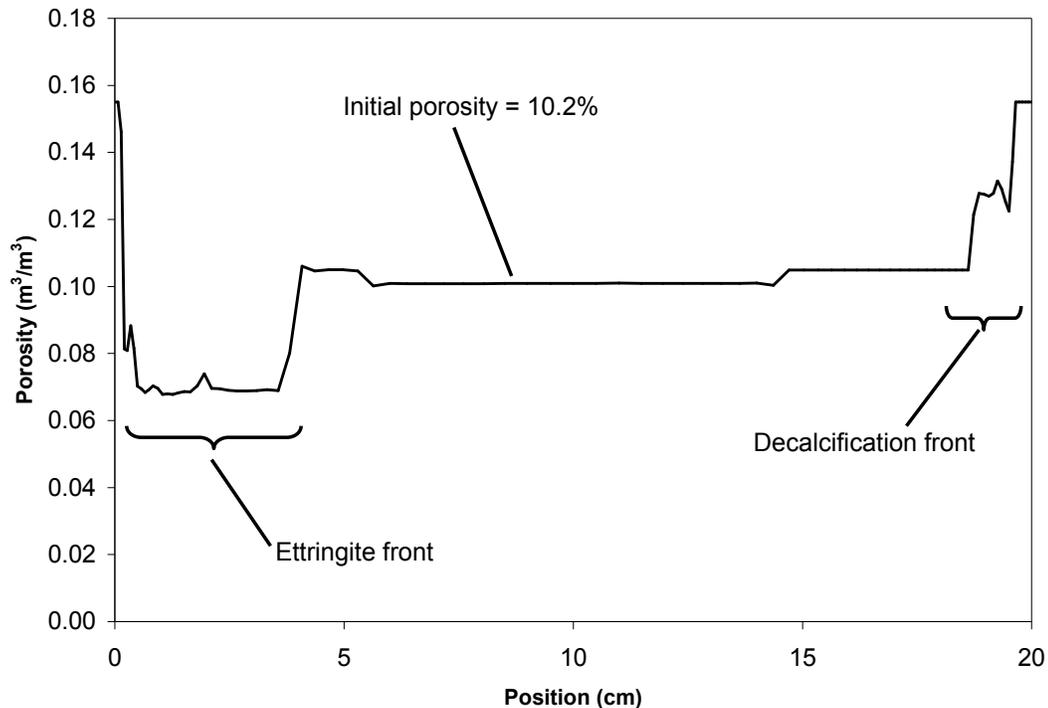


Figure 10 – Mortar bars made with Type I cement and exposed to 5% Na<sub>2</sub>SO<sub>4</sub> solutions. The “distilled water case” corresponds to pure water [20]

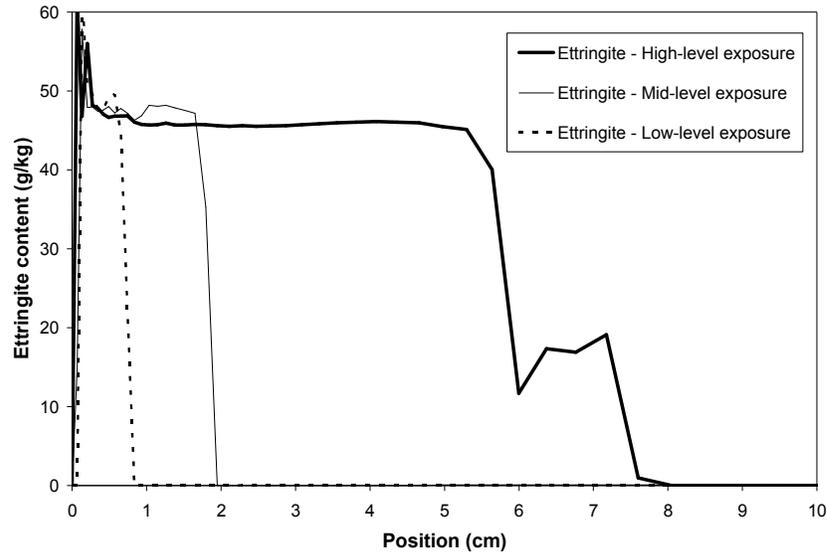


**Figure 11 – Porosity distribution for the phase distribution presented in Figure 6**

In the simulation results presented in this report, the dissolution and precipitation of phases locally modifies the porosity, which in turn affects the transport properties according to the function  $M(\phi)$  in equation (6). Figure 11 shows the porosity distribution corresponding to the solid phase profiles in Figure 6. The formation of an ettringite front from the top surface of the slab reduces the porosity, which lowers the transport property values. According to Figure 11, the porosity goes from approximately 10% to 7%, which gives  $M(\phi)=0.6$ . This means that the transport properties are 60% lower in that area. It is important to emphasize that the calculations performed with STADIUM® do not consider the possible effect of cracking that might be induced by this ettringite front. Tests results reported in reference [9] indicated that the damages resulting from a sulfate exposure could be associated with the presence of a gypsum peak behind the ettringite front. In the present study no such gypsum peaks were predicted by the model. Still, the formation of ettringite could damage the paste and increase the value of the transport parameters. In that case, the rate of ettringite ingress would be more important.

At the other end of the slab, Figure 11 indicates that despite the formation of a small ettringite peak, the decalcification of C-S-H leads to an increase in porosity from 10% to 15%. In that case, damage function  $M(\phi) = 2.2$ . The decalcification of C-S-H at the soil/concrete boundary thus contributes to double the rate of degradation of the material. It should be noted that the porosity variation analysis gives similar result for both materials.

It is important to mention that one side effect of the absence of gypsum formation is that the amount of sulfur bound with the hydrated paste will be, for a given material, independent of the external sulfate exposure. This is due to the fact that the amount of ettringite formed is limited by the amount of alumina present in the material. Consequently, an ettringite front having a fixed height is formed. This is illustrated on Figure 12. In that case, the external sulfate concentration will only influence the rate of ingress of the ettringite front.



