

Effect of Curing Environment on the Performance Properties of Saltstone – 13335

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ABSTRACT

At the Savannah River Site (SRS), the low level radioactive waste (LLW) salt solution is immobilized as a cementitious waste form known as saltstone. Depending on the saltstone formulation, disposal unit size, environmental conditions and pour schedule, the waste form temperature, due to exothermic hydration reactions, can gradually increase by 30 °C to 50 °C above the starting temperature. Previous studies at Savannah River National Laboratory (SRNL) have shown that curing temperature has a negative impact on the hydraulic conductivity and other performance properties of saltstone; specifically, these studies have shown that curing at elevated temperatures results in faster hydraulic conductivities than what is modeled in the saltstone Performance Assessment (PA). SRNL is currently testing the performance of laboratory prepared saltstone cured under controlled conditions (i.e. controlling relative humidity). The PA assumes that the saltstone remains saturated; therefore, some samples are being kept completely saturated while others have a surface exposed to a high humidity environment. The formulation of these samples has been varied to continue studying the impact of processing parameters on the performance properties of saltstone. The final water to premix (w/p) ratio of the saltstone formulation does affect the density, porosity, and compressive strength of the cured saltstone. The saltstone formulations with 0.59 w/p ratios and lower had higher densities, lower porosities, and higher compressive strength than samples formulated at a higher w/p ratio. There is a general trend that the samples formulated at high w/p ratios (0.67 and higher) have the lowest density, highest porosity and lowest strength. However, for hydraulic conductivity, the curing environment had a greater effect on the results than the formulation. Therefore, the impact of elevated temperature is not as detrimental to the performance of the waste form as originally concluded, provided the curing environment is controlled and the waste form is not dried out.

INTRODUCTION

The Saltstone Facility at the Savannah River Site (SRS) is comprised of two facilities, the Saltstone Production Facility (SPF) and the Saltstone Disposal Facility (SDF). The SPF receives low level radioactive waste (LLW) salt solution for treatment. At the SPF, the LLW is mixed with premix (a cementitious mixture of portland cement, blast furnace slag and Class F fly ash) in a Readco-Kurimoto, LLC continuous mixer to produce fresh (uncured) saltstone that is transferred to the Saltstone Disposal Facility (SDF) for permanent disposition in a Saltstone Disposal Unit (SDU). It should be noted that the first SDU's constructed (1 and 4) are referred to as Vaults. The saltstone formulation, including varying water to premix (w/p) ratio, additional water from flushes, and admixtures [1,2] can affect the rate of curing in the SDF. Depending on the saltstone formulation, SDU size and location, environmental conditions and pour schedule, the waste form temperature, due to exothermic hydration reactions, can gradually increase by 30 °C to 50 °C above the placement temperature.

The Saltstone Performance Assessment (PA) models the performance of the waste form and other aspects of the SDF over thousands of years after closure to determine the transport history of radionuclides and

other hazardous constituents in the LLW. The hydraulic conductivity of the waste form is one of the primary inputs into the PA. Previous studies at Savannah River National Laboratory (SRNL) have shown that curing temperature has the largest impact on the hydraulic conductivity of saltstone; specifically, these studies have shown that curing at elevated temperatures results in faster hydraulic conductivities than what is modeled in the PA. Therefore, the conclusion has been that higher curing temperatures have a negative impact on the performance of the waste form. However, the curing conditions were not controlled for these samples and examination of the microstructure shows microcracking due to drying, which could significantly impact the measured performance properties [3]. Because the curing environment was not controlled in previous studies, the impact of elevated temperature may not be as detrimental to the performance of the waste form as originally concluded.

