Projected Impact of Sulfate Attack on the Long-Term Performance of a Concrete Repository

G.P. Flach
Savannah River National Laboratory
Savannah River Site, 773-42A
Aiken, SC 29808

ABSTRACT

Saltstone is a cementitious waste form made by mixing salt solution originating from liquid waste storage tanks at the DOE Savannah River Site with a dry mix containing blast furnace slag, fly ash, and cement or lime. The wet mix is poured into a concrete repository for on-site disposal. Solidified Saltstone is a dense, alkaline, reducing, micro-porous, monolithic, cementitious matrix, containing a solution of salts within its pore structure. Sodium sulfate concentrations in the pore fluid are around 0.15 mol/L, and external sulfate attack on concrete barriers is expected to occur over time. To predict the long-term performance of concrete repositories, the STADIUM® code was used to simulate the reactive transport processes leading to formation of ettringite, an expansive mineral phase often associated with spalling or cracking. STADIUM® is a multi-ionic transport model based on a split operator approach that separates ionic movement and chemical reactions. Ionic transport is described by the extended Nernst-Planck equation for unsaturated media, and accounts for electrical coupling between ionic species, chemical activity, transport due to water content gradient, and temperature effects. STADIUM® does not predict whether physical damage will occur, or the impact on transport properties should fracturing occur. Thus the presence of ettringite was assumed to coincide with physical damage for the purpose of estimating effective transport properties. Effective properties for concrete barriers were estimated assuming complete hydraulic failure behind the ettringite front and unaltered properties ahead of the front. The ettringite front advances at a rate dependent on the diffusion coefficient assumed for the failed zone. A sensitivity study indicates a service life ranging from thousands to tens of thousands of years, depending on the barrier thickness and sulfate exposure conditions among other factors.

INTRODUCTION

The Savannah River Site (SRS) is an 800 km^2 (310 mi^2) U.S. Department of Energy reservation in southwestern South Carolina. Five nuclear reactors were constructed in the 1950's to produce nuclear materials for national defense, primarily tritium and plutonium-239. Supporting facilities included two chemical separations plants, a heavy water extraction plant, a nuclear fuel and target fabrication facility, a tritium extraction facility, and waste management facilities. Today, the SRS is primarily engaged in the processing of legacy nuclear wastes, environmental clean-up, non-proliferation activities, and tritium recycling.

Soluble salts compose most of the legacy radioactive waste in storage tanks at the SRS. Pretreatment of the waste will separate soluble salts from insoluble sludge, and the salt solution will be further treated to remove cesium and strontium. Removal of cesium and strontium leaves a low-activity waste containing less than 0.01 percent of the original radioactivity. The treated salt solution is mixed with cement, fly ash and blast furnace slag to form a solidified waste grout termed Saltstone. The grout is placed into large concrete repositories located near the center of the SRS for on-site disposal.

Sodium sulfate concentrations in the pore fluid of Saltstone are around 0.15 mol/L, and external sulfate attack on concrete barriers encapsulating the grout is expected to occur over time. External sulfate attack ("sulfate attack" hereafter) is characterized by ingress of sulfate ions from an external source, mineral reactions that produce expansive phases such as ettringite and gypsum, and subsequent physical damage such as cracking or spalling [1]. Physical degradation of concrete diminishes the effectiveness of the repository as a waste release barrier. Thus, a model prediction of sulfate attack and associated long-term impacts to concrete barrier properties was desired as part of an overall Performance Assessment of the Saltstone Disposal Facility [2].

Successive sections describe properties of the concrete barrier, the modeling approach used, and the resulting durability predictions.

