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ESTIMATED DURATION OF THE SUBSURFACE REDUCING ENVIRONMENT PRODUCED BY THE Z-AREA SALTSTONE DISPOSAL FACILITY (U)

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1.0 ABSTRACT

The formula for saltstone includes ~25 wt% slag to create a reducing environment for mitigating the subsurface transport of several radionuclides, including technetium-99. Based on laboratory measurements and two-dimensional reactive transport calculations, it was estimated 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. For purposes of comparison, two additional calculations, based on entirely different assumptions, were discussed. The first calculation conducted by Lukens et al. (2004), based on spectroscopy considerations (sans diffusion or aqueous transport considerations), yielded near identical results as above. The second calculation conducted as a first approximation and using unrealistically high groundwater flow rates (discussed in Versions 0 and 1 of this document), concluded that the Z-Area saltstone waste form will maintain a reducing environment likely for more than 10,000 years. Obtaining similar conclusions by three extremely 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.

This version differs from version 1 (WSRC-RP-2003-00362, Ver. 1) in that it includes a more rigorous treatment of the movement of oxygenated groundwater into the simulated reducing saltstone. The calculations in version 1, which are included in Appendix A, were designed to provide a first approximation and early guidance, until the more detailed calculations included in this report were available.

2.0 INTRODUCTION

The nominal blend composition of saltstone is 3 wt% lime source, 25 wt% fly ash, 25 wt% slag, and 47 wt% salt solution (Heckrotte 1988). 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 (MMES 1992). Long-term lysimeter studies have shown that the addition of slag into the saltstone formulation essentially stopped technetium-99 leaching, but did not reduce nitrate leaching (MMES 1992).

2.1 OBJECTIVES

The objective of this study was to estimate how long reducing conditions would exist in the saltstone subsurface environment. Ambient conditions in the Z-Area subsurface 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 (O_2) by infiltrating rainwater.

3.0 MODELING

3.1 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),

$$O + e^- = R \qquad (1)$$

where:

O oxidizing agent, meq $e^- L^{-1}$,
R reducing agent, meq $e^- L^{-1}$, 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, $O_2(aq)$, consumes the saltstone reductant (discussed in more detail below in reference to Eq. (3). Once the reduction capacity is exhausted, the saltstone will no longer be able to bind the targeted radionuclides, such as ^{99}Tc (through the reductive precipitation of Tc(VII) to the sparingly soluble Tc(IV) solid). It is important to note, that the theoretical redox potential, i.e., the intensity term to describe the redox status in a system, 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 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:

$$R_{slag} - O_{salt\ solution} = R_{saltstone}, \tag{2}$$

where:

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

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

$$O_{2\,(aq)} + R_{(saltstone)} \rightarrow RO_{2(saltstone)} \tag{3}$$

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$^-$/gram of solid), and
$RO_{2(salstone)}$	oxygenated saltstone (meq e$^-$/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$^-$/cm^3)/yr) for the above reaction (Eq. (1)) is:

$$R_O = k \cdot C_{O2} \cdot C_R \tag{4}$$

where k is the oxidation rate coefficient in units of 1/(yr·meq e$^-$/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. 2004) indicates that oxidation of slag is a fast reaction. Hence, a simplified one-dimensional (vertical direction) saltstone model was initially established to assess the 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, no diffusion. Table 1 shows that by varying *k* values between 1E+03 to 1E+27 1/(yr·meq e^-/cm^3), that the time required for complete consumption of the slag reduction capacity remained fairly constant, ~400 years.

Table 1. Effect of the Oxidation Rate Coefficient, *k*, on the Consumption of Slag Reduction Capacity

k (1/yr ·(meq e^-/cm^3))	**Time for Complete Consumption (yr)**
1E+01	> 1000
1E+02	610
1E+03	380
1E+04	350
1E+05	380
1E+06	386
1E+07	400
1E+08	410
1E+10	421
1E+12	430
1E+15	440
1E+20	460
1E+25	465
1E+26	460
1E+27	386

The oxidation rate coefficient of 1E+06 was selected in the PORFLOW™ 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. Importantly, 1E+06 cm^3/(yr·meq e^-) is a more conservative selection than larger values.

3.2 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 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 the Saltstone performance assessment revision.

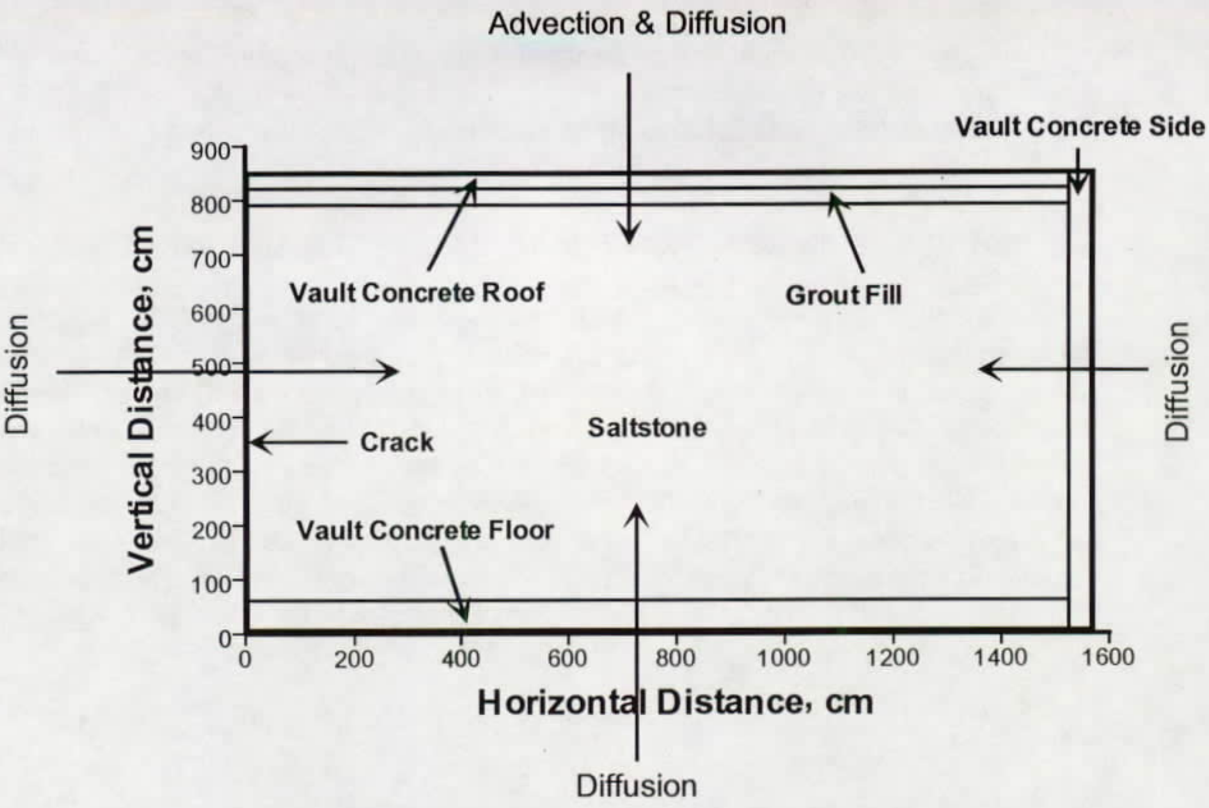

Figure 1. Conceptual Model (Vault is assumed to be cracked in half, i.e., the vault is twice the x-axis. Diagram represents one of the two equally sized vault fragments. Crack is located on the left edge above.)

