Modeling of the Sub-Suface Reducing Environment of the Z-Area Saltstone Disposal Facility at the Savannah River Site

by

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Abstract

Low-level radioactive liquid wastes at the U.S. Department of Energy Savannah River Site are treated by mixing the wastes with Saltstone grout to generate the Saltstone waste form that is poured into the concrete vaults for long-term disposal. The formula for Saltstone includes ~25 wt% slag to create a reducing environment for mitigating the sub-surface transport of several radionuclides, including Tc-99. A two-dimensional reactive transport model was developed to estimate how long the Z-Area Saltstone will maintain a reducing environment, and therefore its ability to sequest Tc-99. The model predicted that ~16% of the Saltstone reduction capacity would be consumed after 213,000 years. Independent calculations published by other researchers yielded nearly identical results. The general modeling approach and the study results are presented in this paper.

INTRODUCTION

The Saltstone Disposal Facility (SDF) at the Savannah River Site (SRS) is a near-surface disposal facility that receives low-level radioactive waste generated at the SRS which has been incorporated into a cementitious form called saltstone. Saltstone grout is produced in Z-Area by mixing an aqueous low-level waste stream containing copious amounts of sodium salts with a dry blend of slag, fly ash and cement. SDF consists of a number of concrete vaults that have been constructed and are being filled with saltstone grout. The saltstone will harden and cure into a monolithic solid waste form with low water conductance properties and high retention properties for some of the radioactive contaminants of concern.

The nominal blend composition of saltstone is 3 wt% lime source, 25 wt% fly ash, 25 wt% slag, and 47 wt% salt solution. The addition of slag to the saltstone formulation provides a chemical reductant (iron(II)) and a precipitating agent (sulfide)

that chemically binds several contaminants as insoluble species, thus reducing the tendency of these contaminants to leach from the solid waste form. Experimentation has shown that leaching of chromium and technetium was effectively reduced to a level that enabled all projected salt solution compositions to be processed into a non-hazardous solid waste. Long term lysimeter studies have shown that the addition of slag into the saltstone formulation essentially stopped Tc-99 leaching.

Ambient conditions in the Z-Area sub-surface are oxidizing, due to the omnipresence of oxygen in air. It is expected that eventually the reducing capacity of the slag will be exhausted by a number of naturally occurring processes, the most important being the oxidation of the slag's reduction capacity by dissolved oxygen in infiltrating rain water.

The objective of this study was to estimate how long reducing conditions would exist in the saltstone sub-surface environment.

MODEL DEVELOPMENT

Chemical Conceptual Model

Electron equivalents are the units used to describe the concentration (more precisely, the activity) of free electrons that can participate in an oxidation-reduction, or redox, reaction. The generalized redox equation is presented in Eq. 1,

$$O + e^- = R \qquad \text{Eq. 1}$$

where:

O	oxidizing agent, meq e^-/L,
R	reducing agent, meq e^-/L, and
e^-	electron.

The greatest concentration of reductant will exist in the

disposal facility when it is initially placed in the ground. Over time, the concentration of reductant will slowly decrease as more dissolved oxygen in the groundwater, $O_{2(aq)}$, consumes the saltstone reductant. Once the reduction capacity is exhausted, the saltstone will no longer be able to sequester the targeted radionuclides, such as Tc-99 (primarily through the reductive precipitation of Tc(VII) to form the sparingly soluble TC(IV)). Based on Eq. 1, the consumption of the reduction capacity is presented in the following reaction.

$$O_{2\ (aq)} + R_{(saltstone)} \rightarrow RO_{2(saltstone)} \qquad \text{Eq. 2}$$
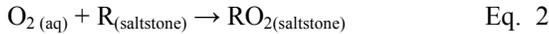
where:

$O_{2(aq)}$ O_2 dissolved in water (meq e$^-$/cm^3 of the fluid),

$R_{(saltstone)}$ reduction capacity of the saltstone (meq e$^-$ per gram of solid), and

$RO_{2(saltstone)}$ oxygenated grout (meq e$^-$ per gram of solid; shown in traditional stoichiometric chemistry as a product of the two reactants, rather than as an oxidized species).

The expression used to calculate the rate of oxidation R_O (meq e$^-$/gram of solid)/yr) for the above reaction (Eq. 2) is:

$$R_O = k \cdot C_{O2} \cdot C_R \qquad \text{Eq. 3}$$

where k is the oxidation rate coefficient in units of $1/(\text{yr} \cdot \text{meq e}^-/\text{cm}^3)$, C_{O2} is the concentration of $O_{2(aq)}$ and C_R is the concentration of reductant in the saltstone.