**Figure 12 – Ettringite content in the ternary concrete after 50 years  
For different exposure conditions**

Assuming that concrete sustains damage from sulfate exposure in high pH conditions, it is possible to provide a rough estimate of the increase in transport properties. Research work ongoing at SIMCO Technologies showed that microcracks ( $< \approx 100\mu\text{m}$ ) caused by cyclic load up to 90% of compressive strength have little effect on diffusion and drying rates. Diffusion coefficients and drying rates were shown to increase by approximately 50% in these conditions. However, recent results of chloride ingress in cracked samples [23] showed that for macrocracks ( $> \approx 100\mu\text{m}$ ), chloride diffuses at a velocity corresponding to its freewater value, which represents approximately a 50-fold increase in diffusion properties.

## 5. CONCLUSION

Simulations based on transport properties evaluated on two concrete mixtures with a water to binder ratio of 0.35 were performed to estimate the long-term durability of material exposed to saltstone waste leachate for an extended period of time. The simulations showed that the presence of sulfate in the leachate is responsible for the penetration of an ettringite front in the structure. No other sulfate-bearing minerals were predicted, including gypsum. According to the simulations, the exposure level (concentration of sulfate ions in the aggressive solution) is the parameter that has the strongest influence on the penetration kinetic.

The potential apparition of microcracks due to the formation of ettringite cannot be taken into account in STADIUM<sup>®</sup>. The simulations thus represent an optimistic situation where ettringite actually reduces the porosity of the material and reduces the rate of ingress of sulfate. In the presence of cracks, the transport properties would increase. Consequently, the rate of degradation would be worst than what was predicted by the model.

It was assumed that the other face of the concrete slab was exposed to pure water in the soil. According to the model, this particular boundary condition caused the decalcification of C-S-H, which could potentially affect the structural integrity of the waste vault. According to the simulations, the degradation could reach 4 cm after 10000 years of exposure.

Characterization of actual concretes exposed to high pH sulfate solutions are required to determine the consequences and damage resulting from exposure of these materials to these unique sulfate solution. Testing is underway in a separate task of this contract.

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**11.0 ATTACHMENT 3**

**Saltstone Vaults 1 / 4 and Disposal Unit 2 Concrete Sample  
Preparations and Fresh Property Characterization**

**Subcontract No. AC48992N Task 2 and 4**

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**SIMCO**

Technologies inc.

Washington Savannah River Company

Subcontract no. AC48992N

Report

Tasks 2 & 4 – Experimental results from Vault Concretes

August 5, 2008

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THE STADIUM<sup>®</sup> MODEL IS A HELPFUL TOOL TO PREDICT THE FUTURE CONDITIONS OF CONCRETE MATERIALS. HOWEVER, ALL DURABILITY-MODELING PARAMETERS HAVE A STATISTICAL RANGE OF ACCEPTABLE RESULTS. THE MODELING USED IN THIS REPORT USES MEAN LABORATORY- OR FIELD-DETERMINED SINGLE VALUES AS INPUT PARAMETERS. THIS PROVIDES A SINGLE RESULT, WHICH PROVIDES A SIMPLE ANALYSIS EVALUATING CORROSION PROTECTION OPTIONS. PREVIOUS CONDITIONS ARE ASSUMED TO CARRY FORWARD IN THE PREDICTION MODEL; THERE ARE NO ASSURANCES THAT THE STRUCTURE WILL BE EXPOSED TO A SIMILAR ENVIRONMENT AS IN THE PAST.

## 1. Objective

This report presents the advancement of experimental Tasks 2 and 4. The objective of Task 2 is to evaluate transport properties for the mixtures used by SRNL for radioactive waste storage, while Task 4 must generate data on exposure conditions under contacting solution to validate modeled results.

The selected mixtures were:

- A. Saltstone Vault 1/4 concrete with a w/b ratio of 0.38 prepared with an ASTM Type I/II cement and slag;
- B. Saltstone Disposal Unit 2 concrete with a w/b ratio of 0.38 prepared with ASTM Type V cement, slag, fly ash, and silica fume.

This report is divided as follow. Section 2 presents the characteristics of raw materials. Section 3 details the formulations and the fresh properties of the mixtures. Section 4 presents the updated measurements performed on the mixtures.

## 2. Raw materials

This section presents the characteristics of the cements, supplementary cementing materials, aggregates, and admixtures used in the concrete mixtures.

Relative density and absorption of Foster sand and Rinker N°67 stone were determined based on CSA A23.2-6A *Relative density and absorption of fine aggregate* and CSA A23.2-12A *Relative density and absorption of coarse aggregate*, respectively.

Terminologies in previous CSA Standards have similar significances such as ASTM C127 *Standard Test Method for density, relative density (specific gravity), and absorption of coarse aggregates* and ASTM C128 *Standard Test Method for density, relative density (specific gravity), and absorption of fine aggregates*. The characteristics of aggregates are presented in Table 1.

**Table 1 – Characteristics of fine and coarse aggregates**

Raw materials		Absorption (%)	Relative density (SSD)	Apparent relative density
Sand	Foster	0.58	2.64	2.67
N° 67 Stone	Rinker	0.62	2.63	2.66

The relative density (specific gravity) of binders is useful to calculate mixture compositions. The data are given in .

**Table 2 – Relative density of binders**

	Type I/II cement Lafarge	Type V cement Lehigh	GGBFS Holcim	Force 10000 SF Grace	Class F Fly Ash SEFA
<b>Relative Density</b>	3.271	3.289	2.990	2.316	2.355

The chemical composition of binders is an input of the chemical equilibrium code in STADIUM<sup>®</sup> to estimate the composition of the hydrated cement paste. Data are given in Table 3. They were evaluated using the X-ray fluorescence technique.

Admixtures such as water reducers and entraining agents can affect the concrete performances and the workability of the fresh mixture. Depending on their dosage, admixtures can affect the setting of the binders, in particular the water reducing admixtures.