3.3 ASSUMPTIONS

In addition to the assumptions listed in Appendix A, the following major assumptions were made in the PORFLOW™ simulations:

- Since the final Saltstone design has not been finalized, the problem is currently 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 monolith, which exists as an initial boundary condition (i.e., exists at time zero), the structure of saltstone is intact during the course of 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. Our laboratory has measured

$O_2(aq)$ SRS groundwater concentration that are appreciably lower, barely detectable in subsurface groundwater.

- The saltstone waste is buried in an unsaturated sediment that has an endless supply of $O_2(g)$ to diffuse into the groundwater.

3.4 NUMERICAL MODEL, BENCH MARKING TESTS, AND INPUT VALUES

The PC-based PORFLOW™ Version 4.0 (dated 14 September 2000) was used in these simulations. PORFLOW™ is developed and marketed by Analytic & Computational Research, Inc. to solve problems 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/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. PORFLOW™ has been widely used at the SRS and in the DOE complex to address major issues related to the groundwater and nuclear waste management.

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

$$\frac{\partial C_k}{\partial t} + \frac{\partial}{\partial x_i}(V_i C_k) = \frac{\partial}{\partial x_i}(D_{ij}\frac{\partial C_k}{\partial x_j}) + R_k \qquad (5)$$

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 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 Eq. (4). This equation is written as:

$$\frac{\partial C_{Sk}}{\partial t} = \frac{\partial}{\partial x_i}(D_{ij}\frac{\partial C_{Sk}}{\partial x_j}) + R_{Sk} \qquad (6)$$

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*

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.

Input values used in the PORFLOW™ simulations are listed in Table 2 and Table 3. These values are consistent with those used in the PA revision.

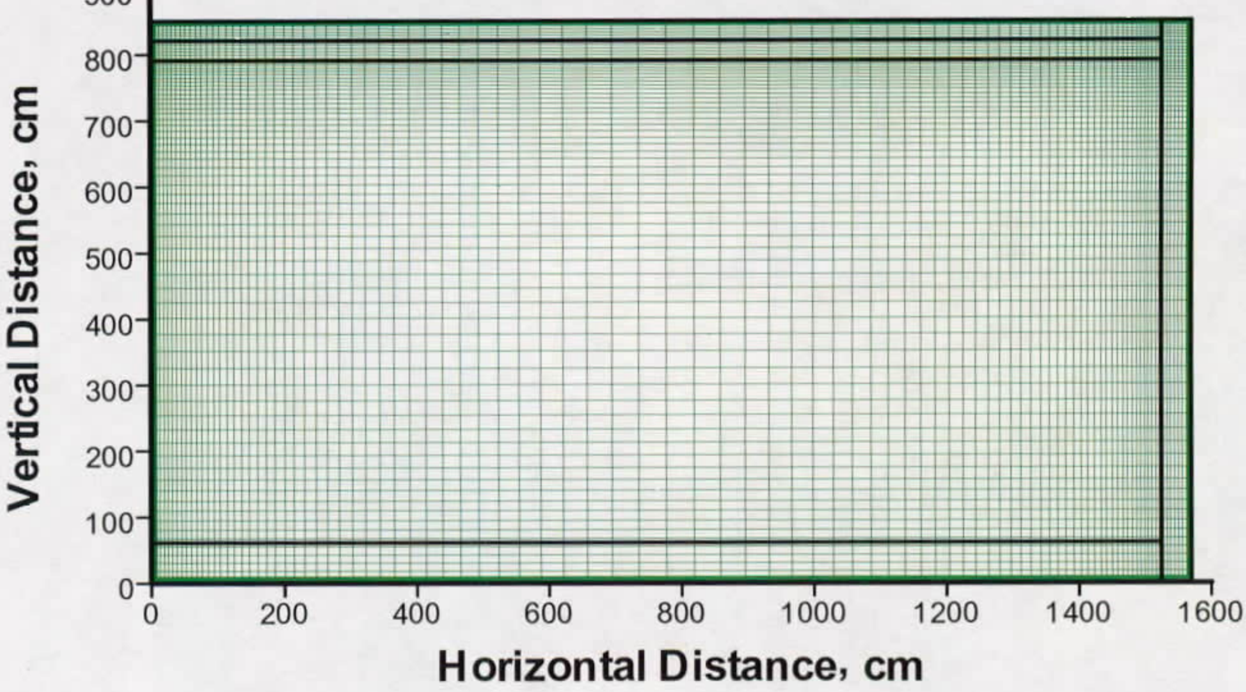

Figure 2. Modeling Grid

PORFLOW™ is capable of modeling chemical reactions. These capabilities were tested by benchmarking the PORFLOW™ results against those obtained from Aspen Custom Modeler™ (ACM), a software package for chemical process modeling provided by Aspen Technology, Inc. The benchmark testing shows excellent agreement between the PORFLOW™ and ACM results. The testing of PORFLOW™ is described in detail in Appendix B. The material properties used in the PORFLOW™ simulations are summarized in Table 2.

Table 2. Model Input Values for Materials

	Vault Concrete	**Grout/Saltstone**
Dry Density (g/cm^3)	2.65	3.148
Porosity	0.18	0.46
Diffusion Coefficient (cm^2/yr)	0.315	0.158
Reduction Capacity (meq e^-/g_{solid}) [a]	9.25E-3	9.25E-03

[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 meq $e^- \cdot [\text{kg slag}]^{-1}$.

