

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

WSRC-STI-2007-00046, REVISION 0

KEY WORDS:

Saltstone

Slag

I-129

Technicium

RETENTION: Permanent

**ESTIMATED DURATION OF THE SUBSURFACE REDUCTION
ENVIRONMENT PRODUCED BY THE SALTSTONE DISPOSAL FACILITY
ON THE SAVANNAH RIVER SITE**

**D. I. KAPLAN
T. HANG**

January 22, 2007

Washington Savannah River Company
Savannah River Site
Aiken, SC 29808

**Prepared for the U.S. Department of Energy Under
Contract Number DE-AC09-96SR18500**



Estimated Duration of the Subsurface Reducing Environment Produced by the Saltstone Disposal Facility on the Savannah River Site

D.I. Kaplan and T. Hang
Savannah River National Laboratory
Aiken, South Carolina 29808
United States

ABSTRACT

The formula for Savannah River Site (SRS) saltstone includes ~25 wt% slag to create a reducing environment for mitigating the subsurface transport of several radionuclides, including Tc-99. Based on laboratory measurements and two-dimensional reactive transport calculations, it was estimated that the SRS saltstone waste form will maintain a reducing environment, and therefore its ability to sequester Tc-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. For purposes of comparison, a second calculation was presented that was based on entirely different assumptions (direct spectroscopic measurements and diffusion calculations). The results from this latter calculation were near identical to those from this study. Obtaining similar conclusions by two extremely different calculations and sets of assumptions provides additional credence to the conclusion that the saltstone will likely maintain a reducing environment in excess of 10,000 years.

INTRODUCTION

The waste in the high-level tanks on the Savannah River Site (SRS) is being evaluated for disposal as vitrified waste form and saltstone. The former would contain ~99% of the radioactivity and would eventually be sent to a high-level waste repository, such as the one proposed for Yucca Mountain. The saltstone would contain ~90% of the waste volume and would be disposed on the SRS. The SRS saltstone facility has been operating intermittently since 1990. It consists of two vaults: the first contains six cells and the second contains 12 cells, where each cell is 33-m length x 33-m width x 8-m height. After each vault is filled, they will be covered with sediment and a geological, water-resistant barrier will be constructed over the facility. As such, the facility will be isolated in the vadose zone.

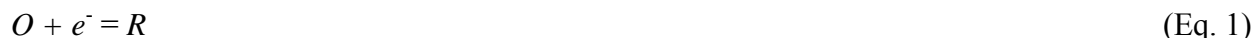
The nominal blend composition of saltstone is 3 wt% lime source, 25 wt% fly ash, 25 wt% slag, and 47 wt% salt solution [1]. The addition of slag to the saltstone formulation provides a chemical reductant and a precipitating agent (iron(II) and sulfide) for binding several contaminants as insoluble species, 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 [2]. A 2.5-year field lysimeter study on the SRS demonstrated that the addition of slag into the saltstone formulation essentially stopped Tc-99 leaching, but did not reduce nitrate leaching [2].

The objective of this study was to estimate how long reducing conditions would exist in the saltstone subsurface environment. Ambient conditions in the SRS subsurface are oxidizing, due to the omnipresence of air in the vadose zone. 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 (O_2) introduced by infiltrating porewater.

MODELING

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 Equation 1,



where:

O oxidizing agent, $\text{meq } e^- \text{ L}^{-1}$,
 R reducing agent, $\text{meq } e^- \text{ L}^{-1}$, and
 e^- electron.

The greatest concentration of reductant will exist in the disposal facility when it is initially placed in the ground and then over time, the concentration of reductant will slowly decrease as more dissolved oxygen in groundwater, O_{2aq} , consumes the saltstone reductant (discussed in more detail below in reference to Equation 3). Once the reduction capacity is exhausted, the saltstone will no longer bind the targeted radionuclides, such as Tc-99 (by reductive precipitation of Tc(VII) to the sparingly soluble Tc(IV) solid). It is important to note, that the theoretical redox potential (the intensity term to describe the redox status in a system and experimentally measured usually as Eh), will remain at a low fixed value until the last mole of reductant in the slag is consumed, at which point the redox potential will make a step-wise increase to a value controlled by the next dominant redox couple, which is likely iron(II/III). Once all the iron(II) has been oxidized to iron(III) then, at pH ~12, manganese(IV/II) will likely control the redox status in the system. This step-wise increase in redox potential will continue until the system is in equilibrium with the surrounding soil/water/air system.

