SRNL-STI-2010-00515 Revision 0

Key Words: Performance Assessment
Saltstone Degradation
Saltstone Microstructure

Retention: Permanent

SALTSTONE CHARACTERIZATION AND PARAMETERS FOR PERFORMANCE ASSESSMENT MODELING

SIMCO TECHNOLOGIES, INC.
TASK 6 REPORT UPDATE

SIMCO TECHNOLOGIES, INC.
SUBCONTRACT SIMCORD08009 ORDER AC48992N (U)

Christine A. Langton

August 27, 2010

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

DISCLAIMER

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REVIEWS AND APPROVALS

Authors:

C. A. Langton, SRNL / E&CPT Date

Technical Reviewer:

G. P. Flach, SRNL / Geo-Modeling Date

SRNL Management Approvals:

H. H. Burns, Project Manager, SRNL / E&CPT Date

A. B. Barnes, Manager, SRNL / E&CPT Date

S. L. Marra, Manager, SRNL / E&CPT Date

Customer Approvals:

T. C. Robinson Jr., SRR / WASTE DETERMINATIONS Date

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ASTM	American Society for Testing & Materials
cm	Centimeters
C-S-H	Calcium silicate hydrate (non to poorly crystalline solid)
CV	Coefficient of variance
d	Day
DI	De-Ionized (water)
E&CPT	Engineering and Chemical Process Technology
g/kg	Grams per kilogram
mg/L	Milligram per liter
mm	Millimeter
mol/L	Mole per liter
m^2	Square meter
m^2/s	Meter squared per second
MCU	Modular Caustic Side Solvent Extraction Unit
Mol/L	Moles per liter
MPa	Mega Pascal
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
Psi	Pounds per square inch
Psig	Pound-force per square inch gauge (pressure relative to the surrounding atmosphere
RI&BM	Regulatory Integration and Business Management
s	Seconds
SIMCO	SIMCO Technologies, Inc.
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
SRR	Savannah River Remediation
SRS	Savannah River Site
STR	Subcontract Technical Representatives
WSRC	Washington Savannah River Company
yr	Year
µm	Micrometer

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1.0 EXECUTIVE SUMMARY

SIMCO Technologies, Inc. was contracted to evaluate the durability of the saltstone matrix material and to measure saltstone transport properties. This information will be used to:

- Parameterize the STADIUM® service life code developed by SIMCO Technologies Inc. to predict service life of concrete structures. The STADIUM® code is a one dimensional diffusion transport code that predicts the rate of penetration of corrosive chemical fronts into concrete. The code is supported by a set of test protocols and is validated by exposure tests of actual structures and on laboratory samples. (SIMCO Technologies Inc. has developed a concrete material data base that is useful for durability screening of a wide range of mix designs.)
- Predict the leach rate (degradation rate) for the saltstone matrix over 10,000 years using the STADIUM® concrete service life code, and
- Validate the modeled results by conducting leaching (water immersion) tests.[1]

The work was originally requested by J. L. Newman, Regulatory Integration & Business Management, and T. C. Robinson Jr., Waste Determinations. Since initiation of this work, Savannah River Remediation (SRR) has assumed responsibility for the liquid waste operations contract at the Savannah River Site. This work was coordinated through H. H. Burns, Engineering and Chemical Process Technology / Savannah River National Laboratory (E&CPT/ SRNL) and will support the Saltstone Performance Analysis (PA).

This report summarizes characterization data for non-radioactive simulated Modular Caustic Side Solvent Extraction (MCU) saltstone prepared with the current saltstone premix reagents and cured for up to 150 days. This saltstone composition is similar to that currently being processed in the Z-Area facility, the simulated MCU saltstone prepared from a premix blend with 45 wt. % slag cement, 45 wt. % Class F fly ash, and 10 wt. % portland cement.

Characterization results for the simulated MCU saltstone material prepared by SIMCO Technologies, Inc. personnel are tabulated in Table 1-1. This material has a higher compressive strength and about 100 X lower porosity, tortuosity, effective diffusion coefficient, and water permeability than a low-slag saltstone[2] which was also prepared and characterized by SIMCO Technologies personnel [Langton, 2009].

