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Evaluating the Chemical Resistance of Saltstone Disposal Unit (SDU) Concrete and Polymeric Coatings – 18494

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ABSTRACT

Saltstone Disposal Units (SDUs) are multi-million liter concrete structures that are used at the Savannah River Site (SRS) for the permanent disposal of low-activity salt solution incorporated in a cementitious grout matrix, termed saltstone. The major chemical constituents of the salt solution include sodium, aluminum, nitrate, nitrite, hydroxide, carbonate, and sulfate. The potential exists for the SDU interior to be chronically exposed to these corrosive constituents resulting in deleterious reactions and physical damage. Sulfate attack is an example of such an interaction whereby aqueous sulfates may penetrate the concrete, and react with hydration products in the cured concrete to form expansive phases that can cause excessive strains and cracking. Recently constructed SDUs have utilized sulfate-resistant Type V cement and polymeric coatings to minimize the potential impacts of SDU concrete exposure to the highly caustic (pH > 13) salt solution. Not only must the concrete and coatings exhibit high resistance to the caustic salt solution but they are also subjected to above ambient temperatures due to the exothermic nature of the grout hydration reaction. As such, both the SDU concrete and the coatings need to be tested with respect to stability in the aforementioned chemical and thermal environments.

Two primary investigations were considered in this work. The first was to evaluate the resistance of two previously used epoxy coatings (Hempel Versiline TL-45 S Novolac and EC-66 elastomeric epoxies) to chemical attack from a simulated salt solution. In addition, a third coating was included in the study, a polyurea coating (Sherwin Williams Envirolastic AR425) that may be considered as an alternative to the epoxy coatings on future SDUs. Each coating was applied to concrete cylinders (actual SDU 6 test cores) and subsequently exposed to saltstone, or full and half strength caustic salt solution; 50% dilution was considered since saltstone processing involves addition of flush water to the SDUs, which is expected to dilute any residual salt solution or bleed water in the SDU. Exposure testing was conducted at 68 °C for 1,000 hours followed by ambient exposure to provide a full exposure time of approximately 90 days. It is important to note that evaluation criteria for the coated materials were only visual in nature. Other than coating discoloration, which was limited to the surfaces, no other visual indications of reactivity between the three coatings and any of the exposure mediums were observed. Cross-sectioned samples indicated no through-thickness coating penetration or reaction, and showed no signs of delamination. The second investigation was to determine if SDU concrete without a polymeric barrier would resist ingress and reaction with salt solution at the elevated temperature. Again, only slight discoloration of the concrete surfaces was observed after the 90-day exposure test irrespective of the salt solution concentration. A requirement of structural concrete in the SDUs is that it possesses a minimum compressive strength of 42 MPa (6,000 psi). The average compressive strength of samples exposed to the full-strength salt solution was recorded at 68 MPa compared to 66 MPa for the unexposed samples thus indicating that the exposure conditions considered in this study were not detrimental to the concrete strength.

INTRODUCTION

The Savannah River Site (SRS) is a U.S. Department of Energy (DOE) facility currently storing 133 million liters (35 million gallons) of Cold War legacy, high-level waste (HLW) with a combined activity of 9.73E+12 megabecquerels (MBq) (263 million Curies). This waste is stored in 43 active underground tanks and will ultimately be dispositioned via vitrification. However, the treatment of HLW at SRS will generate approximately 380 million liters (100 million gallons) of low activity salt solution containing less than 0.1% of the total SRS radionuclide inventory. The radionuclide-containing salt solution is dispositioned at the Saltstone Disposal Facility (SDF) via combination with a mixture of ground-granulated blast furnace slag (GGBFS), Class F fly ash (FA), and Type II ordinary Portland cement (OPC) at the Saltstone Production Facility (SPF) to form a flowable grout referred to as saltstone. Once mixed the radioactive grout is transferred to concrete vaults, termed Saltstone Disposal Units (SDUs) (Fig. 1), where it subsequently cures and encapsulates the waste. The salt solution that is mixed with the cementitious components (and therefore the pore solution of the cured material) contains high concentrations of components such as alkali metals, nitrates, nitrites, hydroxides, and sulfates. After the addition of freshly processed grout to the SDUs, drain water (a combination of bleed water generated from saltstone and process system flush water) may come into prolonged contact with the SDU concrete, particularly in the drain water collection system. In addition, cured saltstone (and hence the pore solution) will be in direct contact with SDU concrete for the lifetime of the SDU structure. Assuming direct contact between saltstone, and/or drain water, and the SDU walls, floor, and columns, there is the potential for corrosive constituents to migrate into the SDU concrete resulting in deleterious reactions and subsequent physical damage over time. Sulfate attack is an example of such an interaction whereby aqueous sulfates may penetrate the concrete, and react with hydration products in the cured concrete to form expansive phases that can cause excessive strains and cracking. Recently constructed SDUs have utilized sulfate-resistant Type V cement and polymeric coatings to minimize the potential impacts of SDU concrete exposure to the highly caustic (pH > 13) salt solution. Not only must the concrete and coatings exhibit high resistance to the caustic salt solution but they are also subjected to above ambient temperatures due to the exothermic nature of the grout hydration reaction. This work was focused towards evaluating the potential of chemical exposure (at elevated temperature) to deleteriously impact the SDU walls and floors when saltstone, and/or saltstone drain water solutions, come into contact with: (1) SDU concrete coated with polymeric barrier layers (as depicted in Fig. 1) and (2) uncoated SDU concrete (to determine if the SDU concrete requires a polymeric barrier layer).