CONCRETE BARRIER

Figure 1 schematically illustrates the design of the cylindrical Saltstone disposal cells currently under construction. Nominal thicknesses for the floor, wall and roof barriers are 30 cm (12 in), 20 cm (8 in) and 20 cm (8 in) respectively. The concrete formulation is shown in Table I. The mix is designed to be resistant to sulfate attack through the use of Type V cement, blast furnace slag, fly ash and silica fume, which minimize the tri-calcium aluminate content of the mix and produce a low permeation concrete. Measurements indicate a hydraulic conductivity lower than 1.E-10 cm/s and an effective diffusion coefficient around 5.E-8 cm^2/s [2]. The permeability is sufficiently low that advective transport is negligible compared to diffusion. After Saltstone disposal cells are filled with waste grout, a low infiltration cover system will be placed over the facility.

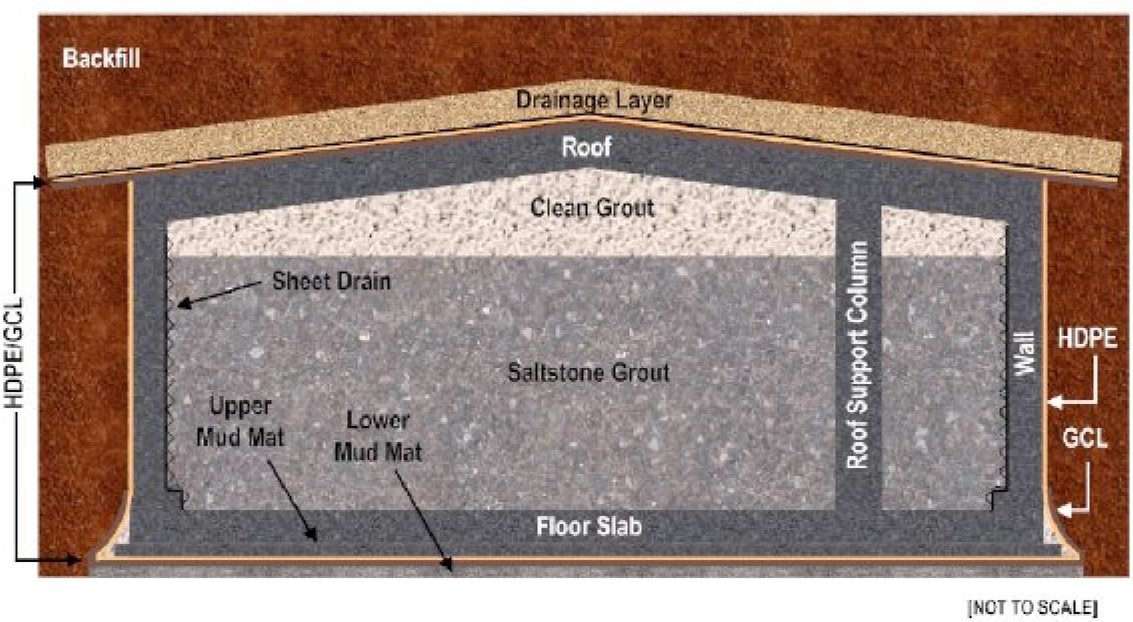

Fig. 1. Schematic diagram of the cylindrical Saltstone repository design.

Table I. Concrete Mix for Cylindrical Saltstone Disposal Cells.

Ingredient	Material Quantity (kg/m^3)	Material Quantity (lbs/yd^3)
Type V cement (Lehigh T-V #2; ASTM C 150)	126	213
Grade 100 Blast furnace slag (Holcim Grade 100 Slagl ASTM C 989	168	284
Silica Fume (W. R. Grace Silica Fume; ASTM C 1240)	28.1	47.3
Type F Fly ash (SEFA Group, Class "F" Fly Ash; ASTM C 618	98.3	165.7
Sand (Natural Washed Sand; ASTM C 33)	540	911
Aggregate (#67 Granite; ASTM C 33)	1098	1850
Water (maximum)	160 L/m^3	32.3 gal/yd^3
Maximum water to cementitious material ratio	0.38	0.38
Grace WRDA 35	325 mL/100 kg c+p*	5 fl oz/cwt c+p
Grace Darex II	26 to 33 mL/100 kg c+p	0.4 to 0.5 fl oz/cwt c+p
Grace Adva 380	196 to 261 mL/100 kg c+p	3 to 4 fl oz/cwt c+p