As a continuation of previous work [3], samples were cured under a temperature profile rather than cured isothermally. Historical SDF Vault 4 data were used as a basis for the temperature profile; however it is important to note that temperatures recorded in previous disposal units vary due to many factors including processing strategy and saltstone formulation. The temperatures that will be recorded in future SDUs will vary from those in Vault 4 due to pour strategy, formulation, and other factors. The intention of this study was to trend saltstone performance properties as a function of curing conditions (relative humidity (RH), temperature) rather than provide information on the performance of material residing in Vault 4 or previous disposal units. Since field conditions vary in the disposal units depending on pour strategy, etc., two curing conditions were investigated. The first was curing saltstone under a defined temperature profile with the surface exposed to a humid environment. The second was saltstone cured under the temperature profile while keeping the surface covered with liquid to maintain saturated conditions as described in the PA [4]. The cured properties (hydraulic conductivity, porosity, density, contaminant retention) of these samples are compared to results from a previous study [3] where samples were cured under the same temperature profile in an environment with uncontrolled humidity.

DESCRIPTION OF METHODS

Data from a typical processing day at the SPF were analyzed to determine the saltstone formulations for this study. The average w/p ratio as well as the average amount of extra water added to the system were determined as baselines for varying the formulation. Extra water is defined for this work as the water from flushes, drain water, and sources other than the LLW salt solution. Throughout processing operations, the mixer, grout hopper, grout pump, and piping to the SDU are flushed with water every 15 minutes to mitigate process upsets. However, this extra water is not accounted for in the water to premix (w/p) calculation for the saltstone formulation. Analysis of a continuous day of processing shows that during a routine operational flush, an instantaneous w/p ratio of 0.73 is being made. During nominal steady-state processing, the w/p ratio target is 0.59 or 0.60. Previous testing has shown that saltstone formulated at a higher w/p ratio has longer gel and set times, more bleed water generated, and generally poor performance properties compared to saltstone made at w/p ratios of 0.6 or lower [3,5-8]. The data were used to calculate instantaneous and cumulative w/p ratios over the given period of processing. Both points were tested to provide snapshots of actual conditions at a given time in the facility.

The w/p ratio, amount of extra water, and admixture dosage are the formulation variables (Table I). The

premix composition and the salt solution chemistry were held constant. The starting w/p was selected by assuming that only the LLW salt solution is being processed with premix to make saltstone slurry. The baseline formulation was a 0.59 w/p ratio with no admix or extra water (WP001) since this is how the SPF has been processing since the third quarter of 2011. The extra water added is the total calculated amount of water added during a full day of processing (8 wt % of the LLW processed) or half of that amount (4 wt %). The final w/p ratio is calculated after the extra water is added to the formulation. The amount of admix added is an average of Daratard 17 (set retarder) dosage to the saltstone formulations from 2008 – 2010 [9,10]. The formulations selected for cured property measurements are representative of the range of starting and final w/p ratios that could be processed through the SPF.

Table I. Experimental Design for Saltstone Formulations Tested

Sample	Starting w/p	Extra Water (wt %)	Final w/p	Admix (wt %)
WP001	0.59	0	0.59	0.00
WP003	0.67	0	0.67	0.00
WP005	0.56	8	0.70	0.05
WP010	0.58	8	0.72	0.05
WP011	0.57	4	0.64	0.00
WP014	0.55	0	0.55	0.00
WP018	0.73	0	0.73	0.00
WP021	0.53	4	0.60	0.05
WP023	0.51	0	0.51	0.00

Sample Preparation and Curing

The nominal premix distribution used in this testing is 45 wt % blast furnace slag, 45 wt % thermally beneficiated Class F fly ash, and 10 wt % portland cement. The salt solution, premix, and admix materials were mixed for approximately three minutes using a paddle blade mixer. The mixing was paused for approximately five seconds after 30 seconds of mixing to allow entrained air to escape from the saltstone. Daratard-17 was added to selected mixes (Table I) at the specified dosage of 0.05 wt %. All admixture dosages are on a wt % basis of the premix in the formulation. The admixtures were added to the salt solution first and then the dry feeds were added. After mixing was complete, the fresh saltstone was poured into sample molds for property testing.