The amount of reductant in the saltstone was calculated by subtracting the amount of oxidant in the salt solution from the amount of reductant in the slag using Equation 2. These results are presented in Table I.

$$R_{slag} - O_{salt\ solution} = R_{saltstone}, \quad (\text{Eq. 2})$$

where:

$O_{salt\ solution}$ electron equivalents of oxidizing agent from salt solution, $\text{meq } e^- \text{ cm}^{-3}$,
 $R_{saltstone}$ electron equivalents of reducing agent in the saltstone, $\text{meq } e^- \text{ cm}^{-3}$,
 R_{slag} electron equivalents of reducing agent from slag, $\text{meq } e^- \text{ cm}^{-3}$.

The total oxidizing capacity was set equal to the amount of dissolved oxygen introduced into the system by infiltrating rainwater and the salt solution used to create the saltstone, as calculated by Equation 2.

Table I. Estimation of Oxidation Capacity of Salt Solution Based on Oxidizing Constituents (Used in Eq. 2)

Oxidizing Ingredient	Saltstone Feed ^(a) (moles L ⁻¹)	e- Equivalents Required to Reduce 1 Mole (meq e- mol ⁻¹)	e ⁻ Equivalents Consumed by Saltstone (meq e- L ⁻¹)	Comments
nitrate	>2.00E+00			Nitrate leaches from lysimeters, thus not reduced by slag
Na ₂ CrO ₄	3.06E-03	3.00E+03	9.18E+00	Cr(VI) not leached from lysimeters, likely reduced by slag; Cr(VI) to Cr(III)
Na ₂ MoO ₄	3.61E-04	2.00E+03	7.22E-01	Mo(VI) to Mo(IV)
Na ₂ SO ₄	1.22E-01			Not reduced by slag
CaSO ₄	3.06E-03			Not reduced by slag
Total ^(b)			9.90E+00	

^(a) Nominal Blend (Table 2.3-3 in reference [2])

^(b) Did not include any salt solution ingredients in calculations that had a concentrations <1.00E-04 molar.

The concentration of reductant present in the slag decreases with time as more dissolved oxygen in groundwater consumes the saltstone reductant. Based on Equation 1, the consumption of the reduction capacity is presented in the following reaction.



where:

O_{2aq} O₂ dissolved in water ($\text{meq } e^-/\text{cm}^3$ of the fluid),
 $R_{saltstone}$ reduction capacity of the saltstone ($\text{meq } e^-/\text{g}$ of solid), and
 $RO_{2\ saltstone}$ oxygenated saltstone ($\text{meq } e^-/\text{g}$ 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 ; $(\text{meq } e^-/\text{cm}^3) \cdot \text{yr}^{-1}$) for the above reaction (Eq. 1) is:

$$R_O = k \cdot C_{O_2} \cdot C_R \quad (\text{Eq. 4})$$

where k is the oxidation rate coefficient in units of $1/(\text{yr} \cdot \text{meq } e^-/\text{cm}^3)$, C_{O_2} is the concentration of $O_{2(aq)}$ and C_R is the concentration of reductant in the saltstone. Previous data [3] indicates that

oxidation of slag is a fast reaction. The oxidation rate coefficient of $1 \times 10^6 \text{ l}/(\text{yr}\cdot\text{meq e}^-/\text{cm}^3)$, was selected in the simulations to support the assumption that oxygen is instantaneously consumed to oxidize slag (*i.e.*, very fast reaction) before being carried downstream to the next node.

Physical and Hydrological Conceptual Model

Fig. 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 at time zero, creating two equally sized blocks. Certainly cracks are known not to be as well defined as depicted here, yet we included it here to permit us an opportunity to evaluate the impact a surface where no vault walls were present and to provide greater conservatism to our calculation by permitting greater surface area for oxygen diffusion. 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 $2.5 \times 10^{-10} \text{ cm yr}^{-1}$ was obtained from the saltstone performance assessment revision.