* c+p = cementitious materials plus pozzolans

MODELING APPROACH

Modeling of sulfate attack is a challenging and ongoing topic of research [1], involving coupled porous medium transport, chemical reaction, and damage mechanics phenomena. A number of empirical, mechanistic and numerical models have been presented in the literature [3-6]. Coupled solute transport and chemical reaction modeling for cementitious materials is relatively well developed, with researchers demonstrating good agreement with laboratory data [5]. However, coupling damage mechanics to reactive transport has proven more difficult, and can be considered an unresolved research topic at present [1].

To estimate the durability of Saltstone barriers to sulfate attack, a three step approach was adopted: 1) detailed, "full-physics", reactive transport simulations for specific conditions, 2) extension of these results to more general conditions through analytic approximations, and 3) simple assumptions for damage. Each step is discussed more fully below.

Reactive Transport

The propietary STADIUM® code [7] was selected for simulating the reactive transport processes in concrete exposed to sulfate. STADIUM® is a multi-ionic transport model based on a split operator approach that separates ionic movement and chemical reactions. Ionic transport is described by the extended Nernst-Planck equation for unsaturated media, and accounts for electrical coupling between ionic species, chemical activity, transport due to water content gradient, and temperature effects.

Simulations were performed for a saturated concrete thickness of 20 cm and exposure to sulfate at three fixed concentration levels at the near face: 0.2, 0.02, and 0.002 mol/L SO_4^{2-}. The sulfate concentration at the far face was set to zero. Figure 2 shows STADIUM® predictions of the depth of ettringite presence for the high, medium and low sulfate concentrations. Ettringite is one expansive mineral phase associated with sulfate attack. The penetration depth for the high sulfate scenario was limited by the thickness of the concrete (20 cm).

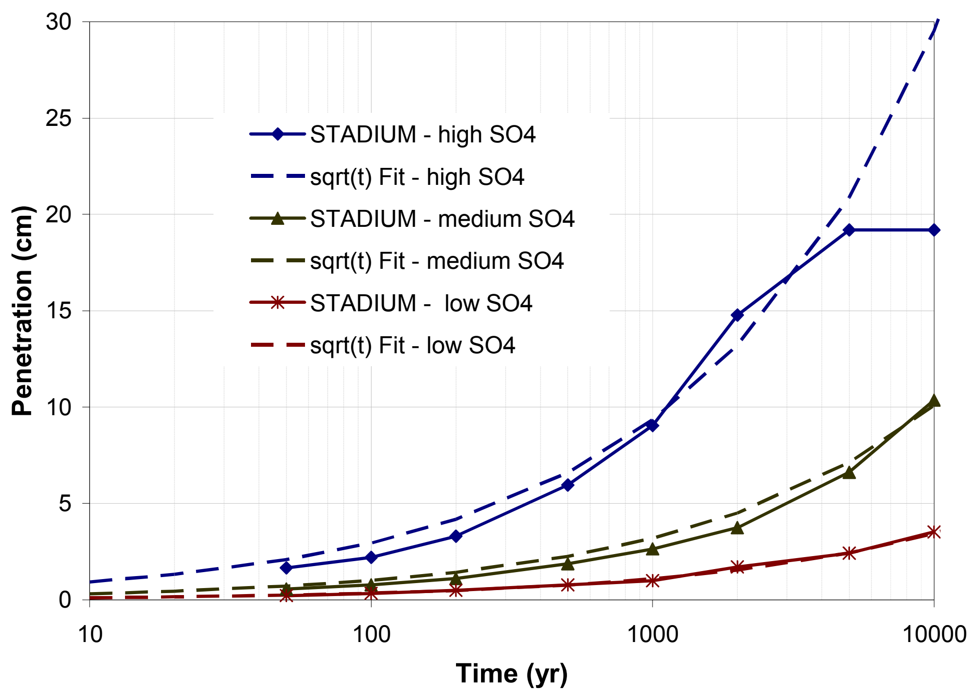

Fig. 2. STADIUM predictions of ettringite penetration depth for high, medium and low sulfate exposure, and analytic approximations.