Samples were cured under profiles based on temperature data from cell K and cell F in Vault 4. To date, the temperatures in cell K are the highest recorded in any of the SDUs and the temperature profile of cell F is typical of temperatures recorded in multiple cells in Vault 4. The data used are actual temperature data recorded by thermocouples in the cells over several months and approximated to a 28 day cure time. Since the processing conditions cannot be replicated and the cure time for simulated saltstone is significantly decreased compared to actual saltstone in cells K and F, the cure profiles in Fig. 1 are only meant to approximate two different processing conditions (pour strategy, etc.) in the SPF. A programmable convection oven was used to achieve the curing profiles (Fig. 1). At the end of the curing profile, the oven temperature was ramped down to room temperature over several days while keeping the humidity high to prevent any drying and cracking of the samples during cooling. Once removed from the oven, samples were

kept in a plastic bag with a wet sponge to maintain humid conditions until the cured properties were analyzed.

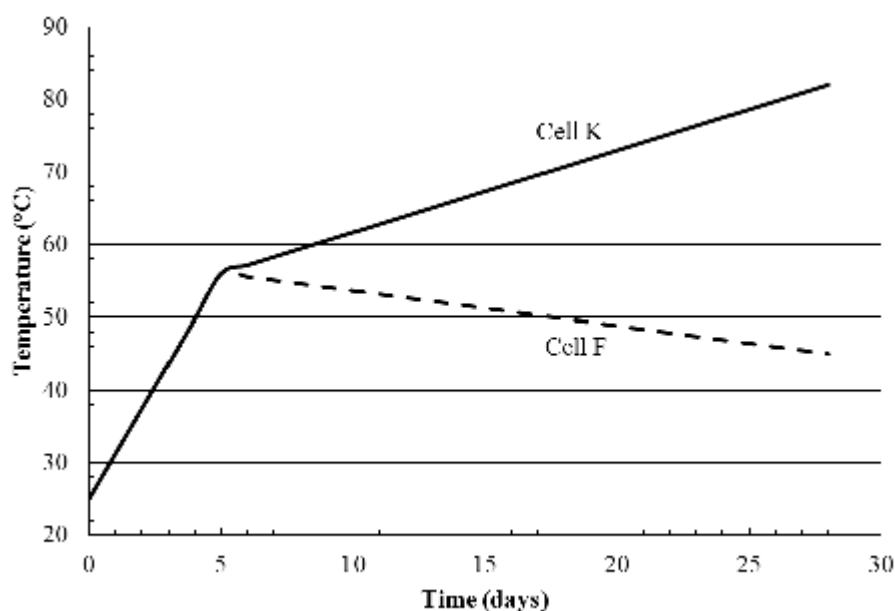


Fig. 1. Modified Cell K and Cell F curing profiles.

Modifications to the oven were made to provide a high humidity curing environment while the samples were heated. A control program was used to keep the chamber of the oven at a high relative humidity. Quadruplicate samples of each formulation were cured in the oven for 28 days. Since field conditions vary in the disposal units depending on pour strategy, etc., two curing conditions were investigated. Two of the samples were kept under saturated conditions by adding liquid on top of the saltstone to maintain complete saturation. The other two samples had the saltstone surface exposed to the humid environment.

Property Measurements

Cured properties were measured after samples cured for 28 days. Grout is considered “cured” after 28 days since the major hydration reactions are complete within that time. Although hydration reactions continue indefinitely, the ratio of strength gain compared to cure time is minimal after 28 days. The cured properties measured on these samples are hydraulic conductivity, compressive strength, porosity, cured density, and leachability index. After the 28 days, the quadruplicate samples were removed from the oven and one sample from each of the curing conditions was used for hydraulic conductivity analysis. The remaining samples were used for the analyzing the other cured properties.

The saturated hydraulic conductivity [11], dry bulk density, and porosity were measured after the samples had cured for 28 days at SRNL. Each 7.62 x 15.24 cm (3 x 6 inch) cylindrical sample was cut in half to create duplicate 7.62 x 7.62 cm (3 x 3 inch) samples and labeled as the top and bottom, respectively. The saturated hydraulic conductivity of the saltstone samples was determined by ASTM D 5084 method F, the

constant-volume falling head using a flexible wall permeameter [11]. The fluid used for testing was the simple salt solution that did not include reactive species such as aluminum nitrate or phosphates. This was used to avoid interactions of the test fluid and the sample during testing. Saturated hydraulic conductivity is a function of the porous medium and the properties of the test fluid as described by Darcy's law [12].