**Table 3 – Chemical composition of binders (%)**

Oxides	Type I/II cement Lafarge	Type V cement Lehigh	GGBFS Holcim	Force 10000 SF Grace	Class F Fly Ash SEFA
CaO	64.3	63.0	35.8	0.50	1.41
SiO <sub>2</sub>	21.0	20.8	39.1	96.6	53.1
Al <sub>2</sub> O <sub>3</sub>	4.91	4.11	10.1	0.21	28.4
Fe <sub>2</sub> O <sub>3</sub>	3.50	4.32	0.36	0.18	7.99
SO <sub>3</sub>	2.64	2.36	1.99	<0.1	<0.10
MgO	0.95	2.40	12.6	0.28	1.00
K <sub>2</sub> O	0.37	0.57	0.27	0.50	2.99
Na <sub>2</sub> O	0.09	0.07	0.22	0.07	0.44
LOI	1.32	1.73	0	1.21	2.39

According to ASTM C494/C494M *Standard specification for chemical admixtures for concrete*, water reducing admixtures can have a retarding effect. Type A water reducer requires that initial and final setting times are not extended by more than 1h30, compared to the same mixture prepared without the admixture. For type D water reducer, the additional setting time allowed is 3h30. The use and the dosage range of admixtures are presented in Table 4.

**Table 4 – Dosage range of admixture for uses defined in ASTM C494/C494M**

Admixture	use	Dosage range <sup>1</sup>	
		for Type A use	for Type D use
MicroAir (BASF)	AEA <sup>2</sup>	-	-
Pozzoloth 200N (BASF)	WR <sup>3</sup>	3 to 4 (195 to 260)	up to 6 (up to 390)
Polyheed 1020 (BASF)	MRWR <sup>4</sup>	3 to 5 (195 to 325)	-
Glenium 3030 NS (BASF)	HRWR <sup>5</sup>	up to 3 (up to 195)	-

(1) in fl oz / 100 lb of binder (in ml/100 kg of binder)

(2) AEA = Air Entraining Agent

(3) WR = water reducing admixture

(4) MRWR = mid-range water reducing admixture

(5) HRWR = high-range water reducing admixture

### 3.0 Concrete Mixtures

The mix designs of two Saltstone Vault concretes were provided by SNRL. Saltstone Vault 1/4 concrete was used to build Vault 1 in the late 1980's, while Saltstone Disposal Unit 2 concrete was designed to construct a pre-cast, reinforced, post tensioned water tank structure.

Samples of Saltstone Vault concretes were prepared based on ASTM C192/192M – 07 *Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory*. Mixtures were cast in plastic cylinders (10 cm diameter, 20 cm length). Two batches of eighty liters (0.1 cubic yard) provided two sets of forty-two cylinders. Methods of consolidation and times of demolding differed between mixtures depending on the slump and on the setting time, respectively. Methods are detailed below. Once demolded, specimens were stored in moist room (100% RH) until testing.

#### 3.1 Saltstone Vault 1/4 concrete

The Master Builders 300N reducing admixture was not available at the time of casting, so we used Pozzoloth 200N, which is another BASF's water reducing admixture. The air entraining admixture was BASF's MicroAir. Table 5 presents the properties of fresh and early age concrete for the two batches.

The Pozzoloth 200N was not efficient enough to reach the specified consistency, i.e. a slump of 75 mm (3 inches). Because the amount of raw materials was limited, it was not possible to try another admixture. It was thus decided to cast this mixture. The concrete cylinders were consolidated on a vibrating table. Table 6 gives the final Saltstone Vault 1/4 concrete formulation prepared for this project.

**Table 5 – Properties of fresh and early age Saltstone Vault 1/4 concrete for the two batches needed to make samples**

Properties	Batch 1V2	Batch 1V3	Differences	
			actual	Allowed <sup>1</sup>
Slump (mm) (in.)	15 5/8	35 1 3/8	20 6/8	51 2.0
Unit weight (kg/m <sup>3</sup> ) (lb/ft <sup>3</sup> )	2,400 150	2,390 149	10 1	40 2.5
Air content (%)	2.5	3.0	0.5	0.8
Time at end of sampling (h:mm)	1:25	0:55		
f <sub>c</sub> 7d (MPa) <sup>2</sup> (psi)	29.4 4,264	37.0 5,366	7.6 1,102	4.0 574
Density at 7d (kg/m <sup>3</sup> ) <sup>2</sup> (lb/ft <sup>3</sup> )	2,370 148	2,390 149	20 1	

(<sup>1</sup>) based on ASTM C192/C192M

(<sup>2</sup>) based on ASTM C39/C39M *Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens*

**Table 6– Saltstone Vault 1/4 concrete formulation**

Raw materials		Formulation	
		(kg/m <sup>3</sup> )	(lb/yd <sup>3</sup> )
Type I/II cement	Lafarge	255	430
GGBFS	Holcim	169	285
Sand	Foster	691	1,164
N° 67 Stone	Rinker	1,096	1,848
Water		162	273
w/b		0.38	0.38
Air content		3 %	3 %
Unit weight		2395 kg/m <sup>3</sup>	149 lb/yd <sup>3</sup>
Slump		35 mm	1 3/8 in.
		(ml / 100 kg of binder)	(fl oz / 100 lb of binder)
MicroAir	BASF	1.2	0.02
Pozzolith 200N	BASF	<b>403</b>	<b>6.2</b>

The differences in slump, unit weight and air content between batches were lower than precision statement of ASTM C192/192M. The difference in early strength was very high. The consolidation of samples does not seem to be the cause of the strength difference since unit weight values of specimen were in acceptable range. On the other hand, the delay before casting the samples of 1V2 batch was very long since we adjusted the water reducing admixture dosage on this batch with several iterations. For the 1V3 batch, we used the total amount of water reducing admixture added in 1V2 batch. However, we added the full amount of admixture at the beginning of mixing and reduced time before casting samples within half an hour. The differences could affect the hardening at early time. We will check if strength development will be recovered at eighty days.

The dosage of the water reducing admixture was above the range for Type D use. Concrete cylinders were too weak to be demolded without surface damage after three days. They were demolded after five days under wet burlap, and then cured in a fog room (100% relative humidity). The compressive strength at seven days was close to the required strength at twenty-eight days (i.e. 4,000 psi). The excess of water reducing admixture slowed the setting of concrete but seemingly did not affect its hardening.

The air content was lower than the specified value (i.e. 3% instead of 5%). The air entraining agent was less efficient due to poor workability of the mixture. Less air content than expected means a little more solid content in the formulation. In this range, variation of entrained air content has little influence on the transport properties of concrete.