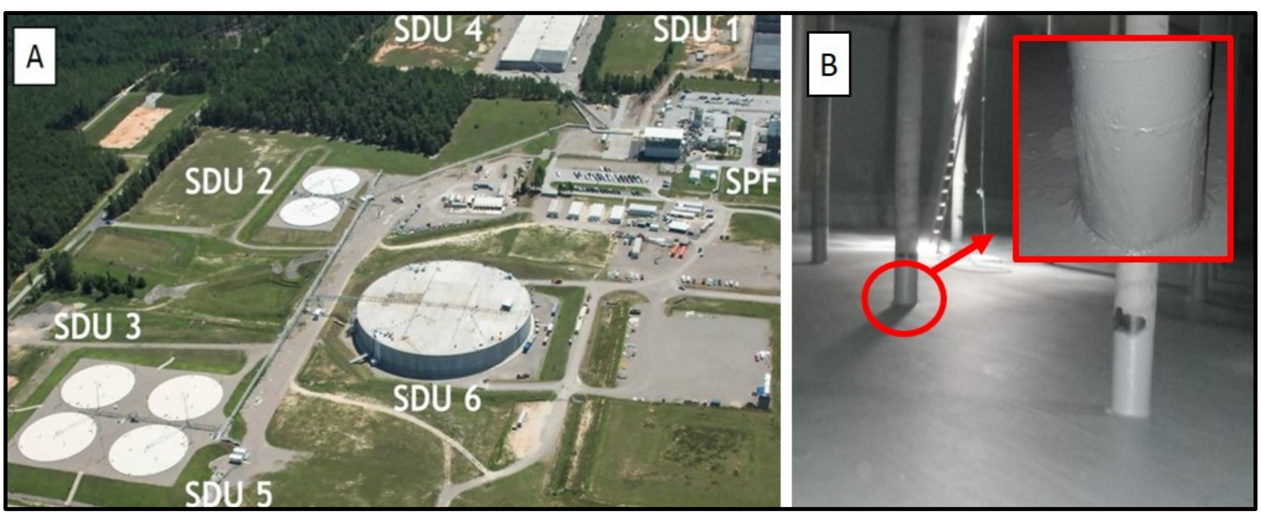

Fig. 1. (A) Aerial view of SDUs; (B) SDU interior with coated floor and roof-support columns.

EXPERIMENTAL DETAILS

The interior walls and floors of SDUs are coated with polymeric coatings prior to grout filling in order to enhance the resistance of the SDU structure to potential chemical attack and subsequent physical deterioration. The coating configuration comprised a fabric-reinforced Novolac epoxy (Hempel Versiline TL-45 S) in direct contact with the concrete SDU interior walls and floors and a subsequent overlying elastomeric epoxy coating in some areas (Hempel Versiline EC-66). Application and integrity testing of the applied coatings is a complex, labor-intensive process (e.g., roller application of polymer compounds and manual embedding of fabric). As such, an alternate spray-applied polyurea coating (Sherwin Williams Envirolastic AR425) is being evaluated with respect to chemical resistance as part of this study, and compared to the performance of the previously utilized Versiline TL-45 S and EC-66 coating systems. A description of the salt solution composition used for this study is briefly detailed in the latter text.

Coated SDU 6 Concrete

The SDU samples evaluated within this study were cast into 10 cm (diameter) by 20 cm (length) cylindrical molds from the mixer trucks in the field during SDU 6 construction (2014 – 2015 timeframe). Samples were transferred to a curing room (maintained between 21 – 25 °C and greater than 95% relative humidity) for long-term storage. The cured samples were subsequently sectioned into 10 cm lengths and coatings applied according to the respective manufacturer instructions by Augusta Specialty Coating Inc. (Augusta, GA). After coating, the samples were exposed to chemical treatment consistent with the sample requirements of ASTM G20-10, *Standard Test Method for Chemical Resistance of Pipeline Coatings* [1]. This standard requires the introduction of two engineered, through-thickness defects (or holidays); two 12-mm diameter holidays were created in the coating using a diamond tipped whole saw on a transverse axis approximately 2.5 cm from the top and bottom of the cylinder (Fig. 2). The holiday provides a consistent defect in the coatings that can be used to evaluate the resistance to coating delamination when the coating-substrate interface is directly exposed to the chemical test environment.