Table 3. Input Values Used in Calculations

	Parameter (symbol; units)	**Value**	**Comments/Source**
Grout	Vault & saltstone height made with reducing grout ($D_{saltstone}$; m)	8.51	WSRC-RP-92-1360; p. 2-62, 2-72
	Grout height, saltstone made with reducing grout ($D_{saltstone}$; m)	7.6	WSRC-RP-92-1360; p. 2-62, 2-72
	Saltstone bulk density ($\rho_{saltstone}$; $kg \cdot m^{-3}$)	1.70E+03	WSRC-RP-92-1360; p. 2-56
	Mass Fraction of slag in saltstone (f_{slag}; kg slag · [kg saltstone]$^{-1}$)	0.25	WSRC-RP-92-1360; p. 2-56
	Reduction capacity of slag (C_{slag}; meq e^{-} · [kg slag]$^{-1}$)	37	Measured, see Figure 3; "Reduction Capacity v1.xls"
Water	Infiltration rate - grout/saltstone ($i_{saltstone}$; $m \cdot yr^{-1}$)	0.40	Dependent variable; WSRC-RP-92-1360; p. 2-72
	Infiltration rate - soil (i_{soil}; $m \cdot yr^{-1}$)	0.40	Dependent variable; Estimate WSRC-RP-92-1360; p. 2-72
	Porosity - vault/saltstone ($\eta_{saltstone}$; vol water · [vol saltstone]$^{-1}$)	0.46	email "saltstone" 21April03, Jim Cook (WSRC)
	Porosity - soil (η_{soil}; m^3 water · [m^3 total]$^{-1}$)	0.46	Average of several materials used in hydraulic barrier
	Volume of infiltrating water/yr – vault-saltstone/yr (L · [yr-m^2]$^{-1}$)	184	Calculated from infiltration rate and porosity
	Volume of infiltrating water/yr – soil (L · [yr-m^2]$^{-1}$)	184	Calculated from infiltration rate and porosity
	Henry's Law Constant for O_2 ($mol \cdot atm^{-1}$)	1.26E-03	Stumm and Morgan (1996); p. 214
	O_2 concentration in air (atm)	2.10E-01	CRC Handbook; 65th Ed.
	O_2 concentration in groundwater (M)	2.65E-04	Near identical to measured values [a]
	O_2 electron equiv. in groundwater ($C_{infiltrating\ groundwater}$; meq e- · L^{-1})	1.06E+00	4 electrons per O_2 molecule [a]
Soil	Soil Cover Depth (D_{soil}; m)	2.90E+00	WSRC-RP-92-1360; p. 2-71
	Soil Reduction Capacity (C_{soil}; meq e- · [kg soil]$^{-1}$)	5.10E+00	Measured, see Figure 3; "Reduction Capacity v1.xls"
	Soil Bulk Density (ρ_{soil}; $kg \cdot m^{-3}$)	1.50E+03	Dragun 1998; p. 10
	Soil Reduction Capacity (C_{soil}; meq e- · [m^3 soil]$^{-1}$)	7.65E+03	

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

Table 4. Estimation of Oxidation Capacity of Salt Solution Based on Oxidizing Constituents (Used in Equation 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**
nitrates	>2.00E+00			Nitrate leaches from lysimeters, thus not reduced by slag
Na_2CrO_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_2MoO_4	3.61E-04	2.00E+03	7.22E-01	Mo(VI) to Mo(IV)
Na_2SO_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 from ITP & ETF (Table 2.3-3 in WSRC-RP-92-1360; page 2-41)

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

4.0 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 collected from the Barnwell/McBean formation, the geological formation where the Z-Area Saltstone Disposal Facility is located. The reduction capacity of the sediment was not used in these calculations, but was used in the preliminary advection calculations presented in Appendix A. Following is a detailed description of the procedure adapted from Lee and Batchelor (2003).

4.1 MATERIALS

1. Z-100 Slag: Provided by Chris Langton, who in turn got it directly from the Saltstone Silos.
2. Glovebag
3. 1000-mL 10 mM $NaHCO_3$: Add 0.84 g $NaHCO_3$ (F.W. = 84) to a 1-L volumetric flask and then bring it up to volume with water.
4. 100-mL 51.5 mM Cr(VI) in 10 mM $NaHCO_3$: Place 1.000 g of K_2CrO_4 (F.W. = 194.2) in a 100-mL volumetric flask and then bring up to volume with 10 mM $NaHCO_3$.
5. 100-mL 1 *M* H_2SO_4: Add 50-mL water to 100-mL volumetric flask. Then add 5.58 mL of concentrated H_2SO_4 to water. Bring to volume with water.
6. 100-mL 1 M NaOH: Add 4-g NaOH (FW = 40) to a 100-mL volumetric flask and bring up to volume with water.
7. Na_2SO_4: Pre-weigh 6 aliquots into weighing boats containing 0.142 g of Na_2SO_4
8. 9 50-mL centrifuge tubes
9. Minilysimeter sediment, a sandy loam soil described in Hawkins (1982).

4.2 METHOD

1. Label 9 tared 50-mL centrifuge tubes as described in Table 5.
2. Add 1.00 g slag to Tubes #21, #22, and #23. Add 1.00 g Minilysimeter sediment to Tubes #27, #28, and #29. Only liquid will go into the 3 controls, Tubes #24, #25, and #26. Record weight to Table 5.
3. Place tubes, solutions #3, #4, #5, and #6, six 0.142-g Na_2SO_4 aliquots, and litmus paper into glovebag for 2 days before proceeding to next step. After one day in the glovebag stir things up to help O_2 gas diffuse out of solids and liquids.
4. Add 10 mL of the 51.5-mM Cr(VI) in 10-mM $NaHCO_3$ solution to each tube.
5. Adjust the pH of each tube to 7 ± 1 by adding NaOH or H_2SO_4.
6. Shake by hand every ~3 hours for 1 day.
7. Add 0.142-g Na_2SO_4 aliquots to each tube.
8. Shake and leave in bag for >0.5 days.
9. Pull tubes out of glovebag, record weight of "tube + solid + liquid" on Table 5, centrifuge, and pass through a 0.45-μm filter.
10. Send to ADS for Cr analysis by ICP-ES.

Table 5. Sample Descriptions and Weights Used to Measure Reduction Capacity (Example Data Table)

ID	Description	Tube Tare Wt (g)	Tube + Solid wt (g)	Tube + solid + liquid (g)
21	Slag, Rep. 1			
22	Slag, Rep. 2			
23	Slag, Rep. 3			
24	Control (just liquid), Rep. 1			
25	Control (just liquid), Rep. 2			
26	Control (just liquid), Rep. 3			
27	Sediment, Rep. 1			
28	Sediment, Rep. 2			
29	Sediment, Rep. 3			

5.0 RESULTS

5.1 LABORATORY MEASUREMENTS

Laboratory measurements of the reducing capacity of an SRS sediment and slag are presented in Figure 3. 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. By way of comparison, Lee and Batchelor (2003) 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 Figure 3.

Also shown in Figure 3 are the reduction potential (Eh) values of 1:1 solid:water suspensions. Reduction potential is an intensity term, i.e., it does not express the total concentration of reducing agents in a system, instead it provides an estimate of the concentration of reducing agents in solution in equilibrium with a solid. Alternatively, and less accurately, it can be thought of as a measurement of the free electron activity, as defined in Eq. (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. (2002) reported that metallic iron (Fe^0) had a reduction capacity of -173 ± 6 mV. This value is consistent with the slag reduction potential value reported in Figure 3.