Previous data (Lukens et al. 2005) indicate that oxidation of slag is a fast reaction. Hence, a simplified one-dimensional (vertical direction) PORFLOW™ saltstone model was initially set up to assess the appropriate value of k to be used to represent a fast reaction. These tests estimated the time required to consume all the saltstone reductant by setting the advection rate very high (40 cm/yr) to expedite calculations, and the oxidation rate coefficient, k, was varied. Importantly, only advection was considered. The exercise showed that the oxidation rate coefficient of 1×10^6 is adequate to support the assumption that oxygen is instantaneously consumed to oxidize slag (i.e., very fast reaction).

Physical and Hydrological Conceptual Model

Figure 1 illustrates the physical and hydrological conceptual model. Half of the saltstone block was modeled

because a crack was assumed to exist in the block center at time zero, creating two equally sized blocks. The crack was assumed to be consistent with past performance assessment calculations and it offered another means to provide greater conservatism by permitting greater surface area for oxygen diffusion. Therefore, the horizontal direction in Figure 1 represented the distance from the crack (on the left) to the vault concrete side. Diffusion of infiltrating, fully oxygenated water, occurred at all sides. Advection however took place only in the vertical direction from the top side to the bottom side. The average velocity value of 2.5E-3 cm/yr was obtained from another Saltstone study (Cook et al., 2005)
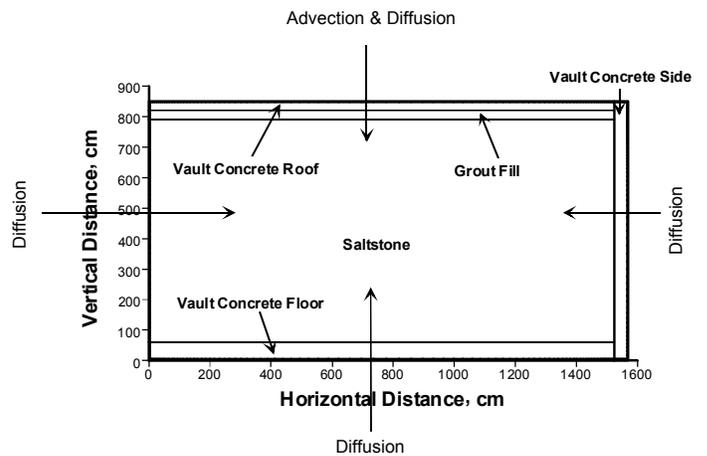

Figure 1. Conceptual model.

Assumptions

The following major assumptions were made in the PORFLOW™ simulations:

- The problem is assumed to be adequately represented in a two-dimensional model.
- Oxidation of the slag by oxygen in infiltrating water is a very fast reaction.
- The advection is primarily in the vertical direction. Hence, negligible velocity component in the horizontal direction is assumed.
- Simulations start at the time when cracks are formed in the saltstone. Consumption of the slag reducing capacity by oxygen prior to this time is assumed to be negligibly small.
- Except for one crack down the center of the saltstone, which exists as an initial boundary condition (i.e., exists at time zero), the structure of saltstone is intact during the course of the simulations.
- The saltstone is saturated with water.

- The water in the sediment in contact with the saltstone is saturated with $O_2(g)$, ~8 mg/L. This is an important conservative assumption. Laboratory data showed that $O_2(aq)$ SRS groundwater concentration is appreciably lower, barely detectable in sub-surface groundwater.
- The saltstone is buried in an unsaturated sediment that has an endless supply of $O_2(g)$ to diffuse into the groundwater.

Numerical Model and Input Values

PC-based PORFLOW™ software Version 4.0, a product of Analytic & Computational Research, Inc. (ACRi), was used in these simulations. PORFLOW™ solves problems involving transient and steady-state fluid flow, heat and mass transport in multi-phase, variable saturation conditions, porous or fractured media flow, and dynamic changes in phases. The porous/fractured media may be anisotropic and heterogeneous. Arbitrary sources (injection or pumping wells) may be present, and chemical reactions or radioactive decay may take place in the model (ACRi, 2002). PORFLOW™ has been widely used at the SRS and in the DOE complex to address major issues related to the groundwater and radioactive waste management.