Assumptions

The following major assumptions were made in the simulations:

- Advection occurs exclusively in the vertical direction.
- The saltstone is saturated with water.
- Oxidation of the slag by dissolved oxygen in infiltrating water is a very fast reaction.
- At the start of the simulations, *i.e.*, as an initial boundary condition, cracks in the saltstone exist.
- Except for one crack down the center of the saltstone monolith, the structure of saltstone is intact during the course of simulations.
- The sediment porewater in contact with the saltstone is saturated with O_{2g} , $\sim 8 \text{ mg L}^{-1}$. This is an important conservative assumption. Our laboratory has measured O_{2aq} concentrations in SRS groundwater to be appreciably lower in deeper waters, and more likely an order of magnitude lower.
- The saltstone waste is buried in an unsaturated sediment that has an endless supply of $\text{O}_2(g)$ to diffuse into the groundwater.
- Redox chemistry was simplified. Such processes as passivation, or the impacts of carbonation/coating on redox chemistry were not addressed primarily because they have not been well studied or quantified in the literature. Changes of water and mineralogical changes with time/aging were not considered.

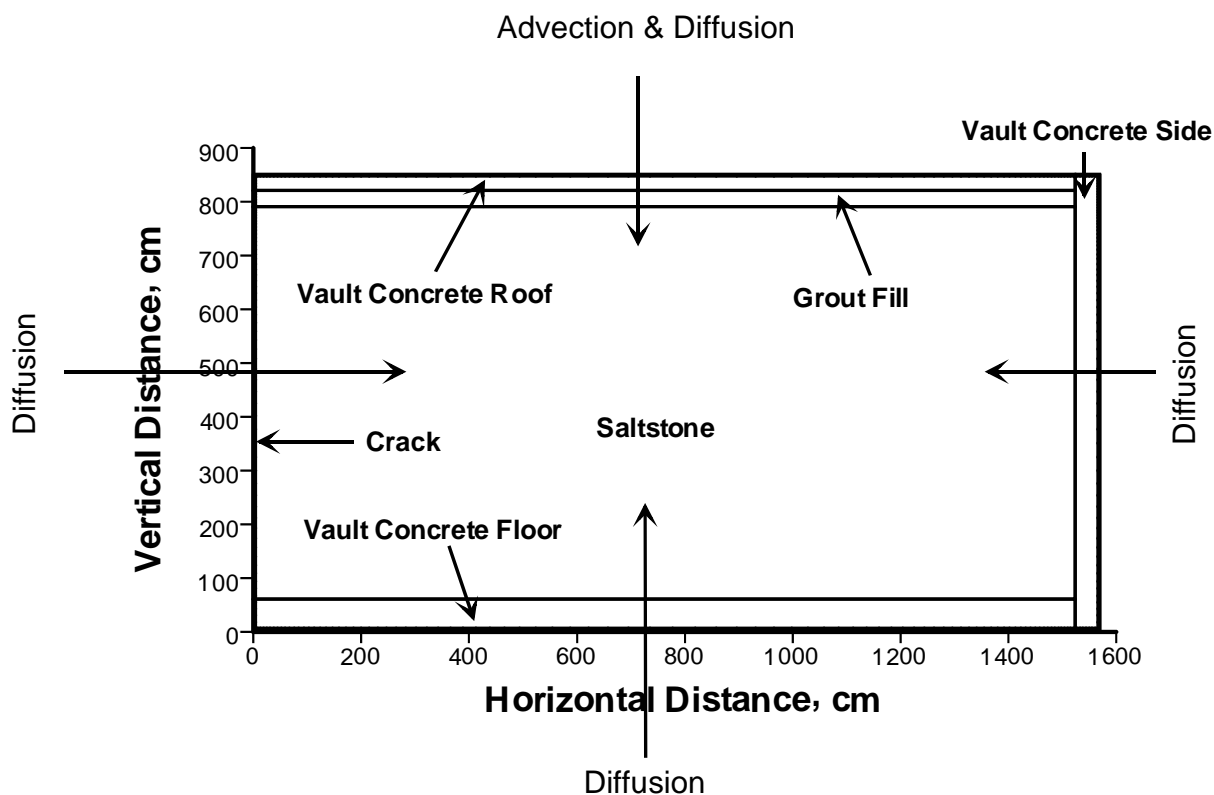


Fig. 1. Conceptual model (vault is assumed to be cracked in half, i.e., the vault is twice the X-axis. Diagram represents one of the two equally sized vault fragments. Crack is located on the left edge.)