The bulk density of the cured samples was measured immediately after the samples were removed from the oven. The cured density of each sample was calculated by dividing the sample mass by the volume of the sample. The compressive strength of the cured samples was measured using a Humboldt CM-3000-LXI compression tester according to ASTM C39 "Compressive Strength of Cylindrical Specimens" [13]. According to the procedure, compressive strength testing of moist-cured specimens shall be made as soon as practical after removal from moist storage [13]. Each sample was centered on the lower block and the load was applied to the sample at a constant rate of 241 ± 48 kPa/s. The compressive load was applied to each sample until the indicator showed a steady decrease in the load and the sample was visibly cracked [13]. The compressive strength was calculated by dividing the maximum load by the cross-sectional area of the sample.

After completion of compressive strength measurements, two fractured pieces from the center of each sample were used for porosity measurements. The porosity was determined by the mass loss [14] upon heating samples to 105°C in a convection oven. The mass loss was monitored until no further mass loss occurred (approximately 24 hours). The water released during heating (m_w) is converted to a volume of simulant by dividing by the ratio of the mass of water to the mass of the simulant then dividing again by the density of the simulant [14]. The reported porosity of the cured samples is the simulant volume divided by the sample volume.

Contaminant movement and release from saltstone is also modeled in the PA. Therefore, after curing, the samples were leach tested using the American National Standard Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure (ANSI/ANS 16.1) [15]. The saltstone samples were suspended in bottles with fresh leachant (deionized water) then lifted out at set times and placed in new bottles with fresh leachant. A blank with just deionized water was created and sampled at each time period to ensure that the leachant was not introducing contaminants into the leachates.¹⁵ The time periods for the leachate testing were 2, 7, 24, 48, 72, and 96, and 120 hours [15]. At the end of each elapsed time period, leachate samples were collected from each bottle for Ion Chromatography (IC) measurements of nitrite (NO_2^-) and nitrate (NO_3^-) concentrations and Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) measurements of chromium and sodium concentrations. Leachate samples were also collected for pH and conductivity measurements.

DISCUSSION OF RESULTS

The impact of curing temperature on the performance (cured) properties of saltstone has been studied extensively [3,6-8,16]. All of the samples analyzed in these previous studies were cured in an environment with uncontrolled humidity, resulting in drying out of the saltstone. These studies showed that the performance properties of saltstone decreased with increasing curing temperatures; however it was unclear whether the deleterious effects of curing at high temperatures were solely due to drying out of the saltstone or whether there were other effects of curing at high temperatures that caused the poor performance

properties [3]. The results presented in this report investigate the impact of curing environment (saturated conditions and exposure to high humidity) and temperature on the cured properties of saltstone formulated with various amounts of extra water as well as with and without admixtures. It should be noted that the samples in the previous study were cured for a total of 90 days prior to analysis whereas the samples in this study cured for 28 days. It is accepted in the grout industry that the majority of the hydration reactions have occurred after 28 days and although curing continues, the performance properties do not change significantly between 28 and 90 days of curing [12,17].

Porosity and Bulk Density

Grout porosity is generally defined as the percentage of total volume of cured saltstone that is not occupied by either the starting cementitious materials (in this case, portland cement, blast furnace slag, and Class F fly ash) or the products that results from reaction of these cementitious materials with water (calcium silicate hydrate, calcium hydroxide crystals, etc.) [12]. The porosity and bulk density are reported in Table II in order of samples formulated with the lowest to highest final w/p ratio. These results support the conclusions from previous studies and literature that the porosity and bulk density of saltstone have an inverse relationship primarily controlled by the w/p ratio [3,7]. Samples formulated at low w/p ratios are denser and have lower porosity than samples at higher w/p ratios (Table II) and have higher compressive strength and lower hydraulic conductivity as discussed in the following sections.