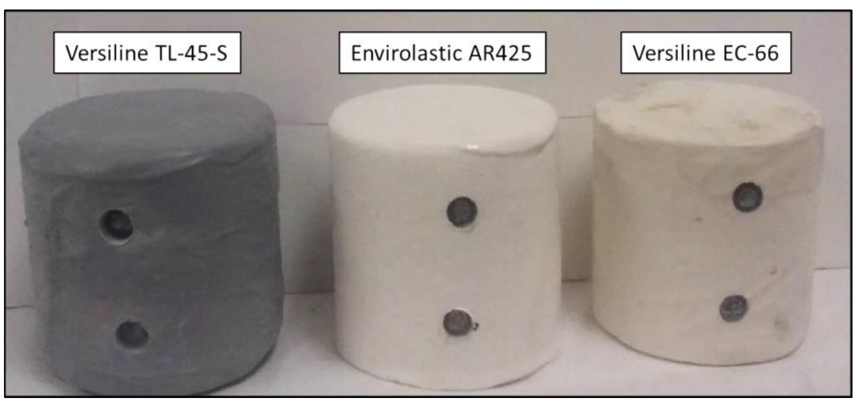

Fig. 2. Examples of coated SDU concrete samples (with pre-engineered defect - holiday) used in chemical exposure testing.

Uncoated SDU 6 Concrete

It is not known if SDU concrete without the addition of a polymeric barrier exhibits sufficient resistance to salt solution ingress and/or chemical reactivity, and thus chemical exposure of uncoated SDU concrete samples was considered in this study. The samples evaluated were cast into 10 cm (diameter) by 20 cm (length) cylindrical molds from the mixer trucks in the field during SDU 6 construction (2014 – 2015 timeframe). Samples were transferred to a curing room (maintained between 21 – 25 °C and greater than 95% relative humidity) for long-term storage. Examples of the SDU 6 concrete cylinders prior to testing are provided in Fig. 3.

Fig. 3. 10 cm dia. by 20 cm high cast SDU 6 concrete cylinders used in chemical exposure testing.

Exposure Conditions

Exposure Chemistry

All aforementioned samples (other than controls) were subjected to the following three chemical treatments:

i. A reference exposure salt solution, termed "S1" throughout this report, accounts for anticipated concentrations of chemical compounds found in salt waste. Table I details the S1 components and their concentrations.

TABLE I. Target concentrations for simulant salt solution (S1).

Chemical Species	Concentration (M)
Na^+	6.73
Al^{3+}	0.22
K^+	0.06
OH^-	2.30
NO_3^-	2.35
NO_2^-	0.90
CO_3^{2-}	0.20
SO_4^{2-}	0.18
Cl^-	0.11
PO_4^{3-}	0.05
$C_2O_4^{2-}$	0.01

ii. A solution with a dilution factor of two (50% S1) was included to account for the aforementioned system flushes; this solution is expected to have reduced reactivity (assuming reactivity occurs between the exposure solution and the concrete) in comparison to the 100% S1 solution.

Note: Uncoated SDU 6 concrete samples were completely immersed in the relevant salt solution during exposure testing (Fig. 4). Coated samples were immersed to cover one holiday while leaving the other holiday exposed to the atmosphere above the salt solution (Fig. 5); the purpose of this is to assess the interaction of evaporative species that may condense on the coating and at the coating-substrate interface within the engineered holiday.

Fig. 4. SDU 6 concrete cylinders fully immersed in salt solution during exposure testing.

Fig. 5. Coated SDU 6 concrete cylinders partially immersed in salt solution (lower holiday immersed; upper holiday open to atmosphere above salt solution).

iii. Saltstone was processed with the 100% S1 salt solution using the standard 45/45/10 mass % blast furnace slag (BFS), fly ash (FA), and cement dry powder mix and a water-to-dry powder ratio of 0.6. Immediately after mixing and prior to gelation the saltstone mixture was poured around the coated and uncoated samples as depicted in Figs. 6 and 7, respectively. The purpose of this test configuration is associated with the fact that the majority of the interior walls and floors of the SDUs will be in direct contact with cured saltstone rather than residual salt solution or bleed water held up in the SDUs. For this scenario it is the salt solution contained within the saltstone pores that may act as the corrosive medium towards the SDU concrete. However, diffusion of species from the sub-micron, tortuous pore network in saltstone is anticipated to be a slow process.

Fig. 6. Uncoated SDU 6 concrete cylinders fully immersed in fresh saltstone during exposure testing.

Fig. 7. Coated SDU 6 concrete cylinders partially immersed in fresh saltstone (lower holiday immersed; upper holiday open to atmosphere above grout).

Exposure Temperature

In addition to chemical exposure, the walls and floors in the SDUs will be subjected to above ambient temperatures due to the exothermic nature of saltstone hydration reactions. Reference 2 has previously prescribed that materials considered for coating the SDU interior be capable of resisting chemical attack at 68 °C for a period of 1,000 hours. As such, exposure tests were conducted in contact with the aforementioned salt solutions, or saltstone, at 68 °C, for 1,000 hours. Exposure temperatures were maintained to ± 2 °C using the circulating heater baths depicted in Fig. 8.

In addition to the elevated temperature exposure, samples were subsequently maintained at room temperature in the same exposure solutions; the time of ambient temperature exposure was somewhat arbitrary but attempted to provide a total exposure time (elevated and ambient temperatures combined) of approximately 90 days.