Numerical Model and Input Values

The PC-based PORFLOW™ Version 4.0 (ACRi -- Analytic & Computational Research, Inc., Bel Air, CA) was used in these simulations. PORFLOW™ is a software that can solve involving transient and steady-state fluid flow, heat and mass transport in multi-phase, variably saturated, porous or fractured media with dynamic phase change. The porous or 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.

The governing mass transport equation of species k in the fluid phase is given by

$$\frac{\partial C_k}{\partial t} + \frac{\partial}{\partial x_i}(V_i C_k) = \frac{\partial}{\partial x_i}(D_{ij} \frac{\partial C_k}{\partial x_j}) + R_k \quad (\text{Eq. 5})$$

C_k Concentration of species k
 V_i Fluid velocity in the i^{th} 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 the convective term is zero and the accumulation term pertains only to the solid phase. (Please note that the symbol k , identifies a different parameter than the symbol k , the oxidation rate coefficient described in Equation 4. This equation is written as:

$$\frac{\partial C_{Sk}}{\partial t} = \frac{\partial}{\partial x_i} (D_{ij} \frac{\partial C_{Sk}}{\partial x_j}) + R_{Sk} \quad (\text{Eq. 6})$$

- C_{Sk} Concentration of species k in the solid phase
- D_{ij} Effective diffusion coefficient for the species
- R_{Sk} Reaction rate of solid species k

The grids were X- and Y-coordinates of the nodes. To provide numerical stability, the meshes had a gradual transition from wider grids to narrower grids near the boundaries and where there were changes in material properties. Input values used in the simulations are listed in Tables II and III.

Table II. Model Input Values for Materials

	Vault Concrete	Grout/Saltstone
Dry Density ($\text{g} \cdot \text{cm}^{-3}$)	2.65	3.148
Porosity	0.18	0.46
Diffusion Coefficient ($\text{cm}^2 \cdot \text{yr}^{-1}$)	0.315	0.158
Reduction Capacity ($\text{meq e}^- \cdot \text{g}_{\text{solid}}^{-1}$) ^a	9.25×10^{-3}	9.25×10^{-3}
^a Reduction capacity in concrete and grout/saltstone is based on slag comprising 25 wt-% of the nominal blend: slag has a reduction capacity of $37 \text{ meq e}^- \cdot [\text{kg slag}]^{-1}$.		

Table III. Input Values Used in Calculations

	Parameter (symbol; units)	Value	Comments/Source
Grout	Vault & saltstone height made with reducing grout ($D_{saltstone}$; m)	8.51	Reference: [2; page 2-62, 2-72]
	Grout height, saltstone made with reducing grout ($D_{saltstone}$; m)	7.6	Reference: [2; page 2-62, 2-72]
	Saltstone bulk density ($\rho_{saltstone}$; $\text{kg} \cdot \text{m}^{-3}$)	1.70E+03	Reference: [2; page 2-56]
	Mass Fraction of slag in saltstone (f_{slag} ; $\text{kg slag} \cdot [\text{kg saltstone}]^{-1}$)	0.25	Reference: [2; page 2-56]
	Reduction capacity of slag (C_{slag} ; $\text{meq e}^- \cdot [\text{kg slag}]^{-1}$)	37	Measured, see Fig. 2.
Water	Infiltration rate - grout/saltstone ($i_{saltstone}$; $\text{m} \cdot \text{yr}^{-1}$)	0.40	Reference: [2; page 2-72]
	Infiltration rate - soil (i_{soil} ; $\text{m} \cdot \text{yr}^{-1}$)	0.40	Reference: [2; page 2-72]
	Porosity - vault/saltstone ($\eta_{saltstone}$; $\text{vol water} \cdot [\text{vol saltstone}]^{-1}$)	0.46	
	Porosity - soil (η_{soil} ; $\text{m}^3 \text{ water} \cdot [\text{m}^3 \text{ total}]^{-1}$)	0.46	Average of several materials used in hydraulic barrier
	Volume of infiltrating water/yr – vault-saltstone/yr ($L \cdot [\text{yr} \cdot \text{m}^2]^{-1}$)	184	Calculated from infiltration rate and porosity
	Volume of infiltrating water/yr – soil ($L \cdot [\text{yr} \cdot \text{m}^2]^{-1}$)	184	Calculated from infiltration rate and porosity
	Henry's Law Constant for O_2 ($\text{mol} \cdot \text{atm}^{-1}$)	1.26E-03	Reference: [4; page 214]
	O_2 concentration in air (atm)	2.10E-01	
	O_2 concentration in groundwater (M)	2.65E-04	Measured values, see Assumptions ^a
	O_2 electron equiv. in groundwater ($C_{infiltrating\ groundwater}$; $\text{meq e}^- \cdot L^{-1}$)	1.06E+00	4 electrons per O_2 molecule ^a
Soil	Soil Cover Depth (D_{soil} ; m)	2.90E+00	Reference: [2; page 2-71]
	Soil Reduction Capacity (C_{soil} ; $\text{meq e}^- \cdot [\text{kg soil}]^{-1}$)	5.10E+00	Measured, see Fig. 2
	Soil Bulk Density (ρ_{soil} ; $\text{kg} \cdot \text{m}^{-3}$)	1.50E+03	Reference: [5]
	Soil Reduction Capacity (C_{soil} ; $\text{meq e}^- \cdot [\text{m}^3 \text{ soil}]^{-1}$)	7.65E+03	Measured, see Fig. 2