Table 1-1 also contains characterization results for the low-slag saltstone material. The microstructure of the simulated MCU saltstone was about 100 X more tortuous (longer pathway connecting pores) which resulted in 100X lower diffusion coefficients and 75 to 100X lower intrinsic permeability (hydraulic conductivity) compared to the low-slag saltstone material. The

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[1] Leaching of non matrix constituents such as radionuclides and hazardous constituents present in trace quantities is not considered in this study. Appropriate representation of soluble constituents that are present in more than trace quantities but do not contribute to conventional cementitious binder phases (e.g. sodium) is still being studied.

[2] The low slag (21 versus 45 wt. % slag) saltstone waste form was mistakenly prepared by SIMCO Technologies, Inc., personnel. The mistake was corrected and the work was repeated at no cost to SRR / SRNL. The hydraulic and physical property data for the low slag saltstone illustrate the beneficial effects of slag cement on microstructure and also provide an indication of the consequences of “off-spec” proportions.

porosity for the low-slag saltstone (21wt. % slag) was about 5% higher than that of the 45 wt. % slag saltstone. Longer term testing including water[3] immersion testing is in progress and will be summarized in a subsequent revision to this report.

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Table 1-1. Summary of Saltstone Physical and Hydraulic Property Characterization.

Materials (kg/m^3)	**Simulated Non-Rad Low Slag Cement Saltstone SIMCO WS-1**	**Simulated Non-Rad MCU Saltstone SIMCO WS-2**
	(kg/m^3)	**(kg/m^3)**
Portland Cement, Type I/II	135	94
Slag Cement, Grade 100	195	423
Fly Ash, Class F	600	423
Simulated MCU Salt Solution	780	796
Water to Binder ratio (cement + slag + fly ash)	0.595	0.60
Properties		
Compressive Strength @28days	3.2 MPa *460 psi* Coef.Variance 6.3%)	5.5 MPa *798 psi* Coef.Variance 6.6 %
Porosity @28 days (vol. %)	65.1 vol. %	60.3 vol. %
Diffusion coefficient for OH^- @28 days	75.0E-12 m^2/s	0.75E-12 m^2/s
Tortuosity @28 days	1.42E-02	1.42E-04
Water diffusivity Permeability @28 days	8941E-22 m^2	119E-22 m^2
Hydraulic Conductivity @28 days*	4.15E-10 cm/s	5.53E-12 (cm/s)

* The intrinsic permeability determined by SIMCO Technologies Inc. for SIMCO saltstone and reported in SRNS-STI-2009-00477 Revision 0 was 4.0E-19 m^2, which is slightly lower than 8.9E-19 m^2 reported here for a sample cured for 28 days. The first value corresponds to a saturated hydraulic conductivity of 1.97E-10 cm/s which is about 20x lower than the value determined for simulated MCU saltstone prepared at SRNL and measured by a Darcy Lay permeation method, 3.4E-09 cm/s [Dixon, 2008], and about 10X lower than the value (2E-09 cm/s) used in the Saltstone PA. The method of determination used by SIMCO Technology is based on a drying isotherm method rather than Darcy-law permeation method. The SIMCO method is a property of the saltstone matrix without micro cracks.

The rate of decalcification and overall durability of the simulated MCU saltstone is expected to be considerably slower than the rate of decalcification of the low-slag material based on the lower permeability and diffusivity of the MCU saltstone compared to the low-slag mix described in SRNS-STI-2009-000477. In addition, the overall durability of both simulated saltstone waste forms is expected to be better than that of portland cement paste with a similar water to cement ratio and a lower total porosity due to the very tortuous microstructure of the saltstone waste form compared to the microstructure of portland cement paste. This conclusion

[3] Deionized water adjusted to a pH of 10.5 is being used as the exposure medium to simulate the important chemistry in anticipated vadose zone water chemistry (water in equilibrium with a moderately aged concrete vault).

was based on the very limited amount of decalcification that was inferred from SEM elemental scans on cross sections of immersed samples. After immersion in DI water with a pH of 10.5, the thickness of the leached zone was estimated to be about 2 mm. Immersion tests for the 45 wt. % slag saltstone samples are in progress and the decalcification rate for this material is expected to be lower than that of the low slag mix because of the more tortuous less porous microstructure.