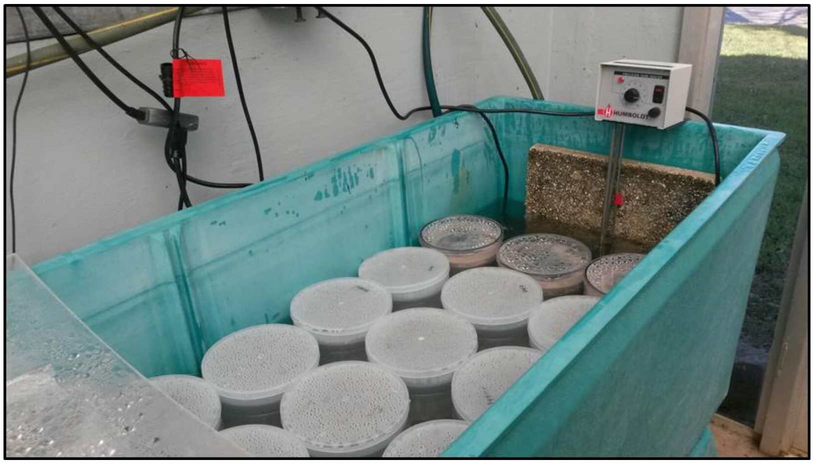

Fig. 8. Heating bath setup used for maintaining samples at 68 °C (± 2 °C).

Evaluation Criteria for Exposed Samples

Coated SDU 6 Concrete

The primary performance requirement of a polymeric coating is to prevent potentially corrosive solutions from interacting with the SDU concrete. Acceptable performance of a coating would be demonstrated by minimal through-thickness interaction between the solution and coating. Additionally, in the presence of potential flaws in the coating that allow solution access to the coating-concrete interface, the coating should resist delamination from the concrete substrate.

Uncoated SDU 6 Concrete

Macro-evaluation of the surfaces of uncoated SDU concrete and shotcrete samples will provide a strong indication of chemical reactivity and physical degradation. Reactive phenomenon typically manifest as surface cracking and spalling due to penetration of the corrosive solution below the concrete surface, and the subsequent formation of expansive phases. However, it should be noted that chemical diffusion of species into the concrete and subsequent reaction does not automatically equate to physical deterioration; adverse physical impacts will be dependent on the reaction products formed, their degree of expansion, and whether the concrete microstructure can accommodate the expansive phases. In addition to visual evaluation, exposed samples were also subjected to compressive strength testing to determine if the exposure treatment resulted in any loss of strength. SDU structural concrete has a minimum compressive strength requirement of 42 MPa.

RESULTS

Coated SDU 6 Concrete

Fig. 9 shows the coated SDU cylinders after the initial 1,000 hours of chemical exposure at 68 °C. All of the coatings (even the control samples exposed to deionized water (DIW) water at 68 °C) displayed surface discoloration in comparison to the pre-exposed samples. There were however no signs of coating cracking or delamination. Fig. 10 shows the four coating treatments at the end of the 90-day test period, which included elevated and ambient temperature exposures with the indicated chemistries. Once again from a visual perspective all coatings exhibited discoloration but no cracks or delaminations were observed.