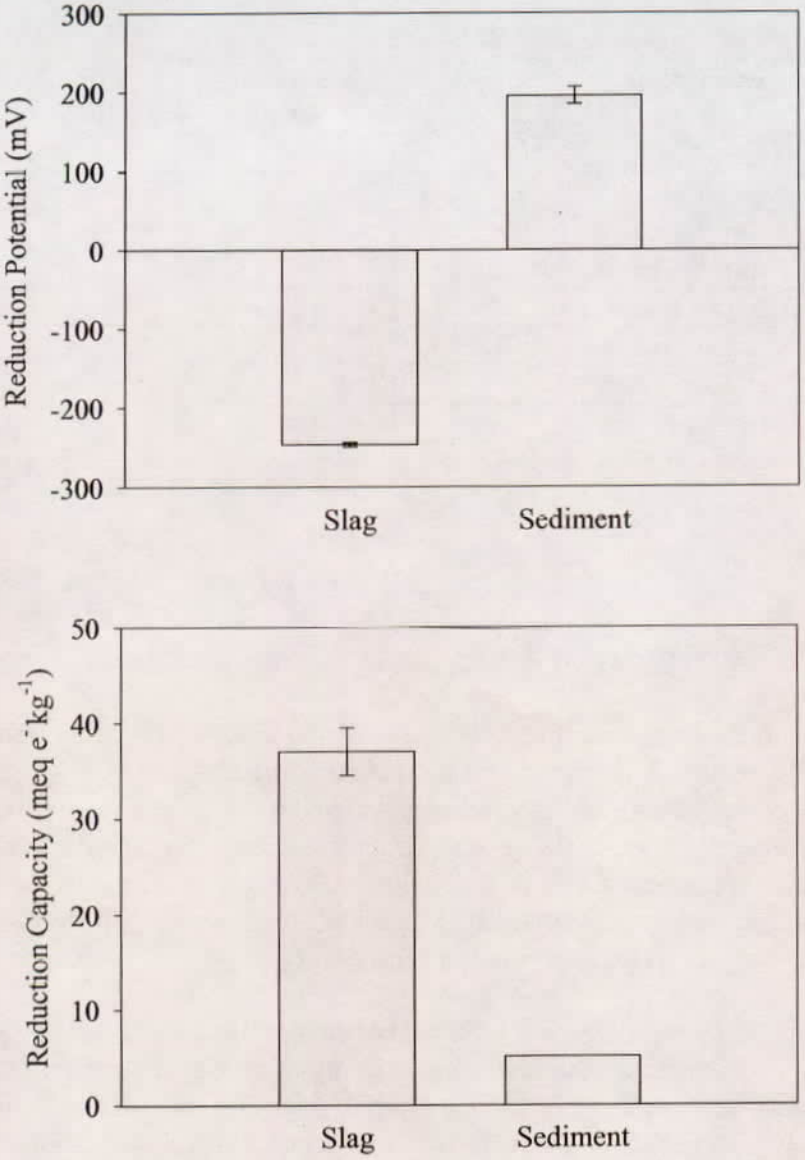

Figure 3.. Reduction Potential and Reduction Capacity of an SRS Subsurface Sediment and the Slag Used to Make Saltstone

5.2 MODELING

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 4 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 5. These data were determined by using the two dimensional PORFLOW™ calculations and the modeling grid presented in Figure 1. Once the final configuration of the saltstone facility has been completed, the values presented in Figure 1 will have to be modified to represent the third dimension. It is expected that these corrections will result in only slight changes in Figure 5.

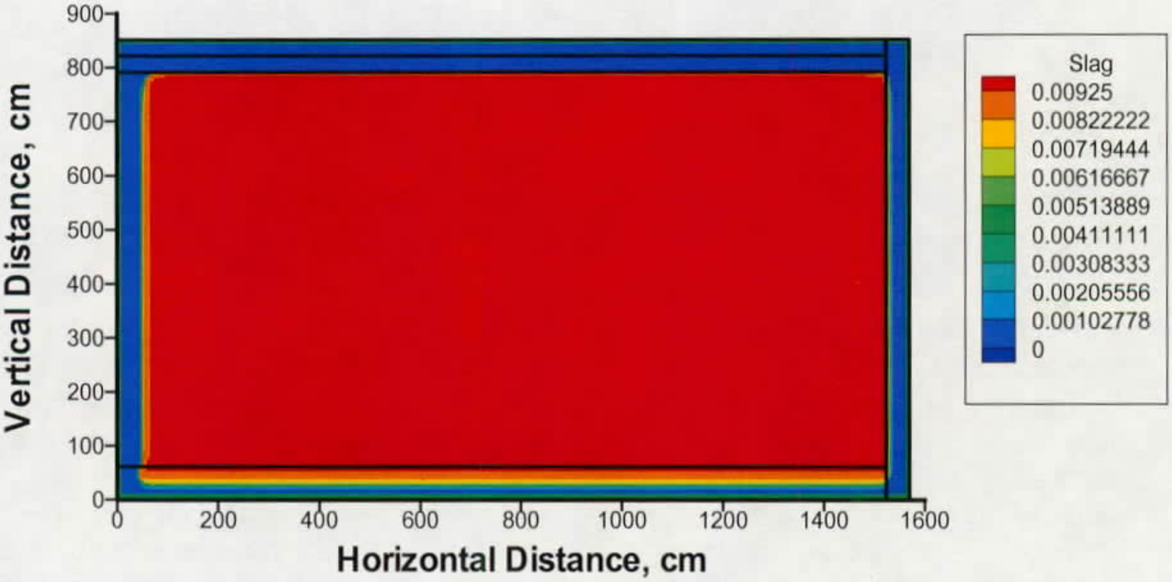

Figure 4. Simulation Result at 250,000 Years (Units in meq e^-/g_{solid}). Red Indicates no Oxidation of Saltstone Occurred and Blue Indicates that Full Oxidation of the Saltstone Occurred.

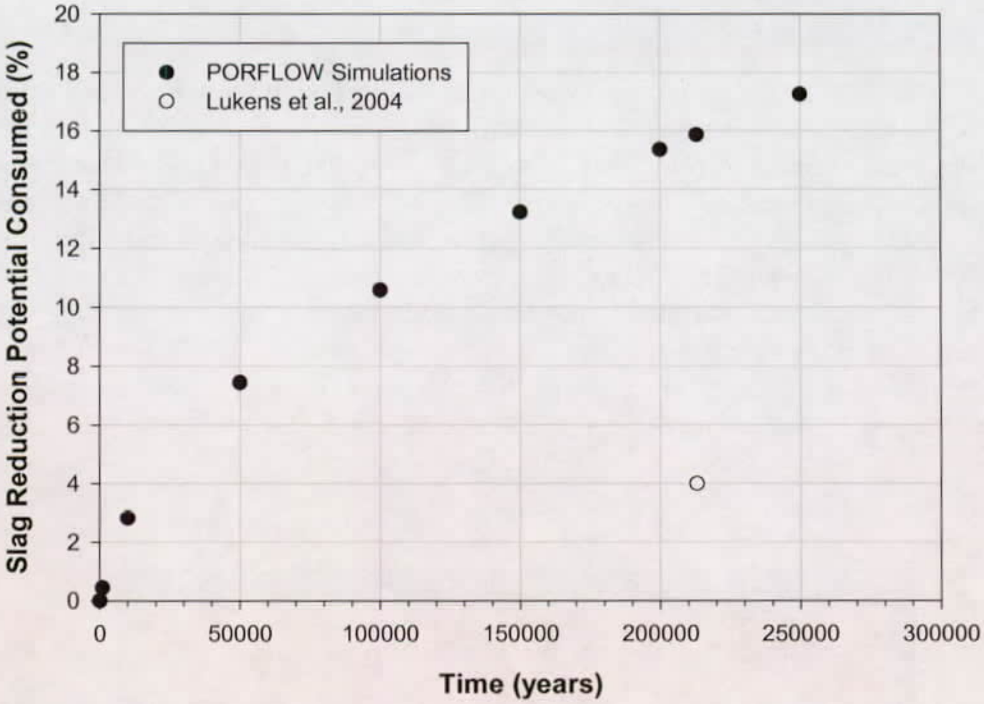

Figure 5. Consumption of Slag Reduction Potential by Oxygen in Infiltrating Water

In Figure 6, the penetration depth is plotted vs. time for all sides. These data can be used to adjust the data in Figure 5 to be consistent with the final dimensions of the saltstone facility. The penetration depth is defined as the distance in the saltstone where oxidation occurred, i.e., the reduction capacity was <9.25E-3 meq e^-/g_{solid}. The penetration depth at the midpoint of the side is presented in Figure 6. 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 6 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 2, hence, resulting in different diffusion pattern.

