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SRNL-L4420-2011-00008
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Subject: Response to NRC VP-2 Comment: Additional basis is required for neglecting disposal unit degradation mechanisms other than sulfate attack.

Summary:

The Materials Science and Technology directorate was requested to evaluate the degradation mechanisms for Saltstone Vaults 1 and 4 (pad and roof). The primary degradation mechanism, sulfate attack, was previously evaluated; however, reinforced concrete structures are susceptible to other degradation mechanisms depending on environment. Other degradation mechanisms observed in concrete structures include (listed in approximate order of importance) carbonation or chloride ingress induced rebar corrosion, alkali-silica reactions, calcium leaching and freeze thaw. An aging study on existing structures at SRS was conducted and other studies have provided data for use in the evaluation of other potential degradation mechanisms for the Saltstone vaults during the timeframe of the performance assessment (i.e., 10,000 years). The aging mechanisms assessed in this work were determined to be similar in importance to sulfate attack for the postulated conditions.

Rebar corrosion:

Corrosion of steel rebar is accompanied by a 3-6X volumetric expansion due to the corrosion products, which leads to cracking and degradation of the concrete cover. Prestressed or high strength steel reinforcement can undergo stress corrosion cracking (SCC) which can lead to premature structure failure. This rarely occurs in conventional structures because the rebar is moderate to low yield strength or not highly stressed and, as such, is not considered susceptible to stress corrosion cracking. General corrosion (or pitting corrosion) is more commonly seen and can result from two mechanisms: carbonation of calcium rich phases and halide (e.g., chloride) induced corrosion. Furthermore the corrosion itself can be divided into two phases: initiation and corrosion phases.

Carbonation induced initiation:

Carbonation of concrete reduces the local pH of the pore water and allows passive film breakdown of the steel reinforcement (i.e., rebar). This phenomenon occurs as a result of the conversion of portlandite ($Ca[OH]_2$: one phase present in cement) to calcium carbonate ($CaCO_3$). Many factors can affect the rate of carbonation, including temperature, relative humidity, and composition of the cement paste. Generally, the depth of carbonation is roughly proportional to the square root of time for concrete kept continuously dry at ambient relative humidity (RH).

$$X_C = A\sqrt{t}$$

Where X_c is the distance of the carbonation front, t is the time and A is a materials constant.[1] The constant, A, can be empirically determined by tracking the progress of the carbonation front.

Papadakis *et al* developed an expression for the rate A for carbonation from theoretical basis.[1]

$$A = \sqrt{\frac{2[CO_2]^0 D_{eCO_2}}{[Ca(OH)_2(s)]^0 + 3[CSH]^0}}$$

D_{eCO2} is the effective diffusivity of CO_2 in the concrete, while $[CO_2]^0$, $[Ca(OH)_2(s)]^0$ and $[CSH]^0$ are the molar concentrations in the concrete. The effective diffusivity of CO_2 is heavily dependent on pore size which, in turn, depends on the water to cement ratio (WCR) used in the concrete mix design. Effective diffusivity, pore fraction and size all decrease with WCR. The WCR for Vaults 1 & 4 was reported to be 0.36 for the floor and 0.56 for the walls and ceiling[2,3] which spans the range of values for reported literature data in Figure 1.

D_{eCO2} is also dependent on relative humidity. As RH increases, the pores become saturated with moisture and the D_{eCO2} is also lowered. However, when concrete is kept dry at intermediate RH, the pores can become unsaturated, which allows CO_2 to diffuse more rapidly into the concrete. In extreme cases of RH below ~40%, carbonation rates are hindered by the lack of any physical water adsorbed to the surface of pores, which assists in the reaction with $Ca[OH]_2$. Hence, the carbonation rate is observed to be maximized in conditions typical of indoor service.

Experimental results of the carbonation of interior and exterior concrete are represented in Figure 1. The carbonation front can be seen in this figure with the aid of a 1% phenolphthalein solution applied to the concrete sample. When this solution is applied to normal concrete it will turn bright pink. If the concrete has undergone carbonation, no color change is observed. The inset of this Figure shows the carbonation front of an interior P-reactor sample. Figure 2 compares the carbonation depth of above grade P-reactor concrete after ~60 years in conditions inside and outside of the same wall. As is evident, the carbonation rate for the interior sample far exceeds that of the exterior sample by an order of magnitude. A structure exposed to the elements (like the current configuration of Vaults 1 and 4) would be similar to the conditions of Figure 2b. A buried structure would be expected to have a carbonation rate much lower than this.[4] This is because the pores in the concrete remain saturated and the carbonation rate is controlled by diffusion in the liquid phase of the pore solution rather than vapor phase. Since Vaults 1 and 4 are expected to be buried, the time required for the carbonation front to reach the rebar would be significantly longer than that of exposed concrete. A time interval for the 3 inch cover to be carbonated in the vaults can be extrapolated from the empirical rate measurement after 60 years. The estimate is in excess of 10,000 years. By comparison, the performance assessment predicted a similar length of time required to degrade the cover by sulfate attack (i.e., 4, 8 or 25 cm in 10,000 years depending on sulfate concentation[2]).