Extensions to More General Conditions

The three STADIUM® simulations involved an isolated thickness of concrete with particular, fixed, boundary conditions. Saltstone disposal cells experience varying sulfate concentrations with waste composition and time. A simplified generic moving-front concept can be used to extend the STADIUM full-physics simulations to more general exposure conditions. Figure 3 illustrates a generic moving front that consumes reactants that are delivered to the front through quasi-steady diffusion. The latter implies that the timescale of diffusion is much shorter than the timescale of the moving front, which is expected for sulfate attack. As the front advances, the diffusion length increases, slowing reactant delivery and advance of the front. A differential equation describing the movement of the generic front is

$$R\frac{dx}{dt} = \frac{nD_e c}{x} \quad \text{(Eq. 1)}$$

where x is front position (e.g. cm), t is time (s), R is a reaction capacity (mol/cm), n is porosity, D_e is effective diffusion coefficient (cm^2/s), and c is a fixed aqueous concentration of reactant at x = 0 (mol/cm^3). The analytic solution to Equation (1) is

$$x = \left[\frac{2nD_e ct}{R}\right]^{1/2} \quad \text{(Eq. 2)}$$

Thus a square root dependence on porosity, diffusion coefficient, exposure concentration, and time in the STADIUM® results can be anticipated, if the conceptual model depicted in Figure 3 is approximately correct.

The position of the ettringite front predicted by STADIUM® was observed to be closely proportional to $t^{0.5}$ as anticipated. However, an exponent slightly lower than 0.5 best captured the effect of exposure concentration. Specifically, the functional form

$$x = Ac^B\sqrt{t} \quad \text{(Eq. 3)}$$

with A = 0.626 ($cm\cdot(mol/L)^{-B}\cdot yr^{-0.5}$) and B = 0.467 (unitless) produced a best-fit analytic approximation to the full-physics STADIUM® results. Figure 2 compares Equation (3) to the original STADIUM® results. The analytic function as plotted does not account for the finite thickness (20 cm) of the concrete for the high sulfate exposure scenario.

The STADIUM simulations assumed a nominal effective diffusion coefficient of ~10^{-7} cm^2/s for ionic transport. Based on Equation (2), Equation (3) can be further generalized as

$$x = Ac^B\sqrt{\frac{D_e}{D_{ref}}}\sqrt{t} \quad \text{(Eq. 4)}$$

where $D_{ref} = 10^{-7}$ cm^2/s is implicitly embedded in the empirical constant A. The rate of change in front position is

$$\frac{dx}{dt} = Ac^B\sqrt{\frac{D_e}{D_{ref}}}\frac{1}{2\sqrt{t}} \quad \text{(Eq. 5)}$$

Equation (4) is based on constant values of sulfate concentration and diffusion coefficient. If the front speed under changing conditions is assumed to follow Equation (5) at any instant in time, then Equation (5) can be generalized to

$$\frac{dx}{dt} = Ac(t)^B\sqrt{\frac{D_e(t)}{D_{ref}}}\frac{1}{2\sqrt{t}} \quad \text{(Eq. 6)}$$

The front position for varying sulfate concentration and diffusion coefficient can be computed by integrating Equation (6) as

$$x = \int_0^T Ac(t)^B \sqrt{\frac{D_e(t)}{D_{ref}}} \frac{1}{2\sqrt{t}} dt \qquad \text{(Eq. 7)}$$

where T is cumulative time. Equation (7) can be numerically evaluated for arbitrary variations in concentration and diffusion coefficient, and provides an approximate generalization of the original three STADIUM® simulations to other conditions.