Additional immersion tests of thin specimens along with SEM and microprobe analyses are required to generate samples that can be used for hydraulic property determination of leached saltstone material. Longer term experiments are required because the matrix alteration rate due to immersion in de-ionized water with a pH of 10.5 is slow. Desorption / adsorption isotherm methods described in this report are suitable for these determinations. Quantitative x-ray diffraction analyses are also required to determine initial and leached phase assemblages. This work is in progress at SIMCO Technologies, Inc. for the 45 wt. % slag saltstone material.

Recommendations include evaluating the cured and immersed samples for chemical, mineralogical, and physical signs of degradation as a function of longer times. Additional work recommended includes the following activities:

- Continue curing the current SIMCO saltstone samples and determine evolution of this material over longer times.
- Continue the SIMCO immersion testing on thin samples and determine the hydraulic properties of immersed (leached) material.
- Verify the modeled water exposure results using actual sample data.
- Determine the composition and mineralogy of the unidentified phase(s).
- Characterize the mineralogical evolution of saltstone exposed to water for multiple pH conditions.
- Evaluate the effects of unsaturated conditions on saltstone mineralogy, microstructure, and hydraulic properties.
- Evaluate the effects of intermittent saturated / unsaturated conditions on saltstone mineralogy, microstructure, and hydraulic properties.
- Develop a technique to stop hydration of the cementitious matrix that does not leach soluble salts out of the sample so the complete material can be characterized. Characterize the mineralogy, microstructure and hydraulic properties of the matrix plus salt samples.

2.0 INTRODUCTION

2.1 Objective

SIMCO Technologies, Inc. was contracted to evaluate the durability of the saltstone matrix material and to measure saltstone transport properties. Saltstone characterization data will be used to:

- Parameterize the STADIUM® service life code,
- Predict the leach rate (degradation rate) for the saltstone matrix over 10,000 years using the STADIUM® concrete service life code, and
- Validate the modeled results by conducting leaching (water immersion) tests.[4]

Saltstone durability for this evaluation is limited to changes in the matrix itself and does not include changes in the chemical speciation of the contaminants in the saltstone.

This report summarized results obtained for non-radioactive simulated Modular Caustic Side Solvent Extraction (MCU) saltstone with premix reagent proportions of 45 wt % slag, 45 wt % fly ash, and 10 wt % cement. The salt solution composition was designed to simulate the MCU product which will be sent to Z-Area for stabilization [Harbour, 2009]. Earlier saltstone characterization performed by SIMCO Technologies Inc. personnel was performed on a low-slag mix with the following premix reagent proportions: 21 wt % slag, 65 wt % fly ash, and 14 wt % cement. Those results are reported elsewhere [Langton, 2009 a and b]. The mistake was acknowledged and new mixes have been prepared and are curing.

This work was originally requested by J. L. Newman, Regulatory Integration & Business Management, and T. C. Robinson Jr., Waste Determinations. Since initiation of this work, Savannah River Remediation (SRR) has assumed responsibility for the liquid waste operations contract at the Savannah River Site. This work was coordinated through H. H. Burns, Engineering and Chemical Process Technology / Savannah River National Laboratory (E&CPT/SRNL) and will support the Saltstone Performance Assessment (PA) [Burns, 2008].

2.2 Background

The saltstone waste form contains high concentrations of sodium salts dissolved in the pore solution of a cementitious matrix consisting of calcium silicate hydrates (C-S-H) and other relatively insoluble hydrated phases. Prediction of the matrix durability over a long time (10,000 years) is required for performance assessment of the Saltstone Disposal Facility.

A subcontract was awarded to SIMCO Technologies, Inc., to use existing expertise, the STADIUM® concrete service life prediction code, and cementitious material characterization methodology to predict the evolution of the saltstone matrix as a function of curing time and to predict the durability. Degradation was assumed to be the result of decalcification of the matrix

[4] Leaching of non matrix constituents such as radionuclides and hazardous constituents present in trace quantities is not considered in this study. Appropriate representation of soluble constituents that are present in more than trace quantities but do not contribute to conventional cementitious binder phases (e.g. sodium) is still being studied.

material. Exposure tests, in which saltstone was immersed in de-ionized water, were performed and are still in progress. Results of the study will be used as supporting documentation for the Saltstone Performance Assessment, which predicts transport of radionuclides from the saltstone waste form into the surrounding environment and water table.