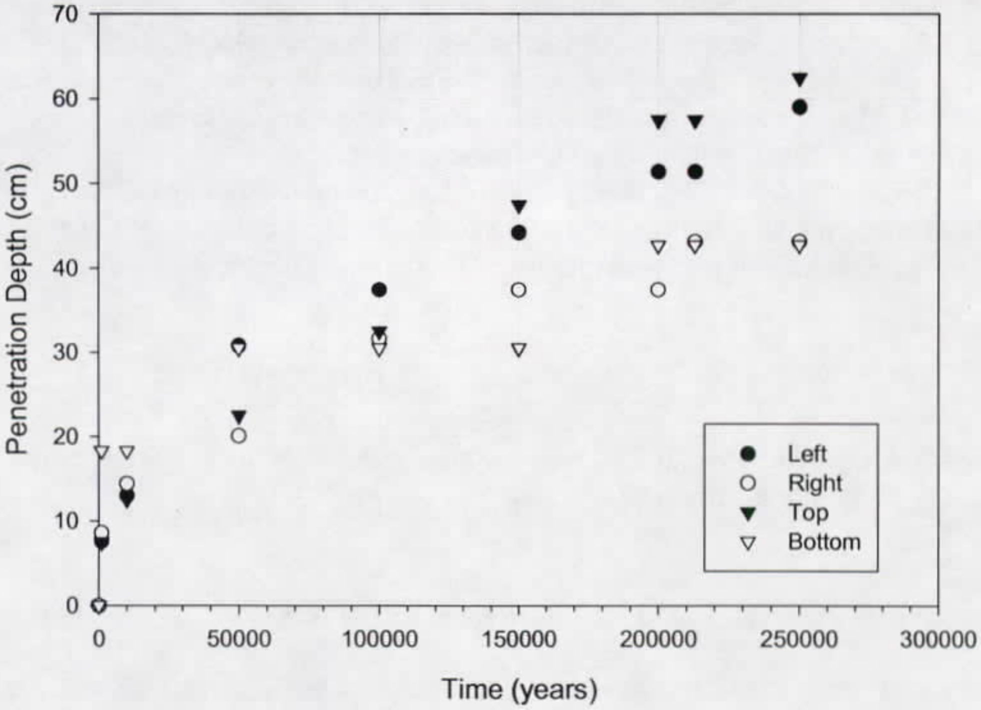

Figure 6. Penetration Depth

6.0 DISCUSSION

There have been two other recent calculations of the longevity of the reducing conditions of the SRS Saltstone waste form. The first was described in the first version of this document and is included in Appendix A. It provided a first approximation 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 in this calculation were that 1) the waste form crumbled at time zero into infinitely small particles that all the reductant was immediately available for oxidation, and 2) that 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 calculation, 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

5 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%.

In summary, obtaining similar conclusions by three extremely 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.

7.0 ACKNOWLEDGEMENTS

We thank Cathy Coffey (WSRC) for her help in the laboratory and Jeff Serne (PNNL) for helpful discussions during various stages of this project.

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9.0 APPENDIX A: CALCULATIONS PRESENTED IN VERSION 1 OF THIS DOCUMENT (WSRC-RP-2003-00362, VER. 1): PRELIMINARY ADVECTION MODEL

9.1 APPROACH: PRELIMINARY ADVECTION MODELING

An equivalent mass balance was conducted to calculate the duration that the Z-Area Saltstone Disposal Facility would remain reduced (Figure 7). Electron equivalents are the units used to describe the concentration (more precisely, the activity) of free electrons that can participate in an oxidiation-reduction, or redox, reaction. The generalized redox equation is presented in Eq A1-1.

$$O + e^{-} = R \qquad \text{(A1-1)}$$

where:

O = oxidizing agent, meq e^{-} L^{-1},
R = reducing agent, meq e^{-} 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 consumes the saltstone reductant. Once the reduction capacity is exhausted, the saltstone will no longer be able to bind the targeted radionuclides, such as technetium-99, in the less mobile reduced form. It is important to note, that theoretically the redox potential, i.e., the intensity term to describe the redox status in a system, 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 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.

For these calculations, it was assumed that the reducing capacity of the saltstone equaled that provided by the slag and the overlying geological material in the moisture barrier. The 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. Once the cumulative amount of oxidizing agent equaled the reducing capacity of the slag and overlying moisture barrier, the capacity of the saltstone to chemically (as opposed to physically) immobilize reducible radionuclides was assumed to be exhausted. The mass balance equation describing these reactions is presented in equation A1-2.

$$O_{infiltrating\ groundwater} + O_{salt\ solution} = R_{soil} + R_{slag} \qquad \text{(A1-2)}$$

where:

$O_{infiltrating\ groundwater}$ = electron equivalents of oxidizing agent from infiltrating groundwater, meq e^{-} m^{-2},
$O_{salt\ solution}$ = electron equivalents of oxidizing agent from salt solution, meq e^{-} m^{-2},

R_{soil} = electron equivalents of reducing agent from soil, meq e^- m^{-2},

R_{slag} = electron equivalents of reducing agent from slag, meq e^- m^{-2}.

The important assumption made for these calculations are presented in Table 6.

Table 6. Important Assumptions for the Preliminary Advection Model

1	The system is well mixed, such that all saltstone reductants at 100% efficiency are available for oxidation by infiltrating water. 100% efficiency of oxygen reducing the slag will not happen; some of the oxygen will not react or will be channeled past reducing areas, thereby leaving some Tc in the reduced form. This is perhaps the most conservative assumption; however, it is necessary because there is no data quantifying the efficiency of this reaction.
2	Formulation of saltstone and especially the concentration of slag remains the same for all saltstone waste forms.
3	No formation of hardened coatings on saltstone to impede oxidation of slag by oxygenated infiltrating water. These will form, thus this is a conservative assumption.
4	Reduction capacity of native soil equals that of moisture barrier. Since the design of the barrier has not been finalized, it is not clear whether this assumption is conservative. As the moisture barrier ages, its reduction capacity will approach that of the native soil. The 2:1 clays commonly used in geosynthetic clay liners will likely have higher reduction capacities than SRS soils.
5	Chromium(VI/III) redox couple used in the reduction capacity measurement is similar to that of groundwater oxygen(0/-II). Chromium standard reduction potential is more negative, hence the measurement underestimates the reduction capacity of the saltstone and native soil, with respect to oxygen. Again, this assumption is conservative because if an oxygen(0/II) probe molecule had been used in the measurement, the reducing capacity of the slag and native soil would have been higher, thereby increasing the estimated longevity of the reducing grout.
6	As a first approximation, important transport processes know to exist in saltstone, such as diffusion, advection and dispersion, were not included in these calculations. Instead the system was conceptualized as a large batch reactor in which oxygenated water was incrementally added. This is likely a conservative assumption, however, a more accurate prediction of the phenomena could be obtained through the inclusion of water and O_2 transport processes along with the chemical reactions used in these calculations.