^a Used to calculate $C_{infiltrating\ groundwater}$;

Laboratory Measurements of Reduction Potential

The objective of the laboratory work was to measure the reduction capacity of the slag used to make saltstone and of a sediment sample collected from the Barnwell/McBean formation, the geological formation where the Saltstone Disposal Facility is located. The reduction capacity of the sediment was not used in these calculations but was included to provide a measure of comparison and will be used in future calculations. The reduction potential was measured using the method described by Lee and Batchelor [6]. Briefly, a slag or sediment suspension is brought up to pH 7, Cr(VI) is added, and at the end of an incubation period in a N₂-glovebox, the amount of Cr(VI) remaining in solution is measured. The amount of Cr(VI)_{aq} removed is assumed to have been reduced by the solid phase. Step-by-step details of the procedures used are provided by Kaplan and Thong [3].

RESULTS

Laboratory Measurements

By way of analogy to the more familiar terms pH and liming capacity, reduction potential (Eh) is to pH what reduction capacity is to liming capacity. Eh and pH are intensity terms whereas reduction capacity and liming capacity are capacity terms. The latter terms provide a measure of how much reductant or acidity is in the system. Eh and pH provide a measure of how much reductant and acidity will be released into the aqueous phase when these solids come to equilibrium. Generally, we need to know both, how much capacity the system has and how reductant it releases to the porewater. This particular calculation is primarily concerned with the capacity term (and assumes that the reduction potential remains constant so long as any reductant is present; as stated earlier, via the step-wise thermodynamic conceptualization).

Laboratory measurements of the reducing capacity of an SRS sediment and slag are presented in Fig. 2. These values indicate that the slag has a very high reducing capacity. Furthermore, it shows that SRS sediments also have a measurable reducing capacity. This reducing capacity is likely the result of naturally occurring iron(II) phases in the sediment, such as magnetite. By way of comparison, Lee and Batchelor [6] reported that a Texas loam and pyrite (FeS) had a reducing capacity of 6.1 and 32 meq kg⁻¹, respectively. These values are certainly consistent with the values reported in Fig. 2.

Also shown in Fig. 2 are the Eh values of 1:1 solid:water suspensions. Again, somewhat inaccurately, reduction potential can be thought of as a measurement of the free electron activity, as defined in Equation 1. The soil and slag had reduction potentials of 196 ± 3 and -247 ± 1 mV, respectively. Reducing systems have lower, more negative, reduction potentials. By way of comparison, Kaplan et al. [8] reported that metallic iron (Fe⁰) had a reduction capacity of -173 ± 6 mV. This value is consistent with the slag reduction potential value reported in Fig. 2.