### **3.2 Saltstone Disposal Unit 2 concrete**

The specified admixtures were not available at the time of casting. Consequently, we used admixtures for which we developed skills in the field of concretes containing supplementary cementing materials at low water to binder ratio.

Small trial batches were prepared to determine HRWRA dosage and check the air content without casting samples. As the effect of HRWRA diminished with time, we targeted higher slump value after ten minutes than required ( $7 \pm 1$  in.). The air content was high due to secondary effect of water reducing and HRWR admixtures. Table 7 presents the properties of fresh and early age concrete for the two batches needed to make cylindrical samples. The concrete cylinders were consolidated by rodding.

**Table 7 – Properties of fresh and early age Saltstone Disposal Unit 2 concrete for the two batches needed to make samples**

Properties	Batch 2V1	Batch 2V2	Differences	
			actual	allowed <sup>1</sup>
Slump (mm) (in.)	210 8 ¼	210 8 ¼	0	51 2.0
Unit weight (kg/m <sup>3</sup> ) (lb/yd <sup>3</sup> )	2,230 139.3	2,190 136.6	40 2.7	40 2.5
Air content (%)	7.4	8.5	1.1	0.8
Time at end of sampling (h:mm)	0:45	0:35		
f <sub>c</sub> 8d (MPa) (psi)	21.0 3,040	19.2 2,785	1.8 261	
Density at 8d (kg/m <sup>3</sup> ) (lb/ft <sup>3</sup> )	2,260 141	2,230 139	30 2	

<sup>(1)</sup> based on ASTM C192/C192M

The differences in slump and early strength between batches were smaller than precision statement of ASTM C192/192M. The precision statement of ASTM C192/192M should be used with caution for air-entrained concrete or concrete with slump over 6 in. (150 mm). The difference in air content between batches was slightly higher than standard precision statement. However, this gap was judged acceptable.

Table 8 gives the Saltstone Disposal Unit 2 concrete formulation. Dosage of WR was in the range for type A use. HRWR dosage was higher than type A use but in the mid-range use (3-6 fl oz / 100 lb of binder) defined by the producer. Concrete cylinders were demolded after two days under wet burlap, and then cured in a fog room (100% RH). We did not observe any important delay in concrete hardening, as observed on the previous mixture.

**Table 8 – Saltstone Disposal Unit 2 concrete formulation**

Raw materials		Formulation	
		(kg/m <sup>3</sup> )	(lb/yd <sup>3</sup> )
Type V cement	Lehigh	121	204
GGBFS	Holcim	162	274
Force 10000 SF	Grace	27	45
Class F Fly Ash	SEFA	95	159
Sand	Foster	548	923
N° 67 Stone	Rinker	1,111	1,873
Water		152	257
w/b		0.38	0.38
Air content		8 %	8 %
Unit weight		2110 kg/m <sup>3</sup>	138 lb/yd <sup>3</sup>
Slump after 10'		210 mm	8 ¼ in.
		(ml / 100 kg of binder)	(fl oz / 100 lb of binder)
MicroAir	BASF	3.1	0.05
Polyheed 1020	BASF	205	3.2
Glenium 3030 NS	BASF	232	3.6

#### 4.0 Concrete Properties Measurements

To this date, Saltstone Vault concretes have been cured over twenty-eight days in a fog room (100% RH). For a given mixture, the cylinders selected for testing were taken from separate batches. The following sections present the results obtained so far. Drying tests (Task 2) and ponding tests (Task 4) are ongoing.

##### 4.1 Compressive strength

Compressive strengths at twenty-eight days were tested based on ASTM C39/C39M *Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens*. Two cylinders were taken from each batch. Four concrete specimens were thus tested for compressive strength. Table 9 presents the results of compressive strength at twenty-eight days for Saltstone Vault concretes.

**Table 9 – Compressive strength for Saltstone Vault concretes**

Properties	Saltstone Vault 1/4		Surrogate <sup>1</sup>	Saltstone Disposal Unit 2	
	Actual average	CV (%)		Actual Average	CV (%)
f <sub>c</sub> 7d (MPa) (psi)	32.1 4650	13	42.7 6190	20.1 <sup>2</sup> 2915	4.5 6030
Density at 7d (kg/m <sup>3</sup> ) (lb/ft <sup>3</sup> )	2380 148	0.5	-	2250 <sup>2</sup> 140	0.7 -
f <sub>c</sub> 28d (MPa) (psi)	59.8 8,670	3.8	54.0 7830	35.2 5,102	2.8 8220
Density at 28d (kg/m <sup>3</sup> ) (lb/ft <sup>3</sup> )	2,390 149	0.1	-	2,250 140	1.0 -

<sup>(1)</sup> from data used in Task 1.

<sup>(2)</sup> measured at 8 d.

The average compressive strength at twenty-eight days for Saltstone Vault 1/4 concrete was 8,670 psi, largely above the minimum strength (i.e. 4,000 psi) specified by design<sup>11</sup>. While compressive strengths at seven days were very different between separate batches, the results at 28 days were close enough to be considered independent of the origin of the batch as the low coefficient of variation (CV) showed.

The average compressive strength at twenty-eight days for Saltstone Disposal Unit 2 concrete was 5,102 psi, slightly above the minimum strength of 5,000 psi specified by design<sup>1</sup>. The dispersion of the results at twenty-eight days was low as shown by the low coefficient of variation.

## 5.0 Task 2 - Transport properties

Cylinders were taken from the chamber and sampled for the different transport property measurements at twenty-eight days of curing period. The transport properties that are evaluated are:

- Porosity: evaluated according to the ASTM C642 standard procedure: *Standard Test Method for Density, Absorption and Voids in Hardened Concrete*,
- Diffusion coefficients: evaluated on the basis of migration test results, which is a modified version of the ASTM C1202 procedure: *Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration*,

<sup>11</sup> Phifer, M. A., Millings, M. R., and Flach, G. P. 2006. Hydraulic Property Data Package for the E-Area and Z-Area Vadose Zone Soils, Cementitious Materials, and Waste Zones, WSRC-STI-2006-00198, Revision 0. Washington Savannah River Company, Aiken, SC. September 2006.