The electron equivalents of oxidizing agent from infiltrating rainwater was assumed to be equal to that provided by dissolved oxygen. Dissolved oxygen concentrations were set equal to 2.65E-4 *M*, a value calculated using Henry's Law and one that is quite similar to those commonly measured in SRS surface sediment porewater (Kaplan and Serkiz 2000). The amount of oxygenated groundwater that came into contact with the saltstone was estimated using infiltration rate and porosity (equation A1-3).

$$O_{infiltrating\ groundwater} = C_{infiltrating\ groundwater} \times 1000 \times i_{saltstone} \times \eta_{saltstone} \times t \qquad \text{(A1-3)}$$

where

$O_{infiltrating\ groundwater}$ = electron equivalents of oxidizing agent from infiltrating groundwater, meq $e^- m^{-2}$,
$C_{infiltrating\ groundwater}$ = oxidant concentration in groundwater, meq $e^- L^{-1}$,
1000 = conversion factor, L m^{-3},
$i_{saltstone}$ = saltstone infiltration rate, m yr^{-1},
$\eta_{saltstone}$ = saltstone porosity, $m^3 m^{-3}$, and
t = time, yr.

The electron equivalents of oxidizing agent in the salt solution were based on the concentration of constituents that are likely reduced by the slag in the nominal blend of ITP and ETF feed solutions at 8:1 mixing (Heckrotte 1988). Molybdenum and chromate in the salt solution were considered reducible. Nitrate and sulfate in the salt solution were not considered reducible because nitrates have been shown to leach from saltstone lysimeters and sulfate is not reduced in grout (MMES 1992). There were several trace constituents, including several radionuclides (e.g., cobalt, iodine, plutonium, and technetium) that were not included in these calculations because their concentrations are extremely low. Their sum contribution to the saltstone electron equivalents is <0.001 wt%. The details for calculating the total concentration of oxidizing agents is presented in Table 4 and the mass balance equation is presented in equation A1-4.

$$O_{salt\ solution} = C_{salt\ solution} \times 1000 \times 1/\rho_{salt\ solution} \times f_{salt\ solution} \times \rho_{saltstone} \times D_{saltstone} \qquad \text{(A1-4)}$$

where

$O_{salt\ solution}$ = electron equivalents of oxidizing agent from salt solution, meq $e^- m^{-2}$,
$C_{salt\ solution}$ = oxidizing constituents concentration in salt solution, meq $e^- L^{-1}$,
1000 = conversion factor, L m^{-3},
$f_{salt\ solution}$ = weight fraction of salt solution in saltstone, kg kg^{-1},
$\rho_{salt\ solution}$ = density of salt solution, kg m^{-3},
$\rho_{saltstone}$ = density of saltstone, kg m^{-3}, and
$D_{saltstone}$ = saltstone height, m.

The reduction capacity of the geological materials above the vaults, R_{soil}, was calculated using Eq. A1-5. R_{soil} was calculated using a value, C_{soil}, measured from a McBean/Barnwell formation sediment, the same geologic formation as the Z-Area Saltstone

Disposal Facility. Being a measured value, as oppose to a calculated value, provides added credibility to it. At this writing, the design for the moisture barrier has not been finalized, but it will likely contain a number of different layered materials. The use of only the one native sediment to approximate these various materials provides a reasonable long term average, and not necessarily a conservative value. More details about this measurement are provided in the next section, Section Laboratory Measurements of Reduction Potential.

$$R_{soil} = C_{soil} \text{ x } \rho_{soil} \text{ x } D_{soil} \qquad \text{(Eq. A1-5)}$$

where

R_{soil} = reduction capacity of soil, meq e^{-} m^{-2}.
C_{soil} = reduction capacity of soil, meq e^{-} kg^{-1},
ρ_{soil} = density of soil, kg m^{-3}, and
D_{soil} = soil height, m.

The value used in these calculations for the reduction capacity of the slag, R_{slag}, was based on a laboratory measurement (described in more detail in the next section, Section Section Laboratory Measurements of Reduction Potential.).

$$R_{slag} = C_{slag} \text{ x } \rho_{saltstone} \text{ x } f_{slag} \text{ x } D_{saltstone} \qquad \text{(Eq. A1-6)}$$

where

R_{slag} = reduction capacity of slag, meq e^{-} m^{-2}.
C_{slag} = reduction capacity of slag, meq e^{-} kg^{-1},
$\rho_{saltstone}$ = density of saltstone, kg m^{-3},
f_{slag} = weight fraction of slag in saltstone, kg kg^{-1}, and
$D_{saltstone}$ = saltstone height, m.

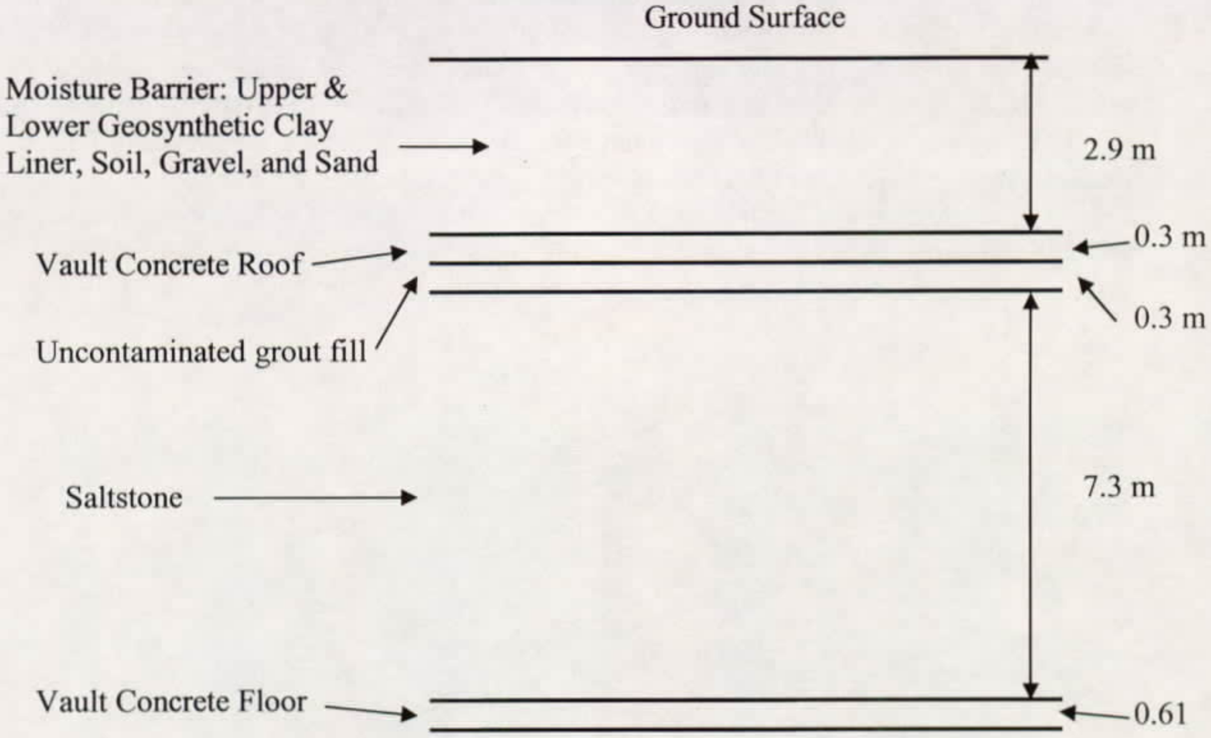


Figure 7. Schematic Representation of the Saltstone System Described by the Preliminary Advection Model