Table II. Bulk density (ρ) and porosity (P) of samples, listed from lowest to highest final w/p ratio, cured under cell K and cell F temperature profiles

Sample	Start w/p ratio	Final w/p ratio	Cell K				Cell F			
			Saturated		Exposed Surface		Saturated		Exposed Surface	
			ρ (g/cm ³)	P (%)	ρ (g/cm ³)	P (%)	ρ (g/cm ³)	P (%)	ρ (g/cm ³)	P (%)
WP023	0.51	0.51	1.787	63.5	1.796	57.5	1.793	55.1	1.789	55.3
WP014	0.55	0.55	1.792	60.9	1.771	61.2	1.789	58.4	1.767	57.1
WP001	0.59	0.59	1.755	64.1	1.736	61.3	1.759	69.9	1.752	59.9
WP021	0.53	0.60 ^{a,c}	1.741	64.9	1.719	62.3	1.732	60.5	1.733	61.3
WP011	0.57	0.64 ^c	1.700	65.3	1.686	60.3	1.722	61.3	1.700	62.5
WP003	0.67	0.67	1.715	67.3	1.692	62.5	1.705	62.1	1.715	63.2
WP005	0.56	0.70 ^{a,b}	1.669	69.6	1.660	64.3	1.659	64.1	1.685	65.8
WP010	0.58	0.72 ^{a,b}	1.677	69.1	1.671	64.7	1.673	68.1	1.642	66.6
WP018	0.73	0.73	1.691	66.2	1.677	64.8	1.703	66.6	1.679	66.8

- ^a Samples with admix included in the formulation
- ^b Formulation with 8 wt % extra water
- ^c Formulation with 4 wt % extra water

In a previous study, it was reported that curing temperature has an effect on the porosity and density of saltstone; however, the mass loss of the sample as a result of curing at elevated temperatures would affect the cured density and therefore the saltstone porosity, since the cured density is used to calculate the

saltstone porosity [3]. Therefore, since these prior study samples were cured in an environment with uncontrolled humidity, the cured properties, specifically density, were more affected by drying than cure temperature alone. In fact, the rapid hydration at higher temperatures leads to encapsulation of porous cementitious materials by a layer of dense hydrated product, causing an overall decrease in saltstone porosity, assuming that the cementitious materials are completely hydrated [12,17]. Therefore, since the samples in this study were cured in a high humidity environment and not dehydrated, the densities of these samples are higher than those cured in an uncontrolled environment. For example, samples in the previous study formulated at 0.55 w/p with no admixtures and cured at 60 °C had densities of 1.711 g/mL and 1.769 g/mL for the low and high aluminate solutions, respectively [3]. In this study, the same formulation was cured to 55 °C and 80 °C under saturated conditions resulting in densities of 1.789 g/cm³ and 1.792 g/cm³, respectively (Table II).

Compressive Strength

Although the compressive strength of saltstone is not an input in to the PA, it is a property that provides insight into other properties of the material, such as hydraulic conductivity, porosity and density. Higher density grouts will have higher compressive strength and lower hydraulic conductivity. This is due to lower void spaces and lower porosity in the saltstone resulting in a higher strength material [17]. There are other factors that determine the compressive strength of a grout that include the microstructure, w/p ratio (including admixtures), the mixing conditions, the curing conditions (especially temperature and RH), the age, and the matter of testing (including water content in the sample [17]. Table III lists the compressive strength of all the samples in order of lowest to highest final w/p ratio. The general trend of the data is that low w/p samples have higher compressive strengths.

Table III. Compressive strength of samples, listed from lowest to highest final w/p ratio, cured under cell K and cell F temperature profiles

Sample	Starting w/p ratio	Final w/p ratio	Compressive strength (kPa)			
			Cell K		Cell F	
			Saturated	Exposed Surface	Saturated	Exposed Surface
WP023	0.51	0.51	20953	20533	18588	18237
WP014	0.55	0.55	20643	22325	16354	16871
WP001	0.59	0.59	21181	20912	11280	15120
WP021	0.53	0.60 ^{a,c}	12018	12666	12666	12093
WP011	0.57	0.64 ^c	13707	11976	13748	13900
WP003	0.67	0.67	11273	15906	10280	9515
WP005	0.56	0.70 ^{a,b}	9777	9935	8474	8729
WP010	0.58	0.72 ^{a,b}	8053	9646	8715	8805
WP018	0.73	0.73	9432	10170	6929	7143
Average			14115	14897	11893	12268
Standard Deviation			5355	5150	3843	3969