This report addresses Task 6 of in Contract SIMCORD08009, 2008.

2.3 Approach

2.3.1 Saltstone Sample Preparation

Samples of the saltstone binder reagents, cement, slag and fly ash, were shipped from SRS to SIMCO Technologies, Inc. and were used to prepare simulated saltstone samples. Chemicals for preparing simulated non-radioactive salt solution were obtained from chemical suppliers.

SIMCO personnel used the following proportions to prepare saltstone premix: 45 wt % slag, 45 wt % fly ash, and 10 wt % cement. They also prepared MCU salt solution according to proportions provided by J. R., Harbour, SRNL [Harbour, 2009]).

The SIMCO personnel prepared simulated saltstone samples according to mix instructions provided by C. A. Langton. Samples were cast in molds and cured for three days under plastic with a source of water to prevent drying. Details of the salt solution composition and saltstone sample preparation are provided in Attachment 1. Samples were cured at a constant temperature (76°F, 24°C) and 100 percent relative humidity until tested.

2.3.2 Initial Mineral Composition

The Stadium® reactive transport model was used to predict the rate of decalcification upon immersion in water. Decalcification was identified as the primary degradation mechanism and the decalcification rate was used as an estimate of durability (service life). The Stadium® code requires an estimate of the mineral composition of the hydrated waste form paste as well as the oxide compositions of the starting materials and combined binder material. Based on the total amount of calcium, silica, alumina and sulfur available to participate in the hydration process, the solid phase assemblage of the hydrated saltstone paste was approximated as consisting of C-S-H and monosulfate (sulfate AFm)[5] in about a 3:1 proportion. The calculation logic for estimating the hydrated phases is provided in Attachment 1.

Descriptions of the property measurement methods are provided in the SIMCO report which is provided in Attachment 1.

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[5] They are crystalline hydrates with general, simplified formula 3 $CaO \cdot (Al,Fe)_2O_3 \cdot CaSO_4 \cdot nH_2O$.

3.0 SALTSTONE CHARACTERIZATION

3.1 Compressive Strength

The compressive strength of the simulated MCU saltstone prepared by SIMCO Technologies personnel was 798 psi after curing for 28 days as shown in Table 3-1. This value is lower than but in the range of values reported by Dixon, 2008, and shown in Table 3-2. For comparison, the 28 day compressive strength of the SIMCO Technologies Inc., low-slag saltstone was 3.2 MPA (460 psi) compared to 5.5 MPA (798 psi) for the MCU saltstone, which indicates that slag is a key cementitious ingredient in the saltstone formulation.

Table 3-1. Compressive strength for MCU Simulated Saltstone.

	Simulated Non-Rad Low Slag Cement Saltstone SIMCO WS-1	Simulated Non-Rad MCU Saltstone SIMCO WS-2*
f_c 28d (MPa) *(psi)*	3.2 *460*	5.5 798
f_c56d (MPa) *(psi)*	*Not available*	*Not available*
f_c 90d (MPa) *(psi)*	*Not available*	*Not available*

*Three 2x2 inch cubic specimens tested per ASTM C 109.

Table 3-2. Compressive Strength for the MCU Saltstone Grout (Cast 3/31/2008)* [Dixon, 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

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

3.2 Pore Solution Composition

Pore solution results for the MCU and low-slag saltstone materials prepared by SIMCO Technologies, Inc., and for an experimental saltstone mix prepared and extracted in 1987 are presented in Table 3-3. Additional data are required to determine the statistical significance of these general observations. However, the results in Table 3-3 show that the pore solution extracted from the MCU saltstone was somewhat less concentrated in soluble ions than the solution extracted from the low-slag saltstone. These results suggest that the slag hydration products incorporate dissolved waste solution ions and/or slag hydration consumes sufficient water so some of the ions precipitate as solid salts. However, more pore solution data are required to identify trends. It should be noted that even with additional data, the pore solution extraction and analysis methods induce experimental errors expected to be in the range detected for the various saltstone samples analyzed. This is due to the large range in dissolved species concentrations in the extract, the very small sample size, and the large dilution factor required for analysis. Solutions were analyzed by atomic absorption, ion chromatography, and pH titration. Details of the extraction method are presented in Attachment 1 and elsewhere [Langton, 2008].