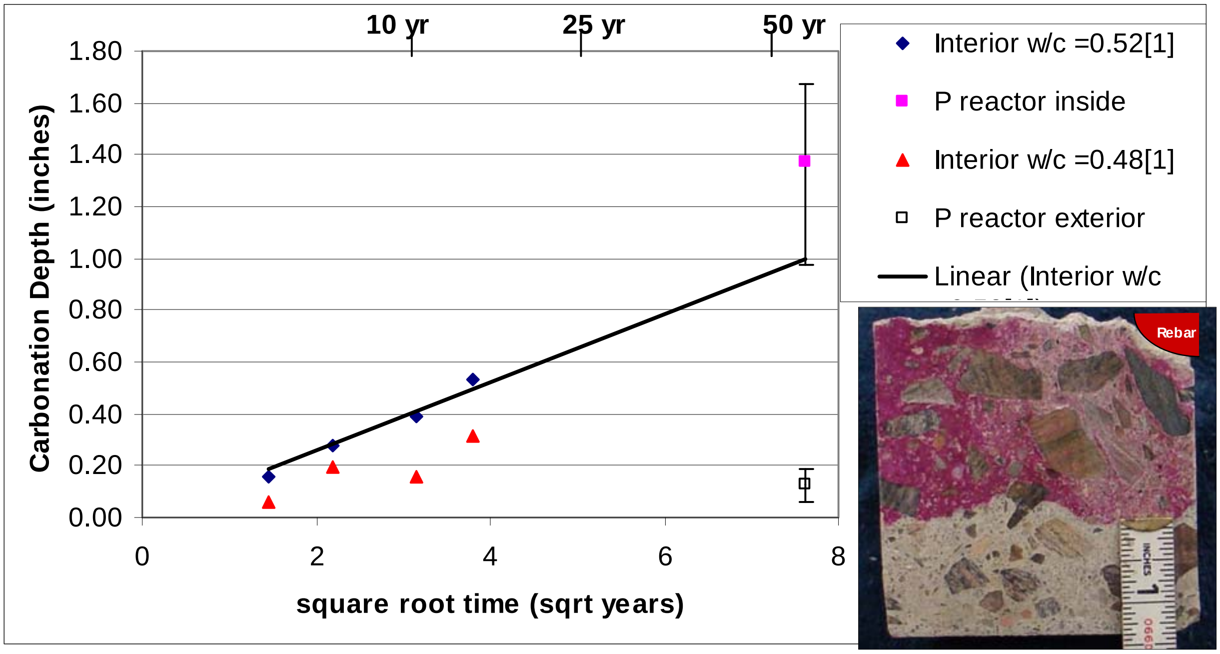

Figure 1: Plot of average carbonation measurements for P-reactor interior and exterior specimens relative to carbonation rates of interior concrete from the literature[5] with photographic insert showing the carbonation layer for an interior P-reactor sample.