- ^a Samples with admix included in the formulation
- ^b Formulation with 8 wt % extra water
- ^c Formulation with 4 wt % extra water

A previous report on the compressive strength of saltstone has shown a decrease in strength as a result of higher curing temperatures (approximately 8549 kPa at 20 °C to 7515 kPa at 40 °C) [8], however, these samples may have been dried out, which would lead to the lower compressive strength. As shown in Table III, the compressive strength of samples cured under high RH and temperature profiles up to 80 °C and 55 °C are greater than or equal to the 8549 kPa recorded from room temperature cured samples [8], indicating that higher cure temperatures benefit the saltstone cured properties, provided the material is not dried out. The data in Table III shows that curing in a high humidity environment is important, more so than if the sample is saturated or has the surface exposed to the environment. The cell K samples have a higher average compressive strength than the cell F samples but the standard deviation indicates the two cure profiles result in saltstone with comparable compressive strengths.

Hydraulic Conductivity

Permeability is defined as the property that governs the rate of flow of a fluid into a porous solid. For steady-state flow, the coefficient of permeability, also known as hydraulic conductivity, is determined by Darcy's Equation [12]. The saturated hydraulic conductivity (Table IV) was measured on the top and bottom of each sample after curing for 28 days under each temperature profile.

All of the samples had a hydraulic conductivity of 4.5E-8 cm/s to 4.3E-10 cm/s. Of the 72 samples analyzed, only three samples had hydraulic conductivities on the order of 1E-7 cm/s (the saturated WP010 sample and both WP003 samples, all cured under the cell K profile). On average, the cell K samples had slightly higher hydraulic conductivities for samples at higher w/p ratios than the cell F samples; however, the majority of the samples have hydraulic conductivities within the range of E-9 cm/s or E-10 cm/s.

As shown in literature, there is an exponential relationship between porosity and the hydraulic conductivity or strength of grout. As the porosity increases, the strength decreases and hydraulic conductivity increases [12,17]. Comparing the results in Table II and Table III, there is a general trend that the samples with the highest porosity (higher w/p ratios) have the lowest strength and therefore highest hydraulic conductivity which indicates the w/p ratio of the formulation effects the cured properties of saltstone. However, for the hydraulic conductivity results reported in Table IV, it is difficult to find a trend in the data based on w/p ratio.

The results from a previous study showed a slight trend of increasing hydraulic conductivity with increasing w/p ratio, but the primary trend was higher temperatures resulted in higher hydraulic conductivities [3]. In that study, a range of sample formulations were cured isothermally at 20 °C, 40 °C and 60 °C for 28 days followed by a 62 day cure at room temperature. These samples had hydraulic conductivities ranging from 1.04E-9 cm/s to 1.90E-6 cm/s, with the majority of the 60 °C samples having hydraulic conductivities greater than 1.0E-7 cm/s [3]. It was determined that those samples were dried out, causing microcracks in the sample and higher hydraulic conductivities [3,17] Comparing the results presented in Table IV to the results from a previous study, the curing conditions have a greater effect on the hydraulic conductivity of saltstone than the w/p ratio. The saltstone in the current study was cured in a high humidity environment which allowed the microstructure to develop without being dehydrated, reducing the formation of microcracks.

Table IV. Hydraulic conductivity of samples, listed from lowest to highest final w/p ratio, cured under cell K and cell F temperature profiles