- Water diffusivity: evaluated from the results of drying tests.
- Water storage: evaluated from small concrete disks equilibrated in boxes maintained at specific relative humidities using saturated salt solutions.

The test procedures to evaluate the diffusion coefficients, water diffusivity water storage are described in the Task 5 report.

The porosity results after 28 days of hydration are given in Table 10.

**Table 10 – Porosity of Saltstone Vault concretes at 28 days**

		Saltstone Vault 1/4	Saltstone Disposal Unit 2
Porosity at 28 days (%)	spec. 1	10.1	10.0
	spec. 2	9.9	10.7
	average	10.0	10.3
Absorption at 28 days (%)	spec. 1	4.4	4.6
	spec. 2	4.3	5.0
	average	4.4	4.8

The analysis of migration tests at 28 days are presented in Figures 1 and 2. The optimal simulation of current using STADIUM model is drawn with experimental curves of current recorded during migration test. The results of the diffusion coefficient analyses are presented in Table 11. The simulations were performed with estimated pore solutions. The actual pore solution analyses are still pending due to problems with the extraction set-up.

These results should be considered with caution. Due to the hydration of the binders, diffusion coefficients usually decrease with time. This time evolution depends on the binder itself. So even though the diffusion coefficients estimated on the vault concretes are lower than those of the surrogate materials, it doesn't mean that the values for the fully hydrated materials will still be lower. We have to wait for tests at later hydration stages to make final assumptions on the transport properties. The comparisons of surrogate and estimated D for this report can be considered to represent similar materials. The values are close enough and should not change the conclusions of the analysis presented in Task 1. Surrogate values are going to be reevaluated with a new method (REFS) rather than the old method used to estimate the values in Report 1.

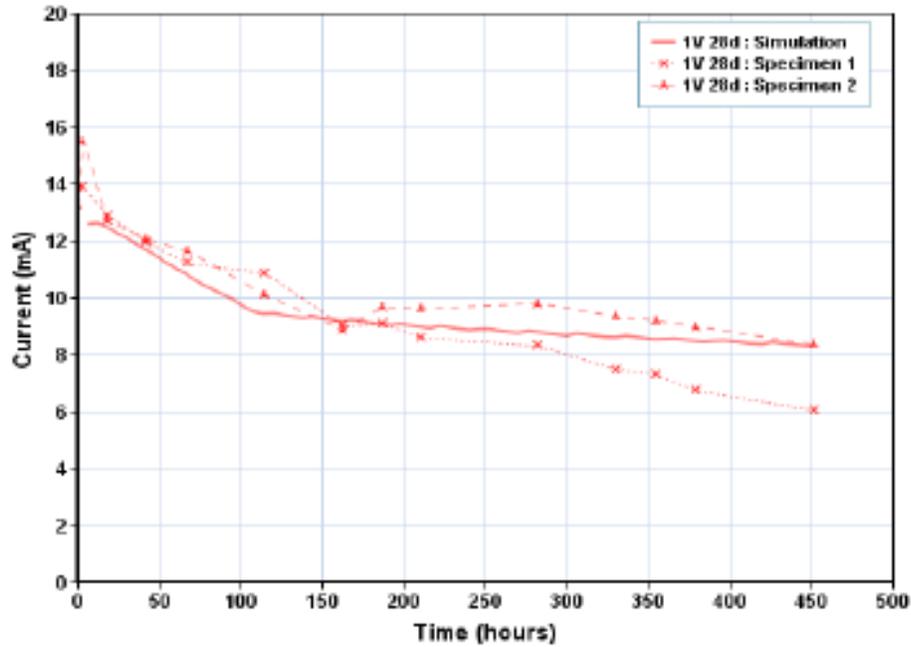


Figure 1– Migration test at 28 days for Vault 1/4 concrete

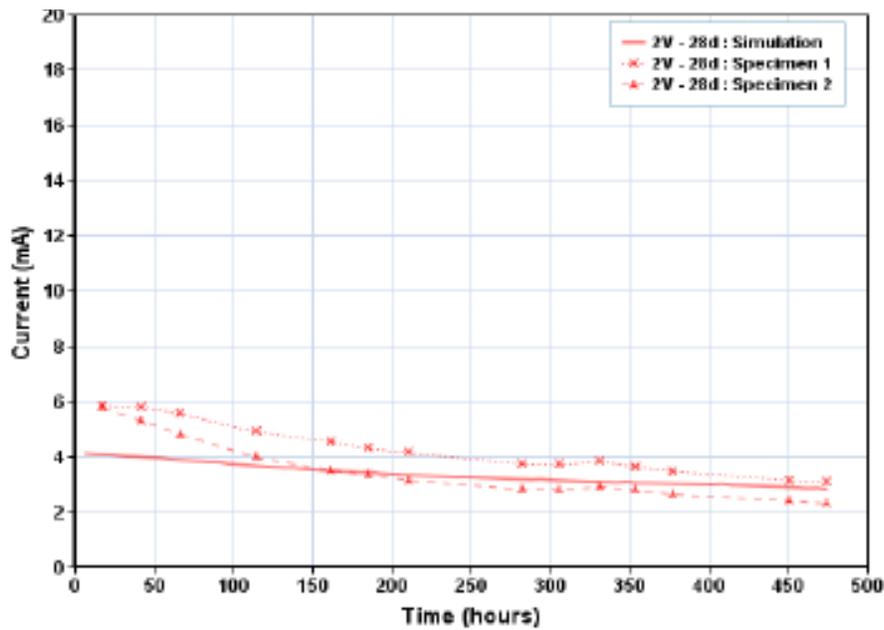


Figure 2 – Migration test at 28 days for Disposal Unit 2 concrete

The drying tests on both concrete mixtures are still ongoing. The mass losses measured so far are presented in Figures 3 and 4. Water diffusivity can not be analyzed before the mass loss for the thin (1 cm) samples is stable.