9.2 RESULTS: PRELIMINARY ADVECTION MODELING

At this writing, the infiltration rates to be used for the various layers at the disposal site (Figure 7) have not been finalized. So to calculate the reducing lifespan of the saltstone system, infiltration rate was used as a dependent variable (Figure 8). Figure 8 shows that the reducing lifespan, if limited by the infiltration rate of the intact saltstone vault (2.54E-07 m yr^{-1}; Phifer 2003), would be 1.29 billion years. Obviously, this infiltration rate will not last for such a long duration because the saltstone vaults will have physically degraded. At the other extreme, the reducing lifespan, if limited by the infiltration rate of intact sediment (0.4 m yr^{-1}; MMES 1992), would be 800 years. This latter scenario is akin to assuming that water will flow through the moisture barrier and vaults at the same rate as water flows through native sediment. A more likely and still reasonably conservative estimate is to assume that the upper geosynthetic clay liner will eventually degrade and then water will flow through the vault at a rate limited by the lower geosynthetic clay liner, 0.0016 m yr^{-1} (Phifer 2003). At this rate, the reducing lifespan of the vault system would be 180,000 years.

Regardless of the infiltration rate, the reducing capacity of the saltstone will account for 77% of the total reducing capacity, whereas the overlying moisture barrier (assumed to have the reducing capacity of native sediment) will account for 14%, and the vault, made from reducing grout, will account for 9% of the total reducing capacity (Figure 9). Thus, relatively little reducing capacity is gained by including slag in the vault cement. The data presented in Figure 8 assumed that the system contained a reducing grout vault. To assume that the vault was not made with reducing grout, all the values shown in Figure 8 would be reduced by 9%. Native sediment offers a relatively large amount of reduction capacity. But it is important to distinguish between capacity, in units of meq $e^- L^{-1}$ and intensity, in units of mV. SRS soil has been shown to reduce oxygen (O_2; Kaplan and Serkiz 2000) and chromate (CrO_4^{2-}; Kaplan and Serkiz 2000), but not pertechnetate (TcO_4^-; Kaplan 2003) or iodide (I^-; Kaplan 2003). So although SRS soils have a measurable reduction capacity, the resulting reduction potential is not sufficiently low to reduce pertechnetate or iodide. Therefore, it would be incorrect to assume that the reducing capacity of the soil beneath the vaults would offer additional protection against pertechnetate or iodide migration.

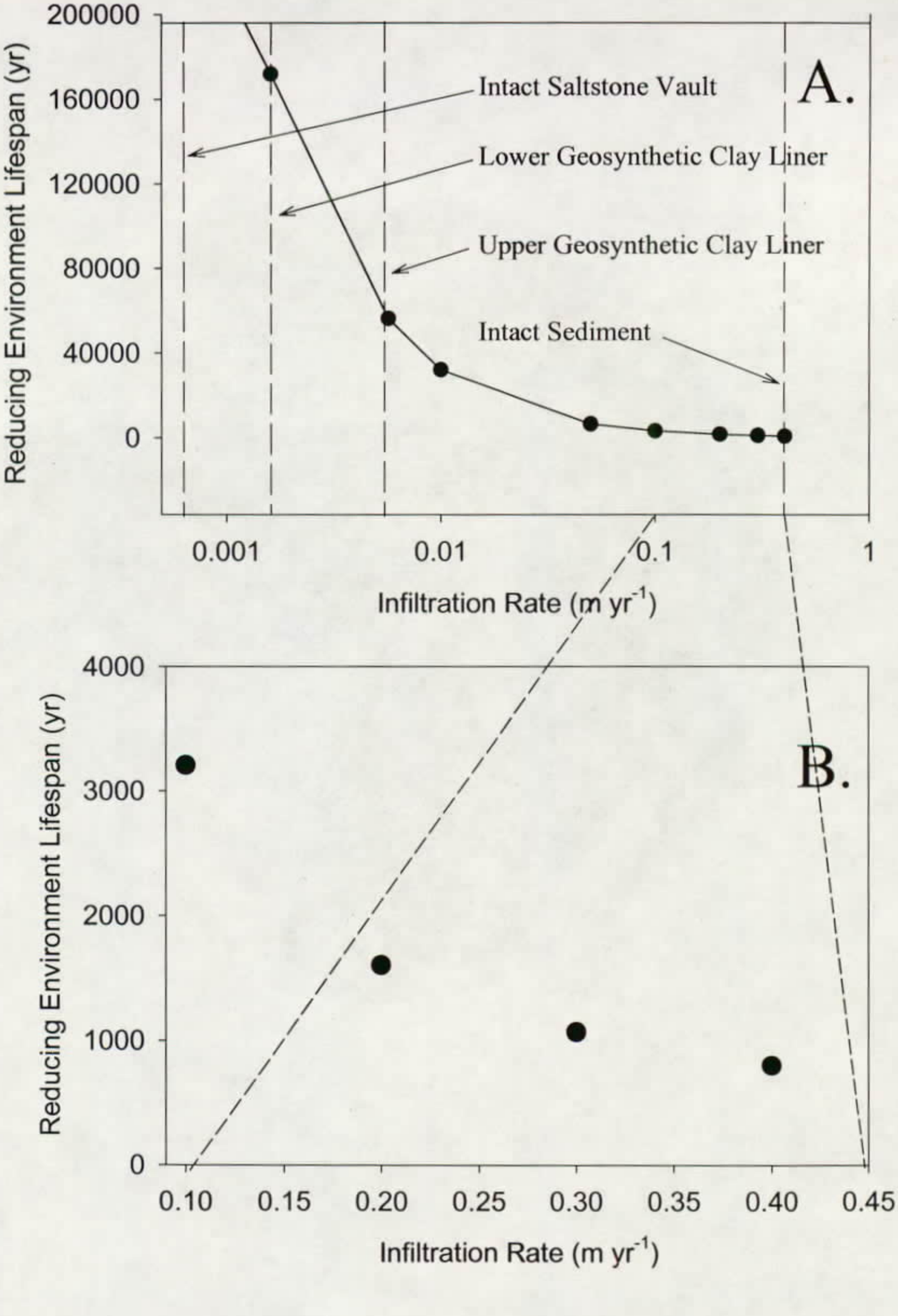


Figure 8. Infiltration Rate Versus Years Until System Becomes Oxidized: (A) Identifies the Infiltration Rates of the Intact Saltstone Vault, Lower Geosynthetic Clay Liner, Upper Geosynthetic Clay Liner, and Intact Sediment; (B) Close up of the Data