Sample	Starting w/p ratio	Final w/p ratio	Sample Section	Hydraulic Conductivity (cm/s)			
				Cell K		Cell F	
				Saturated	Exposed Surface	Saturated	Exposed Surface
WP023	0.51	0.51	top	9.50E-10	5.40E-10	5.80E-09	1.00E-09
			bottom	1.50E-09	3.70E-10	7.70E-10	7.20E-10
WP014	0.55	0.55	top	4.30E-10	3.70E-09	1.30E-09	1.80E-09
			bottom	3.90E-10	4.30E-09	3.70E-09	9.80E-10
WP001	0.59	0.59	top	1.70E-09	4.50E-09	1.40E-09	4.30E-09
			bottom	1.90E-09	3.90E-10	3.60E-09	1.60E-09
WP021	0.53	0.60 ^{a,c}	top	1.70E-09	1.70E-09	4.10E-09	2.10E-09
			bottom	2.10E-09	2.20E-09	3.70E-09	1.30E-09
WP011	0.57	0.64 ^c	top	3.20E-08	4.50E-08	7.00E-09	1.30E-09
			bottom	9.60E-09	1.30E-08	5.00E-09	3.10E-09
WP003	0.67	0.67	top	6.20E-07	4.00E-07	3.50E-09	3.70E-09
			bottom	1.90E-09	9.80E-10	3.00E-09	1.50E-09
WP005	0.56	0.70 ^{a,b}	top	4.30E-10	1.00E-09	7.70E-10	5.20E-10
			bottom	3.10E-10	3.30E-10	7.70E-10	5.20E-10
WP010	0.58	0.72 ^{a,b}	top	2.80E-07	3.60E-09	4.00E-09	3.10E-09
			bottom	3.50E-09	2.60E-09	2.20E-09	2.50E-09
WP018	0.73	0.73	top	7.80E-09	8.00E-09	2.10E-09	4.50E-09
			bottom	2.90E-08	3.30E-09	5.70E-09	7.60E-09

- ^a Samples with admix included in the formulation
- ^b Formulation with 8 wt % extra water
- ^c Formulation with 4 wt % extra water

Another study showed the impact of initial cure temperature on cured saltstone properties. This study showed that saltstone cured at room temperature followed by a high temperature cure had better performance properties than the same saltstone formulation cured at high temperature followed by curing at room temperature.⁸ Therefore, the combination of curing saltstone in a saturated or high humidity environment and under a ramped temperature profile results in slower hydraulic conductivities than saltstone dried out during curing and cured at high isothermal temperature.

Leachability Index

The leachability indices [15] for chromium, sodium, nitrate, and nitrite were determined for the saltstone formulations cured under the cell K profile. The ANSI/ANS 16.1 standard specifies how to calculate the

effective diffusivity ($D_{e,n}^i$) of a leached species when less than 20% of the species leaches (Eq. 1).

$$D_{e,n}^i = \pi * \left[\frac{\frac{a_n}{A_0}}{(\Delta t)_n} \right]^2 * \left[\frac{V}{S} \right]^2 * T \quad (\text{Eq. 1})$$

Where a_n is the amount of species in leachate for leaching interval, n , in grams, A_0 is the total amount of species in the Saltstone Sample initially (grams), $(\Delta t)_n$ is duration of the n^{th} leaching interval (seconds), V is the volume of the sample (cm^3), S is the external surface area of cut saltstone sample (cm^2) and T is the mean time of the leaching interval (seconds). Inserting the leachate masses at the various time intervals (a_n), the initial species masses (A_0), the time intervals $(\Delta t)_n$ and mean leaching times (T), and the volume to surface area ratios (V/S) into Equation 1, the effective diffusivity of the leaching species for each time interval, n , can be calculated. Once the effective diffusivities for the Cr, Na, NO_3^- , and NO_2^- species for the various leaching time intervals for the saltstone samples are defined, the Leachability Index of each species (L_i) can be calculated (Eq.2).

$$L_i = \frac{1}{7} * \sum_{n=1}^i \log_{10} \left(\frac{1}{D_{e,n}^i} \right) \quad (\text{Eq. 2})$$

The Leachability Index based on the ANSI 16.1 standard test for the Cr, Na, NO_3^- , and NO_2^- species in the saltstone samples were calculated using Equation 2 and the effective diffusivities defined by Equation 1 [15]. The Leachability Indices for the saltstone samples with respect to chromium are all greater than numbers since the amount of chromium in the leachate were all below the detection limit of the ICP-ES. The Leachability Indices for Na ranged from 7.0 to 7.9 and the Leachability Indices for NO_3^- and NO_2^- ranged from 6.9 to 7.4 (Table V).