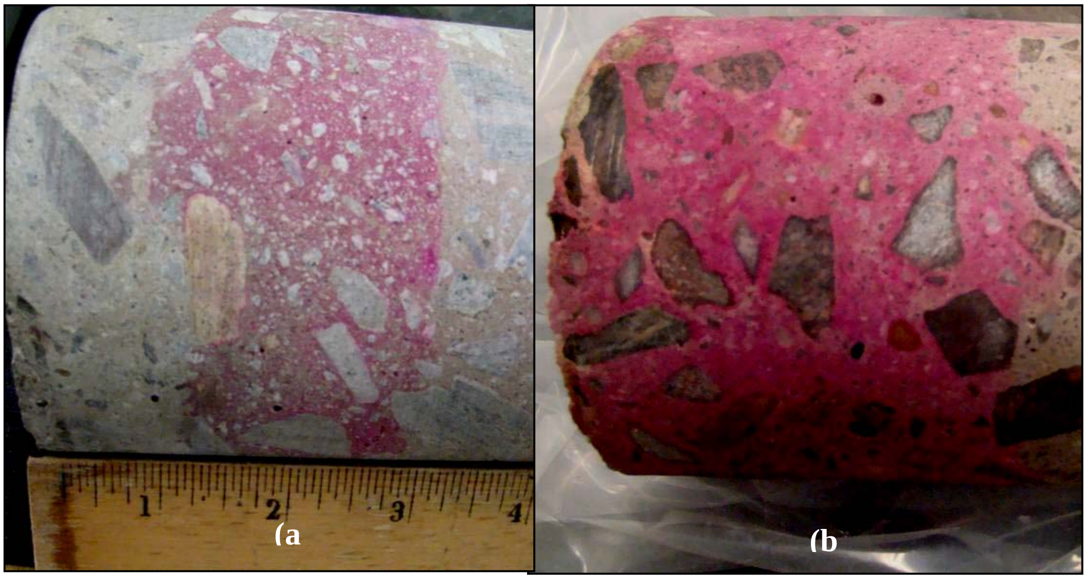

Figure 2: Field Test of (a) interior and (b) exterior core sections from an above grade wall in disassembly basin of P-reactor.

Chloride induced Initiation:

Chloride ingress can cause localized de-stabilization of the passive film of iron oxide that would be present on reinforcement bars embedded in the concrete, and lead to pitting corrosion. If carbonation, would also reach the depth of the reinforcement bars, the oxide film on steel would tend to dissolve, and gross steel corrosion would be expected leading to eventual spallation. That is, chloride ingress alone would cause localized (i.e., pitting) attack, but with carbonation, gross steel corrosion would occur.

Chloride attack has been modeled as a 2-step mechanism. The first step is the initiation time to the onset of corrosion due to chloride diffusion to the rebar. This initiation time can be given by an empirical equation[4].

$$t_c = \frac{129 X_C^{1.22}}{(WCR)\left[Cl^-\right]^{0.42}}$$

t_c = time to onset (yr)
X_c = thickness of concrete cover (in.)
WCR = Water-to-cement ratio (mass)
Cl^- = Cl^- ion concentration at surface of concrete (ppm)

With an assumed concrete cover of 3 inches, a WCR of 0.36, and a chloride ion concentration of 3.3 ppm (an estimate of ground water concentration), the initiation time of rebar corrosion is ~790 years (530 years for WCR = 0.56). This does not consider various additives utilized to reduce permeability in the concrete to chlorides.

Rebar Corrosion:

Once corrosion of the rebar has been initiated, the corrosion rate of rebar is controlled by oxygen diffusion. The reaction kinetics are described for iron corrosion and loss of rebar net section in terms of oxygen diffusion. An oxygen source and water are necessary for the active degradation of the reinforcement bar by general corrosion that can lead to loss of tensile strength and concrete spallation. Such an oxygen/water supply can occur through microcracks in the concrete which can result from mechanical stresses and/or the combined effects of CO_2, C^{l-}, and O_2 species. Figure 3 shows examples of rebar corrosion above grade in various stages of maturity in a structure ~60 years old. Figure 3a) shows the cover beginning to lift off the rebar, most likely as a result of halide induced rebar corrosion. Figures 3 b) and c) are incidences involving more common rain/ground water in leakage at construction/expansion joints. One structural analysis[6] estimated the length of time for rebar failure from the onset of corrosion to be between 150 and 300 years. However, these examples do not adequately apply to the environment associated with Vaults 1 and 4 because the structures associated with the examples are exposed to air and/or near surface water (at least on one surface). Vaults 1 and 4 are currently exposed but will be buried below grade during the timeframe of active corrosion. Once the structure is filled with saltstone and buried, the rebar no longer supports the load for which it was designed but is supported by the backfilled soil/saltstone on either side of it. Hence, rebar corrosion and its eventual failure will not result in structural collapse but in a net section loss of the concrete equal to the depth of cover.

The corrosion rate in the case of a buried structure is limited by oxygen diffusion and, as such, will occur at a much lower rate than that of exposed concrete. A simplified model for rebar corrosion can be utilized to estimate the amount of rebar section that remains after a given exposure. The following relation developed by Walton *et al.*[4] determines the remaining rebar cross-sectional area for a given oxygen diffusion controlled corrosion rate.

$$\%remaining = 100\left(1 - \frac{4\left(9.4\frac{cm^3}{mole}\right)sD_iC_{gw}(t-t_c)}{\pi d^2 x_c}\right)$$

where: s = spacing between reinforcing bars
D_i = oxygen diffusion coefficient in concrete (cm^2/sec)
C_{gw} = oxygen concentration in groundwater
t = time (sec)

t_c = time to onset of oxic corrosion, (sec)
d = diameter of rebar (cm)
x_c = thickness of concrete cover over rebar (cm)

Assuming an intermediate value for D_i (5×10^{-8} cm^2/s), 1 in. diameter (2.54 cm) rebar, spaced at 1 foot spacing under a 3 in. (7.62 cm) concrete cover and a t_c of ~800 years, the length of time required to reduce even 5 % of the rebar section is over 6000 years and 10% reduction is over 10,000 years.