Table 3-3 Pore Solution Analyses for Simulated MCU Saltstone, Low-Slag Saltstone and an 1987 Experimental Saltstone.

Ions	**Simulated MCU Saltstone**		**SIMCO Low Slag Cement Saltstone**		**Trial Simulated Saltstone prepared / characterized at PSU [Langton, 1987]**	
	28 day cure		28 day cure		128 day cure	
	mmol/L	mg/L	mmol/L	mg/L	mmol/L	mg/L
OH^-	383.9	6,528	484.6	8,241	151.18	2,571
Na^+	4,144.2	95,284	4,419.8	101,610	3,639.28	83,667
K^+	120.5	4,712	119.3	4,666	141.84	5,546
SO_4^{2-}	111.7	10,731	120.3	11,558	139.00	13,353
Ca^{2+}	0.1	2	0.9	34	3.88	156
Cl^-	11.9	421	8.9	315	11.50	408
N	3,552.1	214,540	3575.8	215,978	3,153.22	190,471
CO_3^{2-}	46.8	4,683	**115.5**	6,930	97.49	5,850

3.3 Flow and Transport Properties

Transport properties for the non-radioactive simulated MCU saltstone cured for 28 days are summarized in Table 1-1. Test methods and calculations are included in Attachment 1. Properties of the SIMCO low-slag saltstone mix and other saltstone samples previously characterized by SRNL are summarized in SRNS-STI-2009-00477 [Langton, 2009 and Dixon, 2008].

The MCU saltstone was determined to be about 100X more tortuous than that of the low-slag saltstone characterized by SIMCO Technologies, Inc. Intrinsic diffusion coefficients[6] for selected ions are only a function of the material microstructure and not influenced by chemical reactions within the sample. The intrinsic diffusion coefficients were calculated by multiplying

6 Effective diffusion coefficients per SRNL terminology.
The Savannah River Site Performance Assessment and the key supporting documentation, such as WSRC-STI-2006-00198, refer to the free / molecular ion diffusion coefficient multiplied by the tortuosity as an effective diffusion coefficient rather that using the intrinsic diffusion coefficient terminology used by SIMCO Technologies, Inc. and also used in this report which summarizes the SIMCO results.
Furthermore, authors of SRNL reports related to PAs, such as WSRC-STI-2006-00198, apply the term intrinsic diffusion coefficient to the free / molecular ion diffusion coefficient multiplied by the porosity divided by the tortuosity.

the free ion (or molecular ion) diffusion coefficient by the intrinsic tortuosity and were also 100X lower than those reported for the low-slag saltstone. See Table 3-4.

Intrinsic diffusion coefficients for the low-slag saltstone as a function of curing time were reported in SRNS-STI-2009-00477. Time dependent (hydration dependent) results are not available for the simulated MCU saltstone prepared by SIMCO Technologies Inc. personnel.

Table 3-4. Diffusion Coefficients for Selected Contaminant Ions in Saltstone Pore Solution.

Species	**Free Ion Diffusion Coefficient (E-09 m^2/s)**	**Simulated MCU Saltstone Intrinsic Diffusion Coefficients (E-12 m^2/s)**	**Simulated Low-Slag Saltstone Intrinsic Diffusion Coefficients (E-12 m^2/s)**
		28d	**28d**
OH^-	5.273	0.75	75.00
Na^+	1.334	0.19	19.00
K^+	1.957	0.28	27.80
SO_4^{2-}	1.065	0.15	15.10
Ca^{2+}	0.792	0.11	11.30
$Al(OH)_4^-$	0.541	0.08	7.70
Cl^-	2.032	0.29	28.90
Tortuosity		1.42E-04	1.42E-02

NOTE: The Savannah River Site Performance Assessment and the key supporting documentation, such as WSRC-TR-2006-00198, refer to the free / molecular ion diffusion coefficient multiplied by the tortuosity as an effective diffusion coefficient rather that using the intrinsic diffusion coefficient terminology used by SIMCO Technologies, Inc. and also used in this report which summarizes the SIMCO results. Furthermore, authors of SRNL reports related to PAs, such as WSRC-STI-2006-00198, apply the term intrinsic diffusion coefficient to the free / molecular ion diffusion coefficient divided by the tortuosity and multiplied by porosity.