Table V. Leachability Index for Cr, NO_3^- and NO_2^- for saltstone cured under the cell K profile

Sample	Starting w/p ratio	Final w/p ratio	Cr	Na	NO_3^-	NO_2^-
WP001	0.59	0.59	> 10.6	7.7	7.0	7.0
WP003	0.67	0.67	> 10.6	7.9	7.3	7.4
WP005	0.56	0.70 ^{a,b}	> 10.4	7.0	7.0	7.0
WP010	0.58	0.72 ^{a,b}	> 10.5	7.7	7.3	7.1
WP011	0.57	0.64 ^c	> 10.6	7.3	6.9	7.3
WP014	0.55	0.55	> 10.6	7.8	7.4	7.4
WP018	0.73	0.73	> 10.6	7.4	7.0	7.0
WP021	0.53	0.60 ^{a,c}	> 10.6	7.2	6.7	6.8
WP023	0.51	0.51	> 10.6	7.4	6.9	6.9

- ^a Samples with admix included in the formulation
- ^b Formulation with 8 wt % extra water
- ^c Formulation with 4 wt % extra water

A smaller the Leachability Index indicates that a constituent is more easily removed from the saltstone. Based on the formulations tested in this study, the initial formulation of the samples did not influence the rate at which contaminants were released from the saltstone.

CONCLUSIONS

Data from a typical (no setbacks or process upsets) processing day at the SPF was analyzed to calculate instantaneous and cumulative saltstone water to premix ratios over the given period of processing. A series of saltstone formulations were developed and analyzed based on these data and the cured properties (hydraulic conductivity, porosity, density, and contaminant retention) of these formulations were analyzed. Samples were cured under profiles based on temperature data from cell K and cell F in Vault 4. Half of the samples were kept under saturated conditions by adding liquid on top of the saltstone to maintain complete saturation. The other half had the saltstone surface exposed to the humid environment. Based on the results of this study, the relative humidity of the curing environment has the most impact on the performance (cured) properties of saltstone. If the drying of the sample is eliminated or at least minimized, higher cure temperatures can be beneficial for saltstone due to increased reaction rates, formation of denser hydration products, and reduction in porosity.

The final w/p ratio of the saltstone formulation does affect the density, porosity, and compressive strength of the cured saltstone. The saltstone formulations with 0.59 w/p ratios and lower had higher densities, lower porosities, and higher compressive strength than samples formulated at a higher w/p ratio. There is a general trend that the samples formulated at high w/p ratios (0.67 and higher) have the lowest density, highest porosity and lowest strength. However, compared to data from previous studies, the density, porosity, and compressive strength of saltstone are more controlled by curing in a high humidity environment rather than the w/p ratio of the saltstone formulation. The Leachability index for Na, NO_3^- and NO_2^- were calculated for the cured samples using the ANS/ANSI 16.1 standard. Based on the formulations tested in this study, the initial formulation of the samples did not affect the rate at which contaminants are released from the saltstone.

Samples cured for 28 days in controlled humidity environments under temperature profiles up to 55 °C and 80 °C had hydraulic conductivities of 4.5E-8 cm/s to 4.3E-10 cm/s. On average, the cell K samples had slightly higher hydraulic conductivities for samples at higher w/p ratios than the cell F samples; however, the majority of the samples have hydraulic conductivities within the range of E-9 cm/s or E-10 cm/s. Of the 72 samples analyzed, only three samples had hydraulic conductivities on the order of 2.8E-7 cm/s. In a previous study, samples cured isothermally in an uncontrolled environment had hydraulic conductivities ranging from 1.04E-9 cm/s to 1.90E-6 cm/s, with the majority of the 60 °C samples having hydraulic conductivities greater than 1.0E-7 cm/s. Comparing the results presented in this study to the results from the previous study, the curing conditions have a greater effect on the hydraulic conductivity of saltstone than the formulation. The saltstone in the current study was cured in a high humidity environment which allowed the microstructure to develop without being dehydrated, reducing the formation of microcracks. Therefore, the combination of curing saltstone in a saturated or high humidity environment and under a ramped temperature profile results in slower hydraulic conductivities than saltstone dried out during curing

and cured at high isothermal temperatures.

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