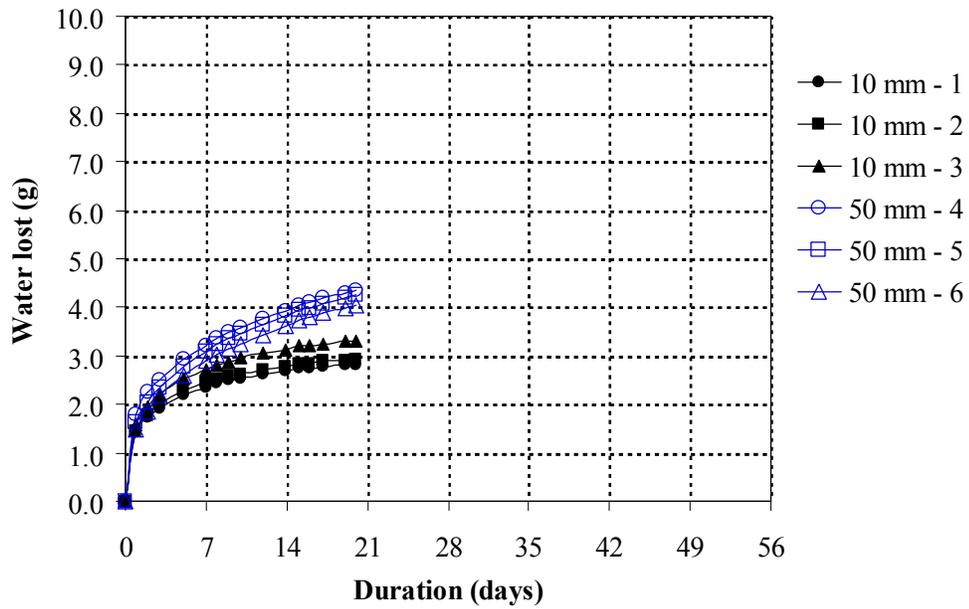


Figure 3– Preliminary results of drying test for Vault 1/4 concrete

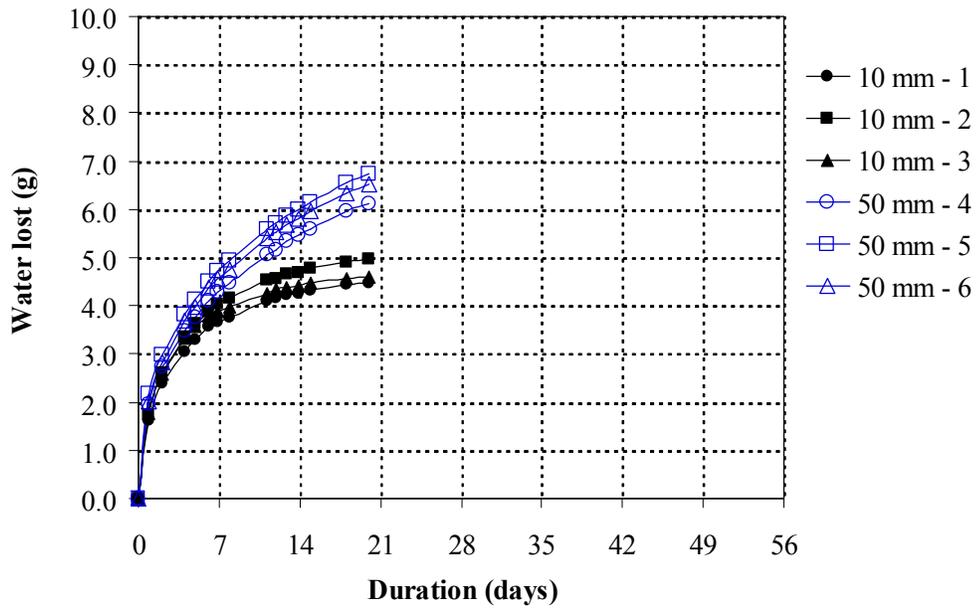


Figure 4 – Preliminary results of drying test for Disposal Unit 2 concrete

Table 11 compares transport properties of actual Vault concrete tested in this project with data used as surrogate concrete in Task 1.

**Table 11– Transport properties for Saltstone Vault concretes at 28 days**

	Saltstone Vault 1/4		Saltstone Disposal Unit 2	
	Actual	Surrogate <sup>1</sup>	Actual	Surrogate <sup>1</sup>
Porosity (%)	10.0	10.0	10.3	10.2
Diffusion coefficients ( $E^{-11} \text{ m}^2/\text{s}$ )				
OH <sup>-</sup>	5.5	13.0	1.3	4.0
Na <sup>+</sup>	1.4	3.3	0.3	1.0
K <sup>+</sup>	2.0	4.8	0.5	1.5
SO <sub>4</sub> <sup>2+</sup>	1.1	2.6	0.3	0.8
Ca <sup>2+</sup>	0.8	2.0	0.2	0.6
Al(OH) <sub>4</sub>	0.6	1.3	0.1	0.4
NO <sub>3</sub>	1.9	4.7	0.4	1.4
NO <sub>2</sub>	1.9	4.7	0.4	1.4
Water diffusivity				
A ( $E^{-13} \text{ m}^2/\text{s}$ )	N/A	4.3	N/A	1.0
B (-)	N/A	80	N/A	80
w @ 50%RH ( $\text{m}^3/\text{m}^3$ )	N/A	0.059	N/A	0.064

<sup>(1)</sup> from data used in Task 1.

Tests for adsorption-desorption isotherms were started at 28 days. At this time, specimens for desorption tests are in boxes at controlled relative humidity while specimens for adsorption tests are still drying at 40°C.

**6.0 Task 4 – Immersion (ponding) test**

The composition (make up chemicals per L of DI water) of undiluted exposure solution for immersion tests (CASE 1) is presented in Table 12.

**Table 12– Product content for undiluted exposure solution**

Chemicals	M.M.	(mmol/L of DI water)	(g/L of DI water)
NaOH	39.99734	959.31	38.37
NaNO <sub>3</sub>	84.9949	3306.19	281.01
NaNO <sub>2</sub>	68.9955	934.67	64.49
Na <sub>2</sub> CO <sub>3</sub>	105.9889	16.66	1.77
Na <sub>2</sub> SO <sub>4</sub>	142.0426	260.25	36.97
Al <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> (9H <sub>2</sub> O)	429.09522	0.04	0.02
Na <sub>3</sub> PO <sub>4</sub> (12H <sub>2</sub> O)	388.124721	1.58	0.6

The exposure solution for cases 2 and 3 of immersion tests consist of the previous solution diluted in lime water at rate of 10:1 and 100:1, respectively. Lime water will be obtained by dissolving 1.5 g Ca(OH)<sub>2</sub> in 1 kg of DI water. For a 1 liter volume of CASE 2 exposure solution, a volume of 100 mL of undiluted solution was mixed with 900 mL of lime water. For a 1 liter volume of CASE 3 exposure solution, a volume of 10 mL of undiluted solution was mixed with 990 mL of lime water.