The porosities of the simulated MCU saltstone and the low-slag saltstone are relatively high, about 60 and 65 volume %, respectively, because of the high water to cement ratios of 0.6. However the microstructure of the low-slag saltstone after curing for 28 days is about 2X more tortuous than that of neat cement paste with a porosity of 52 volume percent [Samson and Marchand, 2007]. Surprisingly, the microstructure of the simulated MCU saltstone is about 100X more tortuous that that of the low-slag saltstone. The low tortuosities of both saltstone samples are attributed to the particle morphology and paste microstructure resulting from slag hydration.

SIMCO Technologies, Inc. used mercury intrusion porosimetry to characterize the pore size distribution of the simulated MCU saltstone and low-slag saltstone samples. Results are illustrated in Figures 3-1. The pore size distributions for these two samples are very different. The simulated MCU saltstone sample has a much finer structure which is the result of the additional slag hydration. A large portion of the pores in the MCU saltstone sample have a radius that is more than 10X smaller than those in the low-slag saltstone material for similar degrees of hydration. Details are provided in SIMCO Technologies Inc., report in Attachment 1.

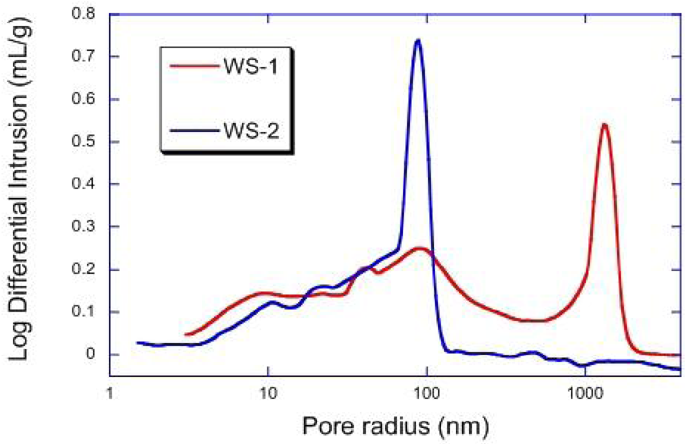

Figure 3-1. Pore Size Distribution for Simulated MCU Saltstone (WS-2) and Low-Slag Saltstone (WS-1).

4.0 CONCLUSIONS AND RECOMMENDATIONS

Chemical Stability: The chemical durability of the simulated MCU saltstone material described in this report is very good. Internal sulfate attack was not observed in the saltstone material and is not predicted based on the very high pH of the saltstone pore solution.

The rate of decalcification of the low-slag saltstone matrix upon immersion in water was found to be lower than that of portland cement paste with a similar water to cement ratio and lower total porosity based on the low-slag saltstone immersion testing previously reported. This conclusion was based on the very limited amount of decalcification data inferred from SEM elemental scans on cross sections of immersed samples. After immersion in DI water with a pH of 10.5, the thickness of the leached zone on the low-slag saltstone material was estimated to be about 2 mm. Longer term immersion tests of thin specimens along with SEM and microprobe analyses are required to obtain hydraulic property characterization data on thicker altered regions.

The durability (chemical stability) of the simulated MCU saltstone material characterized in this report is expected to be better than that of the low-slag saltstone mix described previously [Langton, 2009 a and b] because the intrinsic diffusivity of the simulated MCU saltstone is about 100X lower for the low-slag saltstone. (The rate of ingress of corrosive chemicals in uncracked porous materials is controlled to a large extent by the diffusivity of the material.)

Pore Solution Sulfate Concentrations: Saltstone pore solution is a source of sulfate ions. Consequently, the sulfate concentration in the saltstone pore water is considered important to vault durability. The saltstone vault performance assessment model currently assumes a corrosive fluid composition with a sulfate concentration of 150 mmol/L [Flach, 2009]. Sulfate concentrations in the pore solutions extracted from the low-slag saltstone sample prepared and analyzed by SIMCO Technologies after 28 and 123 days curing were 120 and 139 mmol/L, respectively. The sulfate concentration in the pore solution extracted from the simulated MCU saltstone sample after 28 days curing was 112 mmol/L. All test sample sulfate concentrations were less than what was assumed in the PA analysis.