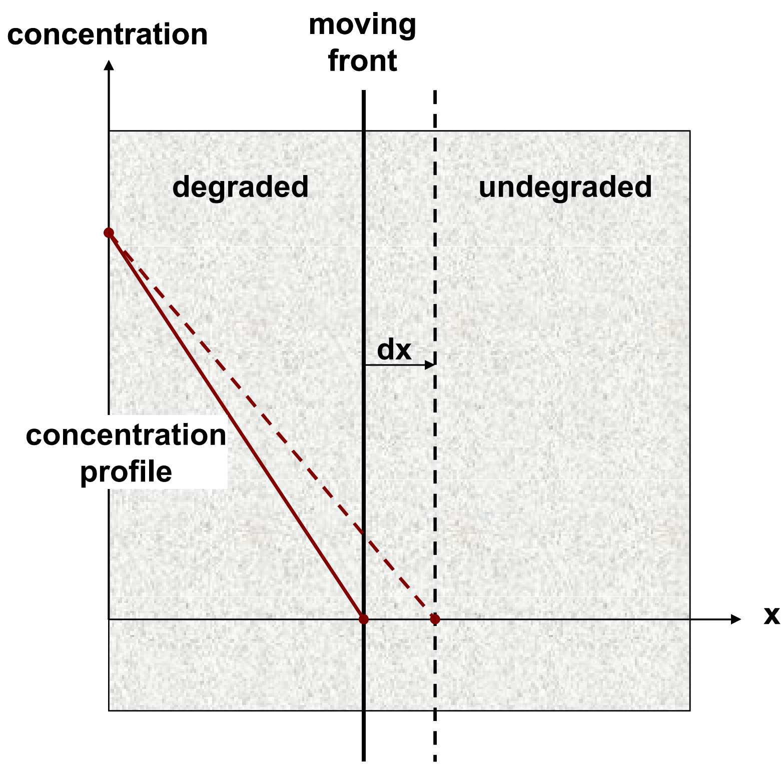

Fig. 3. Generic moving front.

Damage Model

STADIUM® does not predict whether physical damage will occur, or the impact on transport properties should damage occur. To quantify concrete degradation based on the extended STADIUM® results, two key assumptions were made:

1) The presence of ettringite coincides with physical damage to concrete, for the purpose of estimating effective transport properties for waste release.

2) Transport properties, with respect to predicting ettringite front position, are unchanged by passage of the front.

Assumption 1) may be neutral, or conservative if damage does not occur. Assumption 2) would be accurate if ettringite formation does not damage the concrete, or if changes in morphology do not significantly increase transport properties for given exposure conditions. For example of the latter, spalling or cracking under unsaturated conditions may not accelerate sulfate attack, because the fractures would be dewatered with sufficient suction, and relatively inactive. On the other hand, Assumption 2) would not be accurate under saturated conditions, for which cracks/fractures typically dominate solute transport. Thus Assumption 2) may be neutral, or non-conservative if cracking accelerates attack.

With these key assumptions and the front position defined by Equation (7), effective transport properties can be estimated by averaging properties in the intact and degraded regions. Using saturated hydraulic conductivity (K) as an example

$$\Delta x K_{eff}{}^{p} = \Delta x_i K_i{}^{p} + \Delta x_d K_d{}^{p} \qquad \text{(Eq. 8)}$$

or equivalently

$$K_{eff} = \left[\frac{\Delta x_i K_i{}^{p} + \Delta x_d K_d{}^{p}}{\Delta x} \right]^{1/p} \qquad \text{(Eq. 9)}$$

where $-1 \le p \le +1$ and Δx denotes thickness. The subscripts "i" and "d" refer to the intact and degraded regions ahead of and behind the front respectively, and "eff" is the effective (composite) value. Arithmetic averaging corresponds to p = 1 and harmonic averaging is obtained with p = 1. The former is used for transport parallel to the ettringite front, and the latter for transport transverse to the front.