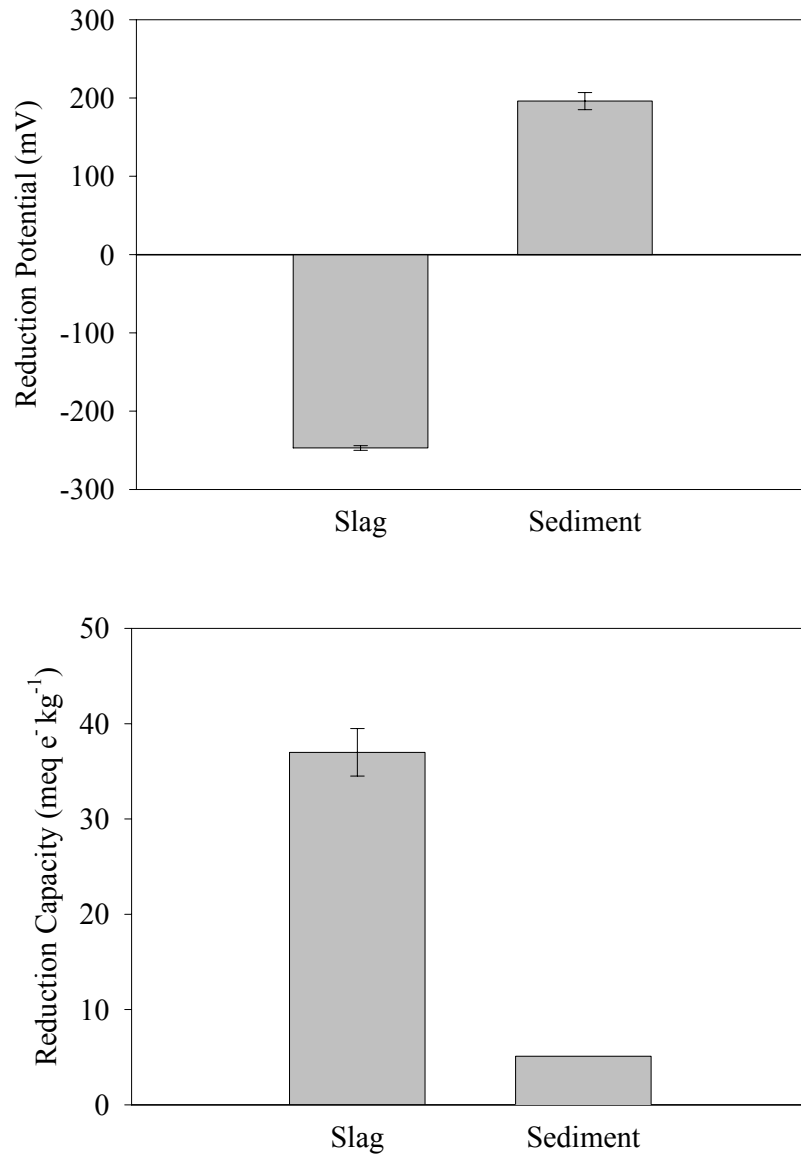


Fig. 2. Reduction potential and reduction capacity of an SRS subsurface sediment and the slag used to make saltstone.

Modeling

Simulations were carried out at varying times ranging from 1000 years to 250,000 years. An example of the output at 250,000 years is presented in Fig. 3. The slag concentration in the saltstone was estimated to range from 0 to 9.25×10^{-3} meq e^-/g_{solid} . Greater oxidation occurred along the upper surface, somewhat less along the sides, and the least from the bottom. The most oxidation occurred at the top because the simulation took into account advective flow. Also, Fig. 3 clearly shows that the left and right sides exhibit different penetration depth. On the left side (crack without the vault wall), 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 II, hence, resulting in different diffusion pattern.