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Implications for Vault Durability: Sulfate attack is a chemical degradation mechanism initially considered the key degradation mechanism in the saltstone vault concrete degradation model. However recent experimental and modeling results indicate that sulfate attack of the saltstone vault concrete due to extended exposure to high pH saltstone pore solution and / or more dilute leachates may not be as corrosive as initially thought, i.e., the sulfate front was predicted to advance about 5 cm in 10,000 years and to result in a corresponding 5 cm thinning of the vault walls [Samson, 2009 and 2010 and Langton 20090 a and b]. The very high quality (low permeability sulfate resistant mixes) of the saltstone vault concretes, in addition to the predicted stable phase assemblages are key factors in the slow ingress of sulfate and resulting damage caused by reactions between the sulfate ions and the concrete matrix phases. The predicted concentration gradient across the saltstone-vault interfacial zone which develops after long exposure times (hundreds to a thousand years) also plays a role in reducing the concentration of sulfate to which the concrete is exposed [Samson, 2010].

Transport Property Parameters: The intrinsic permeability determined by SIMCO Technologies Inc. for the simulated MCU saltstone cured for 28 days was 119 E-22 m^2. This corresponds to a saturated hydraulic conductivity of 5.53E-12 cm/s. This value is about 360X less than the hydraulic permeability currently used in the saltstone PA (2E-09 cm/s) and about 600X less than the value measured for simulated MCU saltstone prepared by SRNL which was measured by Darcy Law permeation method, i.e. 3.4E-09 cm/s as reported by Dixon, et al, 2008.

Permeability values are very sensitive to the measurement technique. This is illustrated in CBP-STI-2009-002-C6. The method of determination used by SIMCO Technology is based on a drying isotherm method rather than Darcy-law permeation method. The SIMCO method is a property of the saltstone matrix.[7] This method minimizes the effects of micro cracking which occur as the result of sample preparation and also general drying. **Recommendations:** Recommendations include evaluating the cured and immersed samples for chemical, mineralogical, and physical signs of degradation as a function of longer times. Additional work recommended includes the following activities:

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- Continue curing the current SIMCO saltstone samples and determine evolution of this material over longer times.
- Continue the SIMCO immersion testing on thin samples and determine the hydraulic properties of immersed (leached) material.
- Verify the modeled water-exposure results using actual sample data.
- Determine the composition and mineralogy of the unidentified phase(s) in saltstone and in the saltstone-concrete interfacial zone. Quantitative x-ray diffraction analyses are required to determine initial and leached phase assemblages. Preliminary mineralogical data are provided elsewhere [Cozzi and Duncan, 2009 and Langton, 1987 and 2005].
- Characterize the mineralogical evolution of saltstone exposed to water for multiple pH conditions.
- Evaluate the effects of unsaturated conditions on saltstone mineralogy, microstructure, and hydraulic properties.
- Evaluate the effects of intermittent saturated / unsaturated conditions on saltstone mineralogy, microstructure, and hydraulic properties.
- Develop a technique to stop hydration of the cementitious matrix that does not leach soluble salts out of the sample so the complete material can be characterized.
- Apply desorption / adsorption isotherm methods described in this report for moisture transport (permeability, tortuosity) determinations of sound material.
- Identify an additional method(s) for characterizing the effects of micro-cracks present in samples and include results as a separate term in moisture transport modeling so that the effects of the material microstructure, micro cracks, and macro-cracks can be addressed as separate parameters.
- Consider evaluating saltstone mix designs containing additional slag since the slag hydration products have a significant contribution to the saltstone microstructure and shift the pore size distribution to smaller pore opening radii and results in lower diffusion coefficients.

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[7] The underlying SIMCO Technologies, Inc. drying method (measurement principle) is expected to be representative of the material and not expected to have induced a strong gradient that would induce osmotic effects.

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6.0 ATTACHMENT 1

Updated Characterization of a Saltstone Mixture

Subcontract No. AC48992N Task 6 Report

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SIMCO Report

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