Figure 3: Examples of degradation associated rebar corrosion from the field at SRS beneath a halide filled window (a), underneath a leaking expansion joint (b) and at the base of a cracked construction joint in a wall below grade (c).

Alkali-Silica Reactions:

Alkali-Silica reactions (ASR) occur between reactive silica present in aggregates and alkali constituents (e.g., Na^+, K^+) in the cement phase(s). In similar fashion to sulfate attack, the alkali constituents form a gel at the aggregate/cement interface, which causes expansion and cracking to occur over time. Water, reactive silica and alkali constituents must be present in the concrete for ASR to occur. Reactive silica (e.g., opal or chalcedony) can exist in aggregates of volcanic origin and are less common in igneous rock. The crystallographic structure may be identical, but the crystal size is much smaller in the case of reactive silica. Sand (a common fine aggregate) is also quartz, but is usually not reactive because it is what is left behind from mechanically and chemically degraded rock. In order to verify the occurrence of ASR, petrography must be performed on samples to identify the gel reaction zones.

Although a detailed analysis has not been performed on concrete from Vaults 1 and 4, the likelihood of ASR resulting in degradation of the structure is believed to be low for the following reasons. First, the large quantities of igneous rock aggregates available in the region suggest that the aggregate is probably igneous in nature (i.e., granite). In addition, Vaults 1 and 4 have been exposed to elements since their construction. The degradation of these vaults by ASR should be evident by now (22 years later) considering the environmental exposure. Finally, ASR has not been documented in other concrete structures on-site. The lack of evidence for this mechanism suggests that it is not a prevalent cause of degradation in this structure.

Calcium Leaching:

Cement components can be leached from concrete only when water passes over the surface or through cracks. Specifically, calcium compounds in the concrete can be dissolved in unsaturated water and washed away. Since the most readily soluble calcium compound in concrete is calcium hydroxide (lime), water can leach lime from concrete. When calcium hydroxide is leached away, other cementitious constituents become exposed to chemical decomposition, eventually leaving behind silica and alumina gels with little or no strength. The extent of the leaching during any given exposure to water depends on the salt content and temperature of the water. Snow melt is considered an aggressive form of water to concrete because it is contains very low levels of calcium and has a high solubility for the ion due to the low temperature. In the present climatic environment this mechanism is not expected to be a significant occurrence because of the temperature ranges of exposure. In addition, Walton *et al.*[4] determined leach penetration rates for ground water with low calcium contents to be less than 1/10 of a cm at 1000 years. Based on these observations leaching of calcium from ground water is not anticipated to be significant in saltstone vaults.

Freeze-Thaw:

Repeated cycles of freezing and thawing may change the mechanical properties and physical form of concrete. The durability of concrete to a freeze-thaw damage mechanism depends primarily on the porosity characteristics of aggregates, the presence of moisture to saturate the fine pores in aggregates, and the permeability of the hardened cement mortar matrix to the passage of water. Mathematical models exist, however they should not be needed since the freeze/thaw degradation is currently not a concern for buried structures in the region. Furthermore, global climatic changes are not expected to impact the area to the extent that freeze/thaw degradation becomes a viable mechanism for breakdown of buried concrete structures.

Conclusion:

Additional basis has been given for neglecting disposal unit degradation mechanisms other than sulfate attack. The degradation mechanisms considered are not expected to exceed the effect sulfate attack from saltstone constituents within the vaults. Therefore, although they may contribute to the degradation of Vaults 1 and 4, they will not result in a large scale difference in degradation rate.from the current degradation model of the structure.

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[1] V. G. Papadakis, C.G. Vayenas and M. N. Fardis**, “***Experimental investigation and mathematical modeling of the concrete carbonation problem,*” Chemical Engineering Science Volume 46, Issues 5-6, 1991, Pages 1333-1338

[2] Performance Assessment for the Saltstone Disposal Facility at the Savannah River Site, Report # SRR-CWDA-2009-00017 Rev. 0, October 2009

[3] C. A. Langton, “Evaluation of Sulfate Attack on Saltstone Vault Concrete and Saltstone” Report# SRNS-STI-2008-00050,

[4] Walton, J. C. et al. “Models for Estimation of Service Life of Concrete Barriers in Low-Level Radioactive Waste Disposal,” NUREG/CR-5542, July, 1990

[5] Nagataki et al., 1986S. Nagataki, H. Ohga and E.K. Kim, Effects of curing conditions on the carbonation of concrete with fly ash and the corrosion of reinforcement in long-terms tests, *Proc. 2nd Int. Conf. on the Use of Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, ACI, SP 91* (1986), pp. 521–539 Madrid.

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