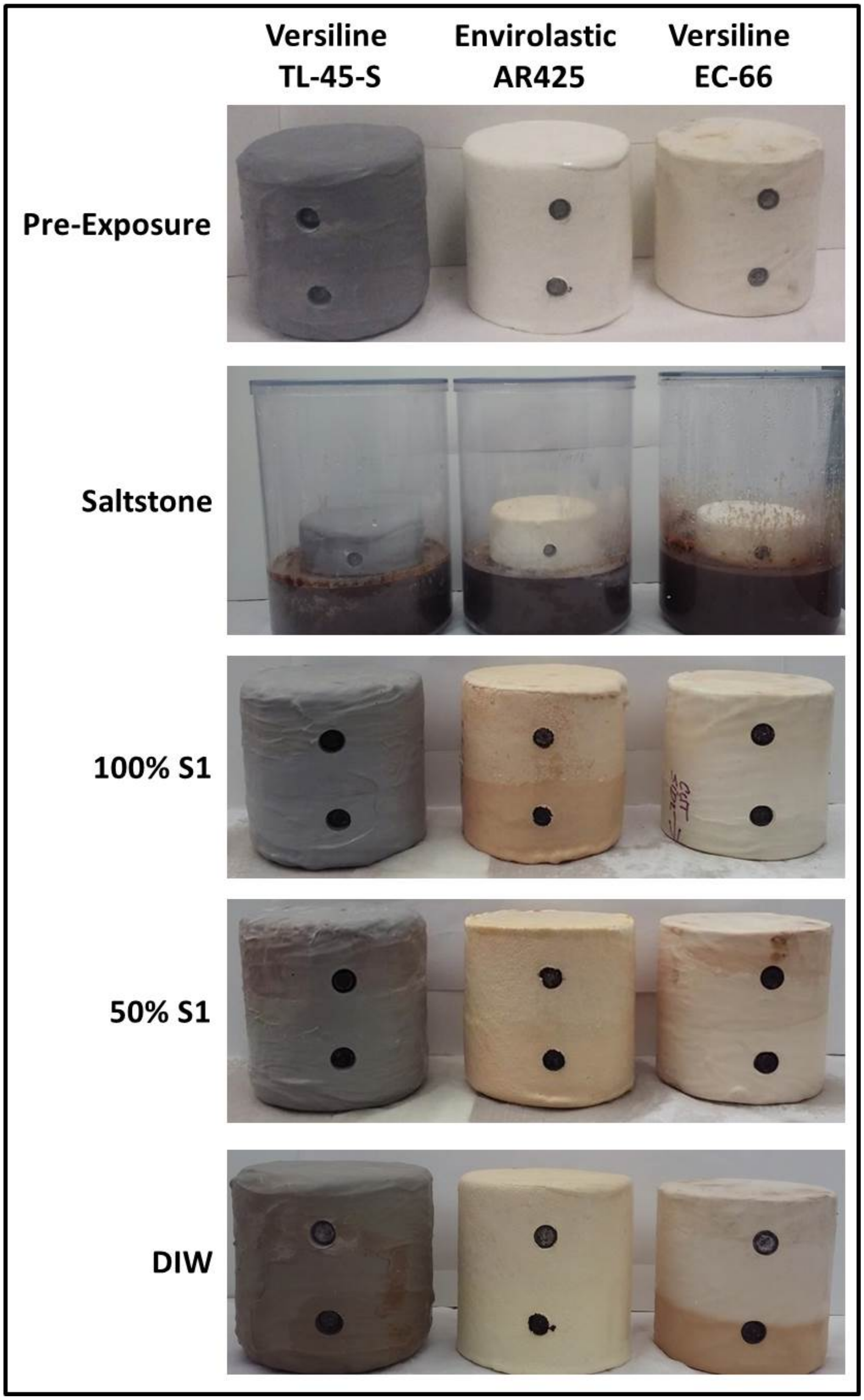

Fig. 9. Coated SDU 6 concrete cylinders after initial 1,000-hour exposure at 68 °C.

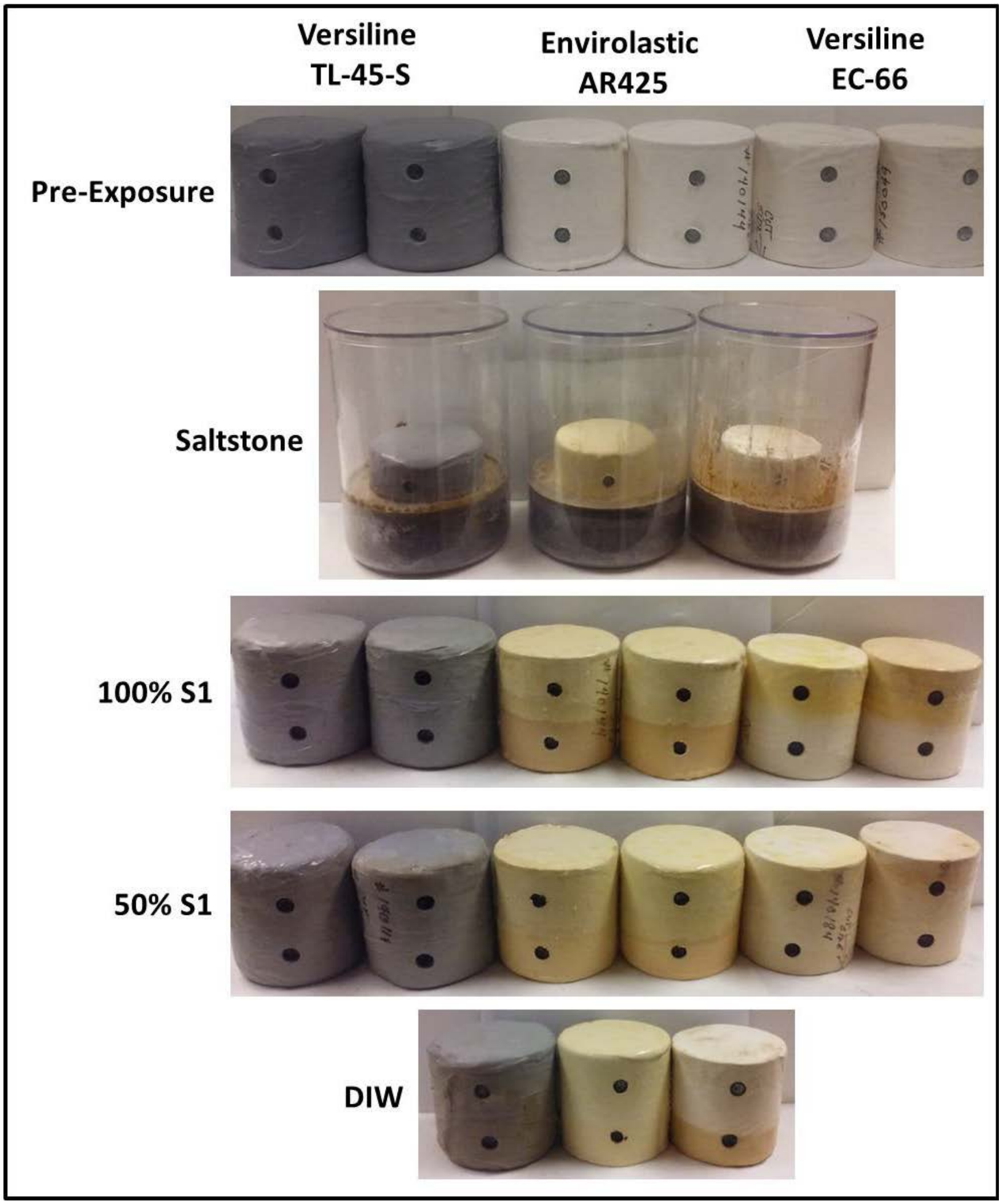

Fig. 10. Coated SDU 6 concrete cylinders after 90-day exposures at elevated (68 °C) and ambient temperatures.