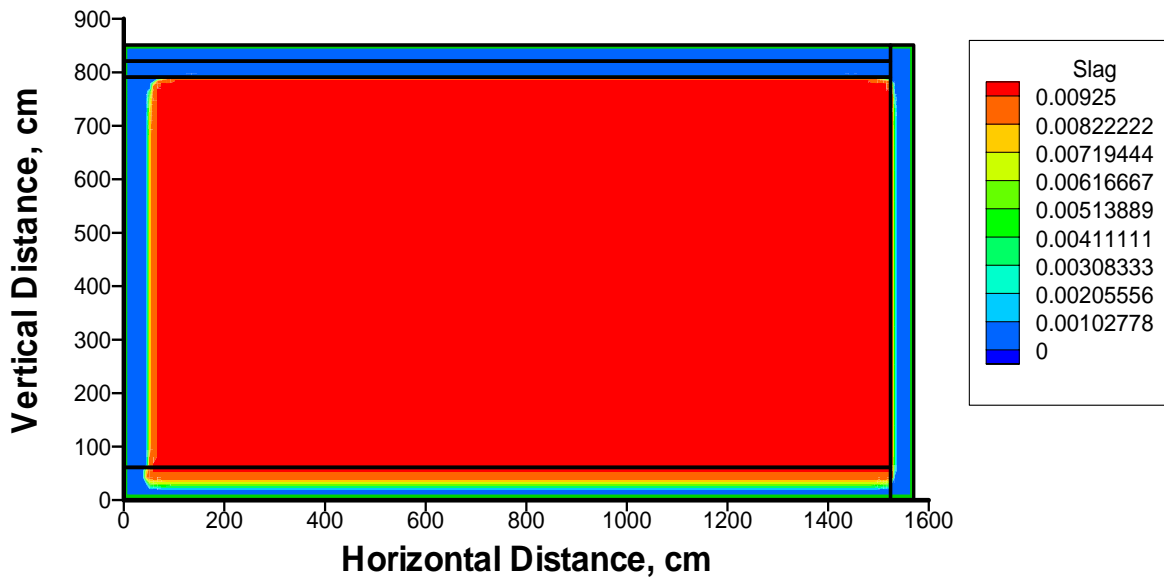


Fig. 3. Simulation result at 250,000 years (units in meq e^-/g_{solid}). Red indicates no oxidation of saltstone occurred and blue indicates that full oxidation of the saltstone occurred.

Fig. 4 shows the percent of slag that is oxidized by infiltrating water. At 250,000 years, 17.2% of the slag reduction potential had been oxidized. At 10,000 years, an important regulatory duration, about 3% of the slag reduction potential had been oxidized.

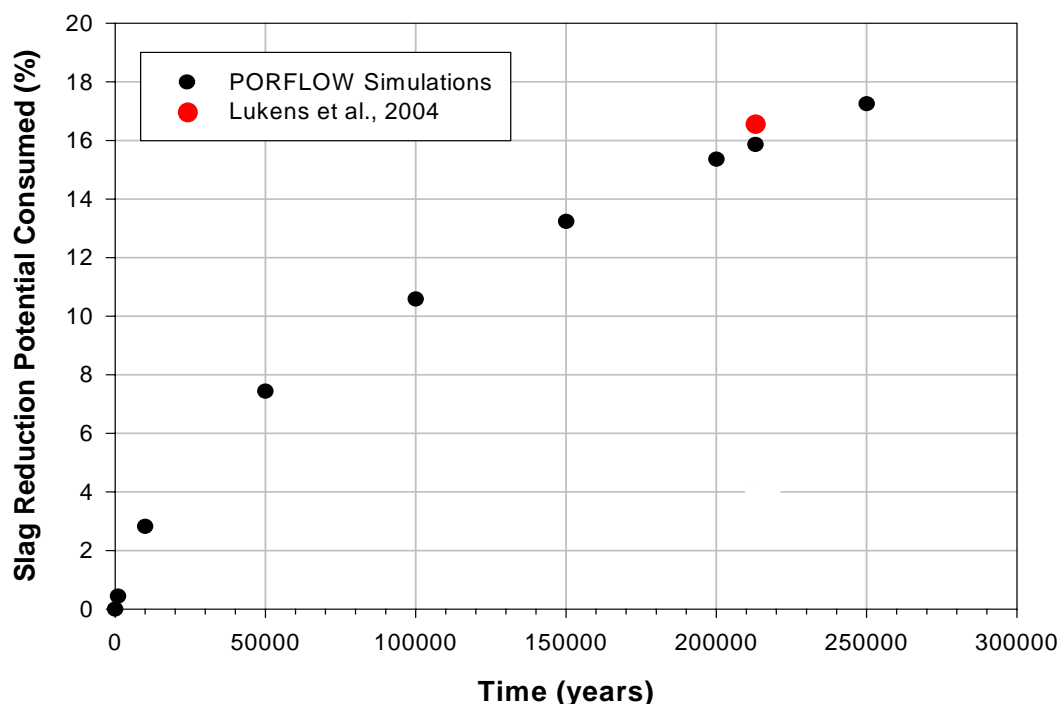


Fig. 4. Consumption of slag reduction potential by oxygen in infiltrating water. Results from Lukens et al. [3] is also presented, which is based on direct spectroscopic measurements (value corrected for diffusion from four direction).