In a 2-dimensional coordinate system, the governing mass transport equation of species k in the fluid phase is given by

$$\frac{\partial C_k}{\partial t} + \frac{\partial}{\partial x_i}(V_i C_k) = \frac{\partial}{\partial x_i}(D_{ij}\frac{\partial C_k}{\partial x_j}) + R_k$$

Eq. 4

C_k	Concentration of species k
V_i	Fluid velocity in the ith direction
D_{ij}	Effective diffusion coefficient for the species
R_k	Reaction rate of species k
i, j	Direction index

The governing mass transport equation of species k in the solid phase is similar to that in the fluid phase except that both convective and diffusive terms are zero and the accumulation term pertains only to the solid phase. This equation is written as:

$$\frac{\partial C_{Sk}}{\partial t} = R_{Sk}$$

Eq. 5

Figure 2 displays the modeling grid used for PORFLOW™ simulations. The grids are X- and Y-coordinates of the nodes. To provide numerical stability, the meshes have a gradual transition from wider grids to narrower grids near the boundaries and where there are changes in material properties. A geometry of 98 (horizontal) and 71 (vertical) nodes were generated for the entire modeling domain.
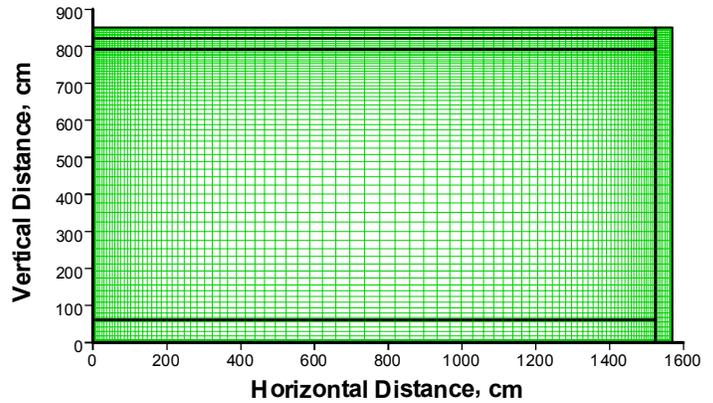

Figure 2. Modeling grid

The material properties used in the PORFLOW™ simulations are listed in Table 1.

Table 1. Model input values for materials

	Dry Density (g/cm^3)	Porosity	Diffusion Coefficient (cm^2/yr)	Reduction Capacity † (meq e$^-$/ g$_{solid}$)
Vault Concrete	2.65	0.18	0.315	9.25E-3
Grout / Saltstone	3.148	0.46	0.158	9.25E-3

†: Reduction capacity in concrete and grout/.saltstone is based on slag comprising 25 wt% of the nominal blend. Slag has a reduction capacity of 37 meq e$^-$/(kg$_{slag}$)

RESULTS

PORFLOW™ simulations were carried out at varying times ranging from 1000 years to 250,000 years. The simulation result at 250,000 years is shown in Figure 3 in which saltstone concentration in (meq e$^-$)/g$_{solid}$ is contour-plotted over the Saltstone geometry. The slag

concentration level ranging from 0 to 9.25E-3 meq e⁻/g$_{solid}$ is colored accordingly.

The consumption of saltstone reduction potential by oxygen in infiltrating water over time is displayed in Figure 4. These data were determined by using the two dimensional PORFLOW™ calculations, such as presented in Figure 3.
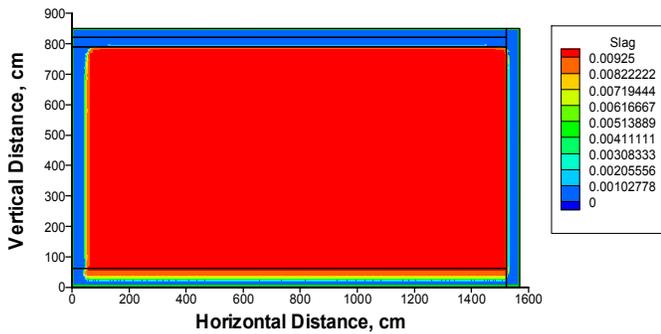

Figure 3. Simulation Results at 250,000 Years (Units in meq e⁻/g$_{solid}$. Red indicates no oxidation of saltstone occurred and Blue indicates that full oxidation of the saltstone occurred)
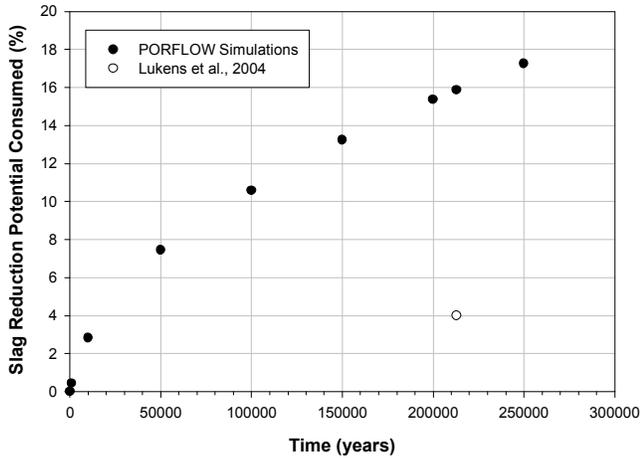