Select coated samples representing the 100% and 50% S1 solution exposures were vertically sectioned through the two holidays for additional inspection (Fig. 11). Cross-sectioning indicated that coating discoloration was a surface phenomenon and no signs of sub-surface solution penetration or reaction were observed. In addition, no delamination at the coating-concrete interfaces was observed for any of the coating treatments. Fig. 12 provides a closer view of the cross-sectioned samples.

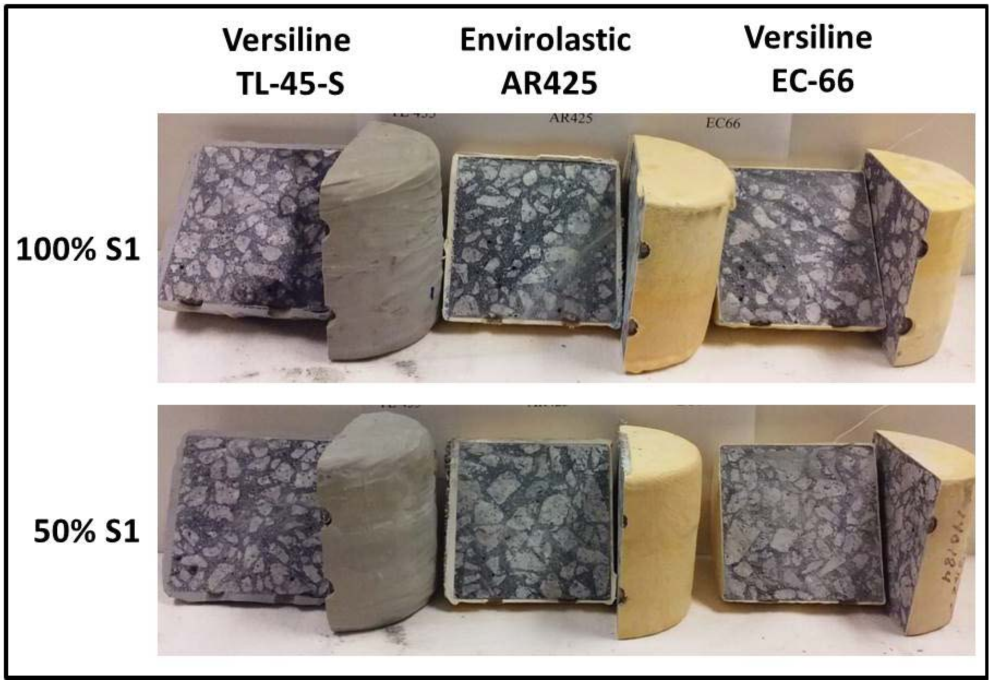

Fig. 11. Cross-sectioned coated SDU 6 concrete cylinders after 90-day exposure testing.

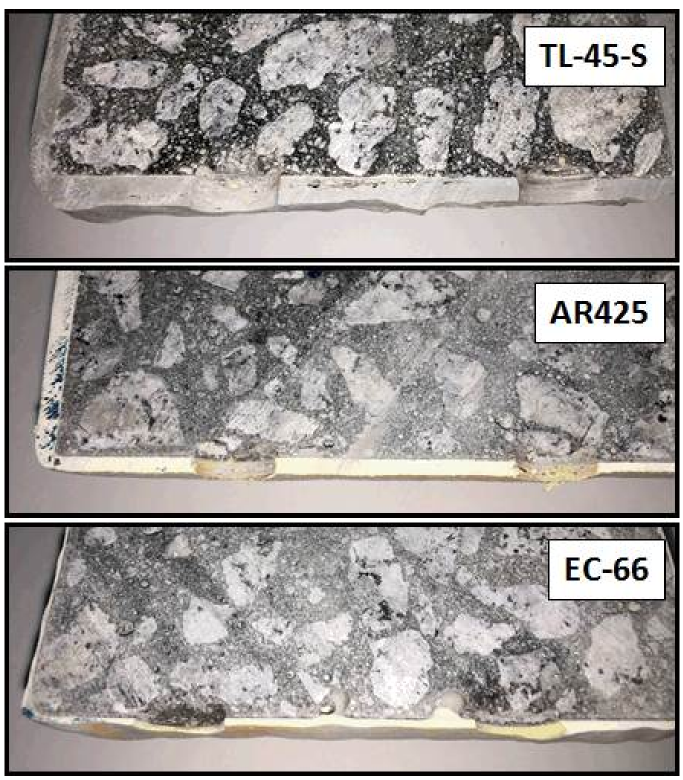

Fig. 12. Close-up view of coating-concrete interface and coating holiday for sectioned samples that had been exposed to the 100% S1 solution.