DURABILITY PREDICTIONS

Durability predictions are shown in Figures 4 and 5. Ettringite advances at the same rate through the floor and wall barriers (Figure 4), which are exposed to the same sulfate concentration. However, the roof is somewhat protected by the presence of a clean grout layer between the waste grout and roof (Fig. 1). Lower sulfate exposure leads to a slower penetration rate. The damage front has minimal effect on the effective conductivity of the barriers, until the front nears the far boundary (Figure 5). In these nominal durability predictions, breakthrough occurs well past the 10,000 year design period of performance for the facility [2].

As noted above, sulfate attack may introduce a feedback mechanism not considered in the STADIUM® simulations, whereby physical damage from expansive mineral phase formation leads to faster delivery of sulfate to the reaction front through cracks. To assess the impact of this possibility, an additional prediction was made assuming the effective diffusion coefficient of the concrete was 10x higher than the nominal value to reflect cracking [8]. As shown in Figure 6, the damage front breakthrough occurs approximately an order of magnitude faster in time, consistent with Equation (4).

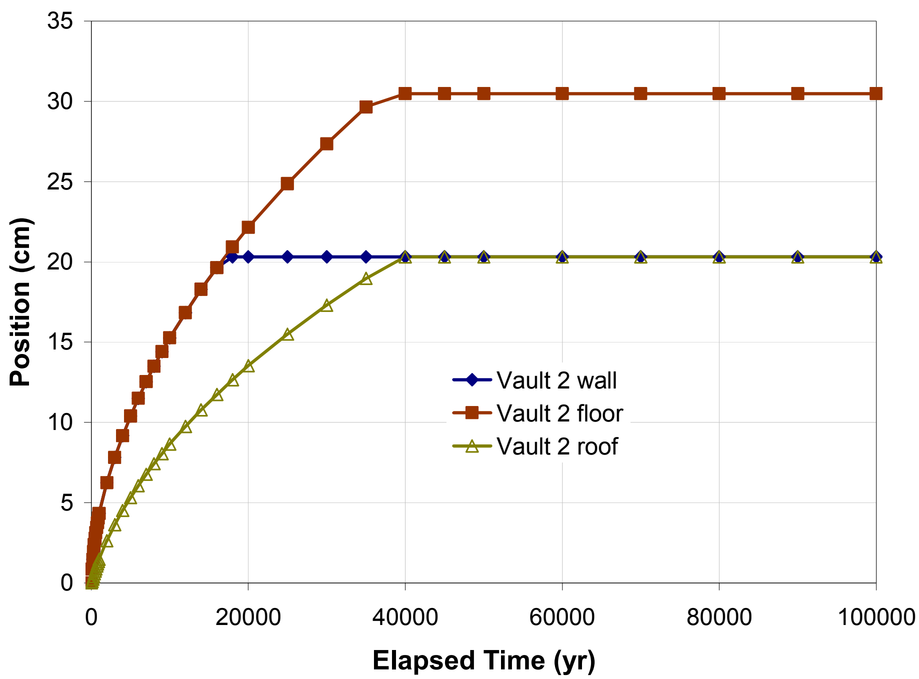

Fig. 4. Ettringite position for the nominal exposure scenario.