Figure 4. Consumption of Slag Reduction Potential by Oxygen in Infiltrating Water

In Figure 5, the penetration depth is plotted vs. time for all sides. The penetration depth is defined as the range within the saltstone where reduction capacity has changed. The range was computed as the distance between where no change, 9.25E-3 meq e⁻/g$_{solid}$ (i.e., initial concentration), and change in reduction capacity occured. The penetration

depth at the midpoint of each side is presented in Figure 5. The data are not smooth due to the very slow nature of the modeled process and the long time required for changes to move from one node to the next. At the expense of appreciably longer simulation times, data smoothness could be improved by rerunning the simulations using a finer mesh size. Also, Figure 5 clearly shows that the left and right sides exhibit different penetration depth. On the left side (cracks), oxygen diffuses directly through grout. On the right side, oxygen diffuses through the vault concrete side first before reaching grout. Concrete and grout have different transport properties as shown in Table 1, hence, resulting in different diffusion pattern.
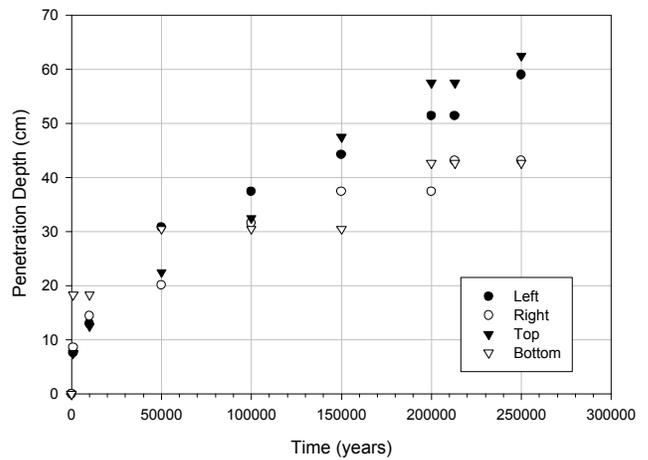

Figure 5. Penetration Depth

There had been two other recent studies of the longevity of the reducing conditions of the SRS Saltstone waste form. The first study provided a simple calculation of the longevity of the saltstone's reducing conditions until the more rigorous and less conservative diffusion calculations presented in this report could be conducted. Two important assumptions were made in the first study: 1) The waste form crumbled at time zero into infinitely small particles that all the reductant was immediately available for oxidation; and 2) Advection, and not diffusion, controlled the movement of dissolved oxygen to the waste form. In this exceedingly conservative calculation, the reduction capacity of the saltstone was not consumed for several thousand years, assuming reasonable unsaturated groundwater flow rates.

In the second study, Lukens et al. (2004) estimated based on a combination of spectroscopic and diffusional

considerations (specifically, the spectroscopic method used to calculate X-ray self-absorption developed by Troger et al., 1992 and the empirical diffusion model developed by Smith and Walton, 1993). In their study, the top of the cuvette was left exposed to air and the Tc oxidation state was measured as a function of time from a 5- to 10-mL cuvette containing simulated SRS reducing saltstone. They observed that Tc(IV) eventually was converted to Tc(VII). Their conclusion was that ~4% of the reduction capacity of the saltstone would be consumed in 213,000 years. This value is shown in Figure 4 and represents the amount of reductant consumed through one-dimensional considerations /measurements. To adjust this value to be compatible to our two-dimensional (four-side diffusion) calculations, we multiplied this percentage by four (an approximation), yielding 16% of the total saltstone reduction capacity would be consumed in 213,000 years. This value is surprisingly similar to our value of 15.8%.

CONCLUSIONS

The two-dimentional reactive transport model was developed to predict that the Z-Area saltstone waste form will maintain a reducing environment, and therefore its ability to sequester technetium-99, for well over 10,000 years. For example, it was calculated that ~16% of the saltstone reduction capacity would be consumed after 213,000 years. The conclusion of this study was positively confirmed by comparison with two other studies.

In summary, obtaining similar conclusions by three different types of calculations and sets of assumptions provides additional credence to the conclusion that the Z-Area saltstone will likely maintain a reducing environment in excess of 10,000 years.

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