Uncoated SDU 6 Co0000ncrete

Fig. 13 represents the uncoated SDU 6 concrete after exposure to the indicated treatments at 68 °C for 1,000 hours. Similar to the coated SDU 6 concrete the primary change observed for the samples was discoloration after initial exposure to the 100% and 50% S1 salt solution; it is possible that the reddening of the surface is associated with oxidation of iron species in the concrete. For some samples salt precipiates were also observed on the surfaces, which is expected based on the highly concentrated salt solution. No physical degradation, such as cracking or spalling, was observed for the samples.

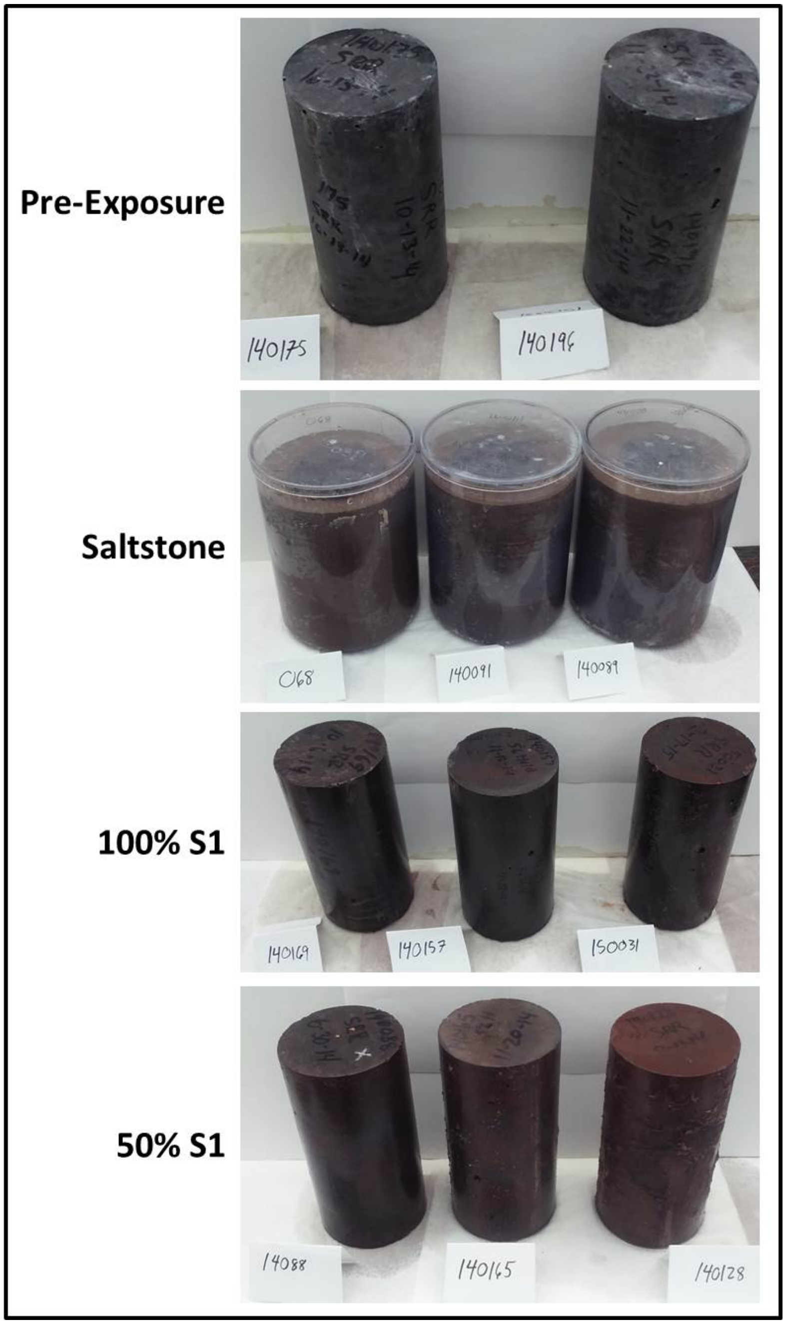

Fig. 13. Uncoated SDU 6 concrete cylinders after exposure to the indicated treatments for 1,000 hours at 68 °C.

Fig. 14 represents the uncoated SDU 6 cylinders after full duration (90-day) exposure to the 100% and 50% S1 solutions (the samples embedded in saltstone were no different in comparison to those observed after elevated temperature exposure). Some discoloration (again potentially associated with iron oxidation) and salt buildup was noted on both the 50% and 100% S1 treatments. It is important to note that one cylinder exposed to each of the 50% or 100% S1 solutions indicated a surficial material the origin of which was not immediately obvious; however, it appears that this may be the result of residue from the saturated wrapping paper in which these two cylinders were stored in prior to testing.

Fig. 14. Uncoated SDU 6 concrete cylinders after elevated (68 °C) and ambient temperature exposure to the indicated treatments for 90 days.

Three cylinders from the 100% S1 treatment, three cylinders from the 50% S1 treatment, and the two control cylinders were subject to compressive strength testing according to ASTM C39-16b *Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens* [3]. The results from compression tests are summarized in Table II. No significant reduction in compressive strength was observed for the SDU 6 cylinders after exposure to the 100% or 50% S1 treatment solutions compared to the control cylinders, and all cylinders maintained a compressive strength greater than 42 MPa.