After 56 days of curing, specimens for ponding tests were prepared following the procedure detailed in the Task 5 report. For each Vault concrete mixture, eight specimens were immersed in 30 liters of solution for each exposure solution. The ionic penetration will be determined after 90 days of exposure. DUE TO LOW PERMEABILITY/TORTUOSITY. OTHER SAMPLES WILL BE TESTED AFTER LONGER EXPOSURE DURATION – TO BE DETERMINED.

**Appendix A – Samples**

Table A.1 – Use of cylinders for Vault 1/4 concrete

Batch 2		Batch 3	
1V 201	Imm 56d	1V 301	fc 7d
1V 202		1V 302	iso 28d
1V 203		1V 303	
1V 204		1V 304	
1V 205		1V 305	Imm 56d
1V 206		1V 306	
1V 207		1V 307	
1V 208		1V 308	
1V 209		1V 309	
1V 210		1V 310	Imm 56d
1V 211	poro-mig 28d	1V 311	iso 28d
1V 212		1V 312	iso 28d
1V 213	fc 7d	1V 313	iso 28d
1V 214		1V 314	
1V 215		1V 315	
1V 216	Imm 56d	1V 316	Imm 56d
1V 217	Imm NaCl	1V 317	
1V 218	fc 7d	1V 318	
1V 219		1V 319	
1V 220		1V 320	dry 28d
1V 221	iso 28d	1V 321	iso 28d
1V 222	iso 28d	1V 322	
1V 223	Imm 56d	1V 323	fc 28d
1V 224		1V 324	
1V 225		1V 325	Imm 56d
1V 226		1V 326	
1V 227		1V 327	
1V 228		1V 328	
1V 229		1V 329	
1V 230		1V 330	iso 28d
1V 231	Imm 56d	1V 331	Imm 56d
1V 232	fc 28d	1V 332	fc 28d
1V 233	Imm 56d	1V 333	
1V 234	Imm 56d	1V 334	
1V 235	iso 28d	1V 335	
1V 236	dry 28d	1V 336	
1V 237	iso 28d	1V 337	
1V 238		1V 338	
1V 239		1V 339	
1V 240	iso 28d	1V 340	Imm 56d
1V 241	fc 28d	1V 341	
1V 242	iso 28d	1V 342	poro-mig 28d
1V 243		1V 343	
1V 244		1V 344	

Table A.2 – Use of cylinders for Disposal Unit 2 concrete

Batch 1		Batch 2	
2V 101		2V 201	
2V 102		2V 202	
2V 103		2V 203	
2V 104		2V 204	
2V 105		2V 205	
2V 106	Imm 56d	2V 206	
2V 107		2V 207	
2V 108		2V 208	
2V 109	iso 28d	2V 209	
2V 110		2V 210	
2V 111		2V 211	
2V 112	Imm 56d	2V 212	
2V 113		2V 213	
2V 114	Imm NaCl	2V 214	
2V 115	iso 28d	2V 215	
2V 116		2V 216	iso 28d
2V 117	iso 28d	2V 217	
2V 118		2V 218	
2V 119		2V 219	
2V 120		2V 220	
2V 121	iso 28d	2V 221	Imm 56d
2V 122	Imm 56d	2V 222	
2V 123	iso 28d	2V 223	
2V 124		2V 224	iso 28d
2V 125		2V 225	
2V 126	fc 8d	2V 226	
2V 127		2V 227	
2V 128		2V 228	Imm 56d
2V 129		2V 229	dry 28d
2V 130	dry 28d	2V 230	Imm 56d
2V 131	Imm 56d	2V 231	Imm 56d
2V 132		2V 232	iso 28d
2V 133		2V 233	
2V 134		2V 234	
2V 135		2V 235	
2V 136		2V 236	Imm 56d
2V 137	fc 8d	2V 237	iso 28d
2V 138	fc 28d	2V 238	poro-mig 28d
2V 139	fc 28d	2V 239	fc 28d
2V 140	Imm 56d	2V 240	iso 28d
2V 141	Imm 56d	2V 241	Imm 56d
2V 142	poro-mig 28d	2V 242	fc 28d
2V 143	iso 28d	2V 243	iso 28d
2V 144		2V 244	fc 8d

**12.0 ATTACHMENT 4**

**Saltstone Characterization Results**

**SUBCONTRACT NO. AC48992N TASK 6**

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Washington Savannah River Company

Subcontract no. AC48992N

Report

Task 6 – Characterization of a saltstone mixture

August 15, 2008

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THE STADIUM<sup>®</sup> MODEL IS A HELPFUL TOOL TO PREDICT THE FUTURE CONDITIONS OF CONCRETE MATERIALS. HOWEVER, ALL DURABILITY-MODELING PARAMETERS HAVE A STATISTICAL RANGE OF ACCEPTABLE RESULTS. THE MODELING USED IN THIS REPORT USES MEAN LABORATORY- OR FIELD-DETERMINED SINGLE VALUES AS INPUT PARAMETERS. THIS PROVIDES A SINGLE RESULT, WHICH PROVIDES A SIMPLE ANALYSIS EVALUATING CORROSION PROTECTION OPTIONS. PREVIOUS CONDITIONS ARE ASSUMED TO CARRY FORWARD IN THE PREDICTION MODEL; THERE ARE NO ASSURANCES THAT THE STRUCTURE WILL BE EXPOSED TO A SIMILAR ENVIRONMENT AS IN THE PAST.

## Objective

The objectives of Task 6 are to measure transport properties for the saltstone slurry designed by SNRL and to generate data on the leaching behavior of saltstone in contact with water to validate modeling results.