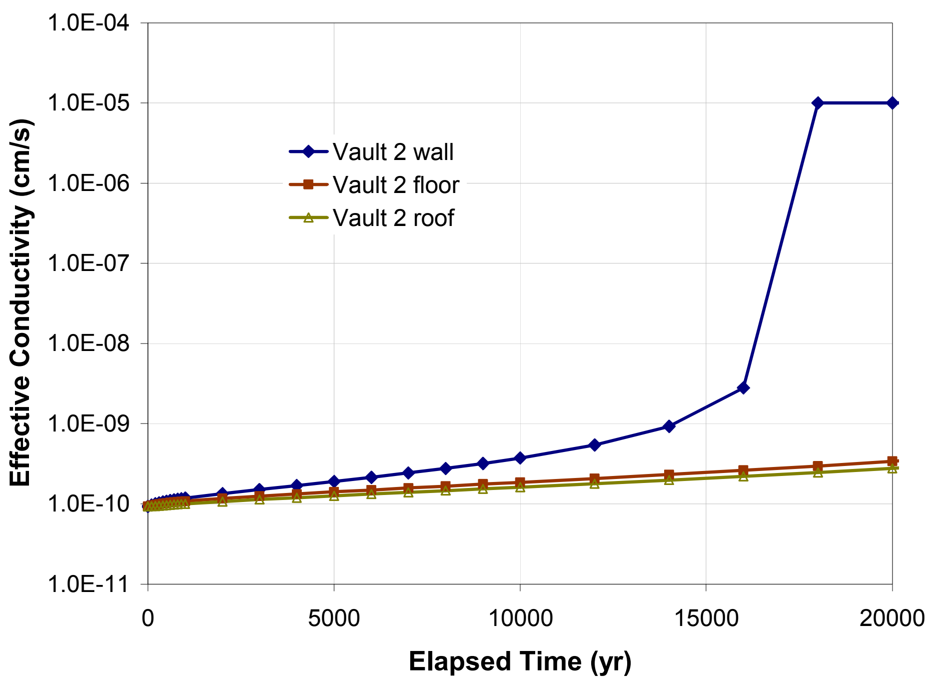

Fig. 5. Effective conductivity for the nominal exposure scenario.

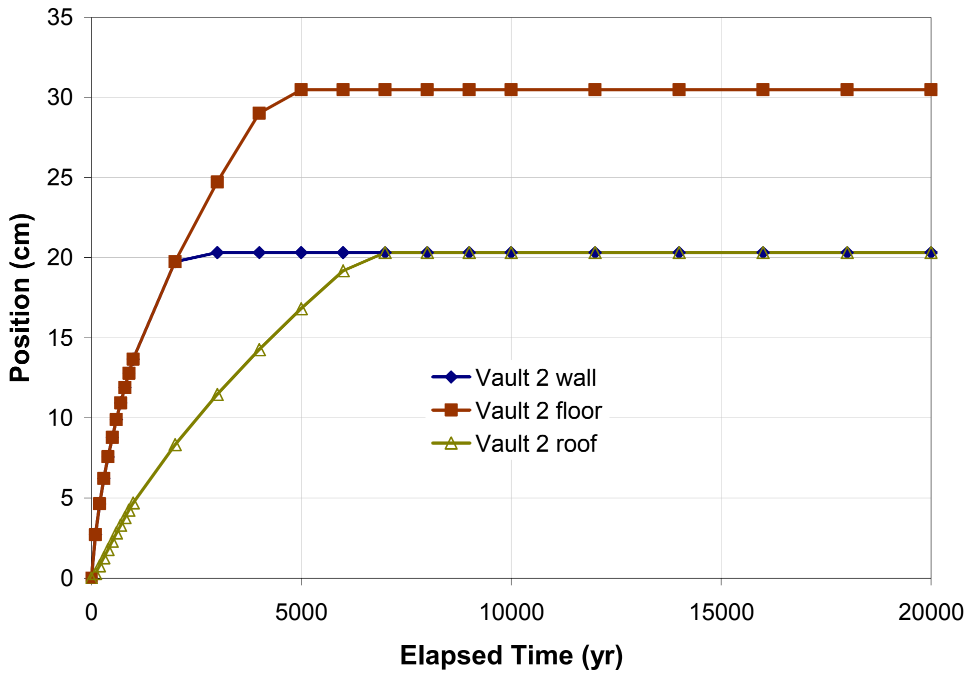

Fig. 6. Ettringite position for the accelerated sulfate attack scenario.

CONCLUSIONS

The nominal durability predictions presented herein suggest a Saltstone service life readily surpassing the 10,000 year design period of performance for the facility, with respect to external sulfate attack. A sensitivity analysis using pessimistic assumptions indicates a shorter service life on the order of a few thousand years. Both scenarios have been considered in a Performance Assessment of the Saltstone Disposal Facility [2]. Additional research is needed to enable more accurate prediction of reactive transport in cementitious materials coupled with damage mechanics.

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