TABLE II. Compression test results for SDU 6 cylinders.

Exposure Condition	SDU 6 Cylinder ID	Cylinder Age (Days)	Compressive Strength (MPa)	
			Absolute	Mean (St. Dev.)
No Exposure Control	140175	617	64.8	65.9 (1.6)
	140196	577	67.0	
50% S1	140070	750	62.7	65.0 (5.9)
	140080	740	71.8	
	140088	722	60.6	
100% S1	140199	573	73.3	68.2 (5.5)
	150004	523	62.4	
	150031	490	68.9	

One remaining cylinder from the 50% S1 treatment, one remaining cylinder from the 100% S1 treatment, and one of the three samples embedded in saltstone were sectioned using a masonary saw to investigate the presence of visual indications of chemical attack/physical deterioration. Fig. 15 shows the cross-sectional image of the sectioned samples representing the three main treatments, with Fig. 16 providing a close-up view of the SDU concrete cylinder surface. No obvious changes in structure were observed for the three samples.

Fig. 15. Sectioned SDU 6 concrete after 90-day exposure in the indicated treatments.

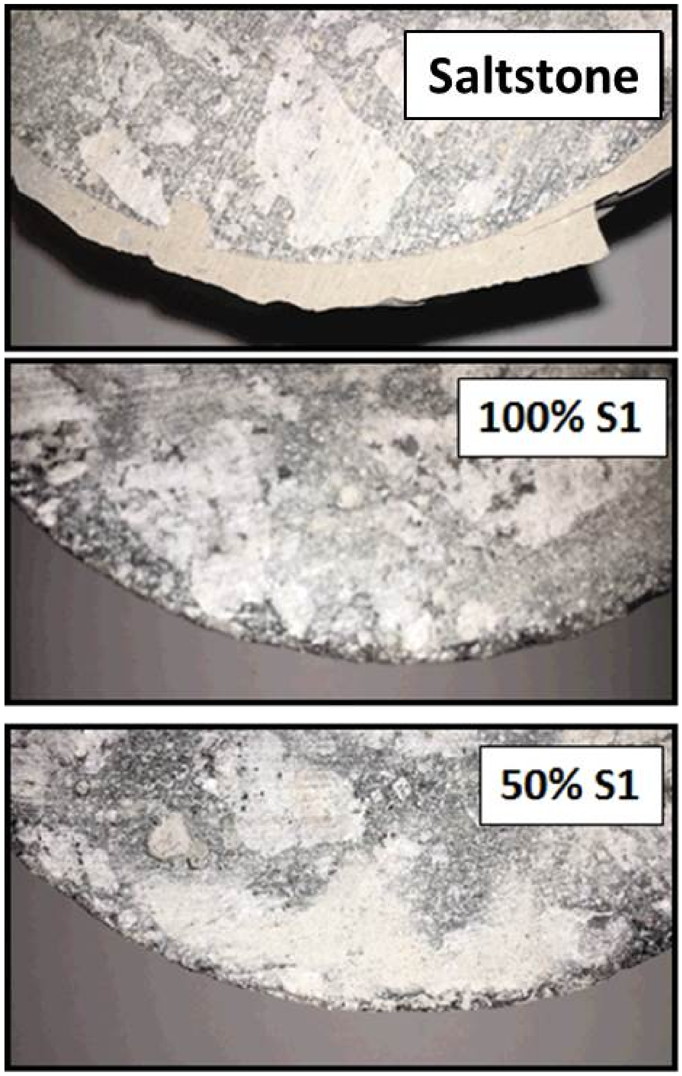

Fig. 16. Close-up view of sectioned SDU 6 concrete after 90-day exposure in the indicated treatments.

CONCLUSION

The intent of this chemical exposure study was two-fold consisting of evaluating the potential interactions between a conservatively predicted SRS salt solution composition and:

1. Historically-used and proposed protective polymers coated onto SDU 6 concrete, and
2. Unprotected SDU 6 concrete (i.e., no polymer barrier coating).

Three coatings were evaluated, namely Hempel Versiline TL-45 S Novolac and EC-66 elastomeric epoxies (utilized on previous SDUs) and an alternate polyurea coating (Sherwin Williams Envirolastic AR425). All coatings indicated surface discoloration after exposure to the salt solutions at 68 °C but this was a surface-limited phenomenon with no indication of sub-surface interaction between the coatings and the caustic salt solutions. In addition, no delamination was observed around pre-engineered through-thickness defects. This data supports the applicability of all three coating types in future SDUs.

For the uncoated SDU 6 concrete slight discoloration of the sample surface was observed following exposure to the salt solutions at 68 °C but sectioned samples again indicated that the phenomenon was restricted to the surface. No signs of physical deterioration at or below the concrete surface were apparent. Compressive strength testing also indicated no apparent impact when comparing exposed and non-exposed samples and all samples maintained a compressive strength above the 42 MPa specified for SDU 6 structural concrete. This data suggests that uncoated SDU 6 concrete exhibits resistance to chemical and subsequent physical degradation when exposed to a chemical/thermal environment that can be considered conservative to anticipated service conditions. As such, for future SDUs it is possible that the use of polymer coatings on the SDU interior can be negated.

REFERENCES

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