This report is divided as follow. Section 2 presents the characteristics of raw materials. Section 3 details the formulation of the mixture and the procedures of mixing and curing. Section 4 describes the experiment and gives the first available results.

## Raw materials

This section presents the characteristics of the cements, supplementary cementing materials, and salt solution used in the saltstone mixtures.

The relative density (specific gravity) of binders is useful to calculate mixture compositions. The data are given in Table 1.

Table 1 – Relative density of binders

	<b>Type I/II cement Lafarge</b>	<b>GGBFS Holcim</b>	<b>Class F Fly Ash SEFA</b>
<b>Relative Density</b>	3.271	2.990	2.355

The chemical composition of binders is an input of the chemical equilibrium code in STADIUM<sup>®</sup>. Data are given in table 2. They were evaluated using the X-ray fluorescence technique.

**Table 2 - Chemical composition of binders (%)**

Oxides	Type I/II cement Lafarge	GGBFS Holcim	Class F Fly Ash SEFA
CaO	64.3	35.8	1.41
SiO <sub>2</sub>	21.0	39.1	53.1
Al <sub>2</sub> O <sub>3</sub>	4.91	10.1	28.4
Fe <sub>2</sub> O <sub>3</sub>	3.50	0.36	7.99
SO <sub>3</sub>	2.64	1.99	<0.10
MgO	0.95	12.6	1.00
K <sub>2</sub> O	0.37	0.27	2.99
Na <sub>2</sub> O	0.09	0.22	0.44
LOI	1.32	0	2.39

### Mixture

The mix design of saltstone slurry was provided by SNRL. The solution for mixing with premix blend of Saltstone was prepared following the composition presented in Table 3.

**Table 3 - Product content for Saltstone mixing solution**

Chemicals	M.M.	(mmol/L of DI water)	(g/L of DI water)
NaOH	39.99734	1590	63.6
NaNO <sub>3</sub>	84.9949	3160	268.58
NaNO <sub>2</sub>	68.9955	370	25.53
Na <sub>2</sub> CO <sub>3</sub>	105.9889	180	19.08
Na <sub>2</sub> SO <sub>4</sub>	142.0426	60	8.52
Al <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> (9H <sub>2</sub> O)	429.09522	50	21.45
Na <sub>3</sub> PO <sub>4</sub> (12H <sub>2</sub> O)	388.124721	10	3.8
TOTAL			410.56

The salt solution was prepared one day before batching. All of the ingredients were dissolved during the mixing. The relative density of the solution at 24°C was 1.2235.

Table 4 gives the saltstone slurry formulation. Special procedure for mixing and casting samples of the saltstone slurry was adapted based on ASTM C938 – 02 *Standard Practice for proportioning grout mixture for preplaced-aggregate concrete* as follow:

- We premixed the 3 solid binders. We weighed the necessary quantity for a batch of ten liters and transferred them to a 5-gallon plastic bucket. We shook the container to mix the ingredients.
- The solution was weighed into a mixing container (5-gallon plastic bucket).
- The premixed blend was poured over less than 1 minute while stirring using a helicoid impeller.
- The slurry was mixed for 5 minutes. Then, it was poured into plastic cylinders (4 in. diameter, 8 in. length) and 2-in. cubic molds.

**Table 4- Saltstone slurry formulation**

Raw materials		Formulation	
		(kg/m <sup>3</sup> )	(lb/yd <sup>3</sup> )
Type I/II cement	Lafarge	135	230
GGBFS	Holcim	195	330
Class F Fly Ash	SEFA	600	1015
Salt solution		780	1320
DI water		553	935
Salt		227	385
w/b		0.595	0.595

Table 5 presents the properties of the fresh saltstone slurry. Four batches of ten liters (0.35 cubic foot) provided four sets of six cylinders and three cubic specimens.

**Table 5 – Properties of fresh Saltstone slurry**

Properties	Values
Unit Weigth (kg/m <sup>3</sup> )	1680
(lb/ft <sup>3</sup> )	105
Relative Yield (ft <sup>3</sup> /yd <sup>3</sup> )	27.6

For the initial curing phase, the cast samples were kept in the molds and placed under a plastic sheet in the lab. We placed damp burlap beside the samples under the plastic sheet to maintain high RH conditions. When the slurry was set, we covered the molds directly with

the damp burlap without marring the top surface of the material and placed a plastic sheet over the burlap. After three days, we sealed the molds (cylinders and cubes) within plastic bags and put them in moist room (100% RH).

We demolded the cubic samples for compressive strength after five days. We wrapped each specimen with plastic film before putting them into sealed plastic bag and stored them in moist room until testing.

## Experiments

Prior to testing, the samples were cut using water for safety concern. The various specimens were kept in sealed bag directly after sawing. It is assumed that all samples are saturated before testing.

## Compressive strength

Compressive strength at twenty-eight days was tested based on ASTM C109/C109M *Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)*. Three cubic specimens were tested for compressive strength. Table 6 presents the results of compressive strength for Saltstone slurry.

**Table 6 - Compressive strength for Saltstone slurry**

	average	CV (%) <sup>1</sup>
f <sub>c</sub> 7d (MPa) (psi)	2.1 300	7.4
f <sub>c</sub> 28d (MPa) (psi)	3.2 460	6.3

(1) for three cubic specimens

The average compressive strength at twenty-eight days for Saltstone slurry was only 460 psi. Moreover, the cohesion of the saltstone was very weak.

## Transport properties

Cylinders were taken from the chamber and sampled for different transport properties at twenty-eight days of curing period. The transport properties that were evaluated are:

- Porosity: evaluated according to the ASTM C642 standard procedure: *Standard Test Method for Density, Absorption and Voids in Hardened Concrete*.

- Diffusion coefficients: evaluated on the basis of migration test results, which is a modified version of the ASTM C1202 procedure: *Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration*.
- Water diffusivity: evaluated from the results of drying tests.
- Adsorption-desorption isotherms: evaluated from small disks equilibrated in boxes maintained at specific relative humidities using saturated salt solutions.

The test procedures to evaluate the diffusion coefficients and water diffusivity are described in the Task 5 report. At this time, all the tests at 28 days are still ongoing.



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