DISCUSSION

There has been another recent calculation of reducing condition longevity in SRS saltstone by Lukens et al. [3]. Lukens et al. [3] estimate was based on a combination of spectroscopic (taking into consideration synchrotron X-ray self-absorption [9]) and the empirical diffusion model developed by Smith and Walton [10]. In their study, the top of a 5- to 10-mL cuvette filled with a SRS reducing-saltstone stimulant was left exposed to air and the Tc oxidation state was measured as a function of time. This method has the advantage that it is a direct measurement of the phenomena of interest. The shortcoming of this approach for calculating the longevity of saltstone reducing longevity is that these very careful and difficult results obtained from studies that lasted <14 months had to be extrapolate to 213,000 years, an extrapolation of >182,000 fold. In comparison, the calculation made in this paper was based on an entirely different set of assumption; namely, on calculated movement of water, assumed simplified chemistry, and a few property measurements (not direct chemical phenomenon measurements).

Lukens et al. [3] 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. In the scenario described in Fig. 4, where oxidation is occurring along four fronts, one may approximate that this one-dimensional diffusion would result in the consumption of ~16% of the reduction capacity. This value is surprisingly similar to our value of 15.8%.

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

REFERENCES

1. HECKROTTE, R.W. "Project S-1780 – Savannah River Plant – 200-S Area Defense Waste Processing Facility – Sludge Plant Request to Modify the DWPF Saltstone Industrial Solid Waste Permit," Inter-office Memorandum, PP-001183, DuPont, Savannah River Plant, Aiken South Carolina (1988).
2. MMES (Martin Marietta Energy Systems, Inc., EG&G Idaho, Inc., Westinghouse Hanford Company, and Westinghouse Savannah River Company). "Radiological Performance Assessment for the Z-Area Saltstone Disposal Facility," WSRC-RP-92-1360, Westinghouse Savannah River Company, Aiken, South Carolina (1992).
3. LUKENS, W.W., J.J. BUCHER, D.K. SHUH, and N.M. EDELSTEIN. "Evolution of Technetium Speciation in Reducing Grout." *Environmental Science Technology* 39: 8064-8070 (2005).
4. STUMM, W., and J.J. MORGAN. "Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters," 3rd edition, John Wiley and Sons, Inc., New York, New York (1996).
5. DRAGUN, J. "The Soil Chemistry of Hazardous Materials," 2nd Edition, Amherst Scientific Publishers, Amherst, Massachusetts (1998).
6. LEE, W., and B. BATCHELOR. "Reductive Capacity of Natural Reductants." *Environmental Science Technology* 37: 535-541 (2003).
7. KAPLAN, D.I., and T. HANG. "Estimated Duration of the Subsurface Reducing Environment Produced by the Z-Area Saltstone Disposal Facility," WSRC-RP-2003-00362, Westinghouse Savannah River Company, Aiken, South Carolina (2003).
8. KAPLAN, D.I. "Influence of Surface Charge of an Fe-oxide and an Organic Matter Dominated Soil on Iodide and Per technetate Sorption." *Radiochim. Acta* 91:173-178 (2003).
9. TROGER, L., D. ARVANITIS, D. BABERSCHKE, H. MICHAELIS, U. GRIMM, and E. ZSCHECH. "Full Correction of the Self-absorption in Soft-fluorescence Extended X-ray-Absorption Fine Structure." *Phys. Rev. B.* 46: 3283–3289 (1992).
10. SMITH, R.W., and J.C. WALTON. "The Role of Oxygen Diffusion in the Release of Technetium from Reducing Cementitious Waste Forms." *Mat. Res. Soc. Symp. Proc.* 294:247–253 (1993).