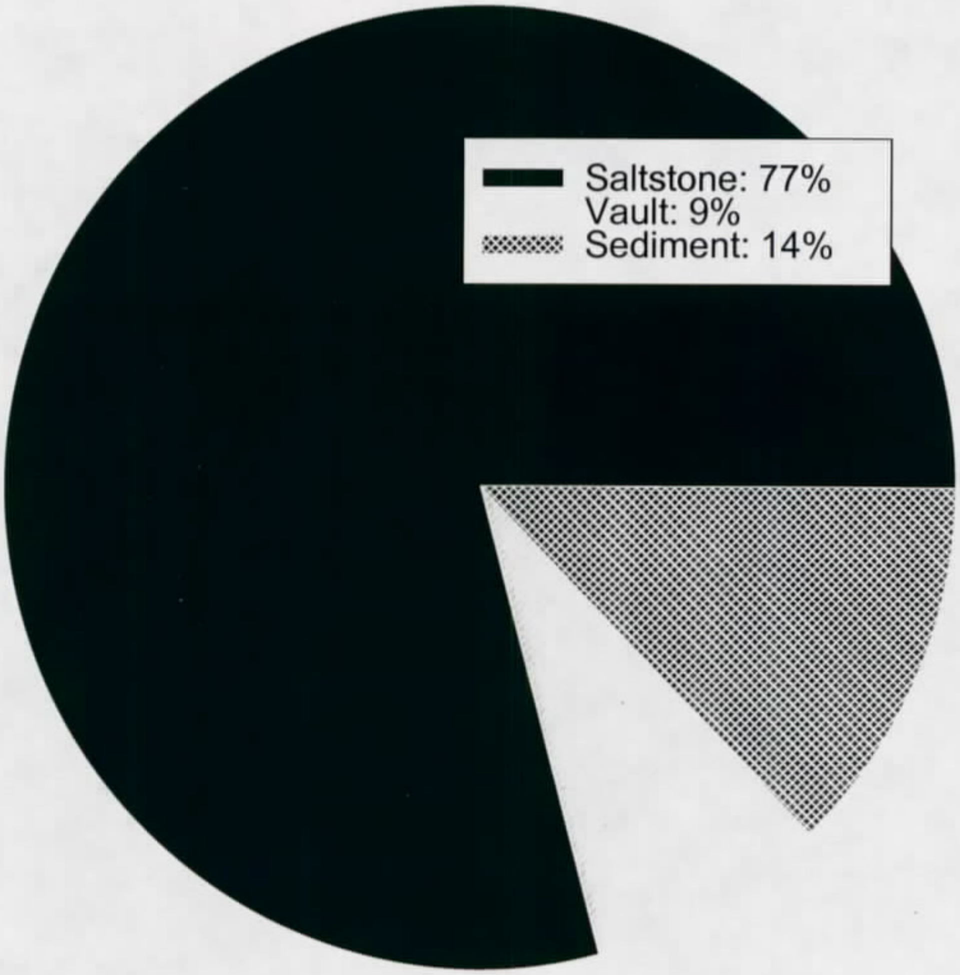


Figure 9. Mass Balance of Reduction Capacity in the Saltstone Disposal Facility

10.0 APPENDIX B: TESTING OF PORFLOW™

10.1 TESTING OF PORFLOW™

PORFLOW™ provides capabilities to model chemical reactions. These capabilities were tested by benchmarking the PORFLOW™ results against those obtained from Aspen Custom Modeler™ (ACM), a software package for chemical process modeling provided by Aspen Technology, Inc. ACM has been extensively used to model major facilities at the SRS.

Two test cases relevant to the reactions considered in the current study were set up. In the first test case, a species A in the liquid phase precipitates to the solid species B. In the second case, a species A in the liquid phase reacts with a solid species B to form a solid species C. The two test cases show excellent agreement between the PORFLOW™ and ACM results.

10.1.1 Test Case 1

$A_{liquid} \rightarrow B_{solid}$

Reaction rate: 0.01 C_A
Porosity: 0.4
Total volume: 1 cm^3
Liquid volume: 0.4 cm^3
Solid volume: 0.6 cm^3
Liquid density: 1.5 g/cm^3
Solid density: 2.65 g/cm^3
Initial C_A: 1.06 $mol/cm^3{}_{liquid}$

Time (hours)	PORFLOW C_A ($mol/cm^3{}_{liquid}$)	ACM C_A ($mol/cm^3{}_{liquid}$)	PORFLOW C_B (mol/g_{solid})	ACM C_B (mol/g_{solid})
0	1.06000000E+00	1.0600000E+00	0.00000000E+00	0.0000000E+00
1	1.04940563E+00	1.0495141E+00	2.66534451E-03	2.6379728E-03
2	1.03897671E+00	1.0390702E+00	5.28919199E-03	5.2653480E-03
3	1.02863923E+00	1.0287288E+00	7.89007512E-03	7.8669729E-03
4	1.01840461E+00	1.0184906E+00	1.04650803E-02	1.0442626E-02
5	1.00827182E+00	1.0083552E+00	1.30144651E-02	1.2992401E-02
6	9.98239845E-01	9.9831744E-01	1.55384843E-02	1.5517625E-02
7	9.88307687E-01	9.8838026E-01	1.80373903E-02	1.8017545E-02
8	9.78474350E-01	9.7854366E-01	2.05114330E-02	2.0492160E-02
9	9.68738852E-01	9.6880619E-01	2.29608599E-02	2.2941839E-02
10	9.59132068E-01	9.5915966E-01	2.53779021E-02	2.5368640E-02

10.1.2 Test Case 2

$A_{liquid} + B_{solid} \rightarrow C_{solid}$

Reaction rate: 0.01 C_A C_B
Porosity: 0.4
Total volume: 1 cm^3
Liquid volume: 0.4 cm^3
Solid volume: 0.6 cm^3
Liquid density: 1.5 g/cm^3
Solid density: 2.65 g/cm^3
Initial C_A: 1.06 $mol/cm^3{}_{liquid}$
Initial C_B: 9.25 mol/g_{solid}

Time (hours)	PORFLOW C_A ($mol/cm^3{}_{liquid}$)	ACM C_A ($mol/cm^3{}_{liquid}$)	PORFLOW C_B (mol/g_{solid})	ACM C_B (mol/g_{solid})
0	1.06000000E+00	1.06000000E+00	9.25000000E+00	9.25000000E+00
1	9.66052207E-01	9.66507790E-01	9.22636393E+00	9.22647990E+00
2	8.81069383E-01	8.81395690E-01	9.20498501E+00	9.20506810E+00
3	8.03632649E-01	8.03980640E-01	9.18550446E+00	9.18559260E+00
4	7.33138278E-01	7.33495440E-01	9.16777036E+00	9.16786050E+00
5	6.68941042E-01	6.69304190E-01	9.15162038E+00	9.15171170E+00
6	6.10459488E-01	6.10825020E-01	9.13690827E+00	9.13700000E+00
7	5.57169007E-01	5.57533610E-01	9.12350204E+00	9.12359340E+00
8	5.08595759E-01	5.08958140E-01	9.11128251E+00	9.11137310E+00
9	4.64311325E-01	4.64663470E-01	9.10014190E+00	9.10022980E+00
10	4.24056243E-01	4.24258730E-01	9.09001490E+00	9.09006510E+00

11.0 APPENDIX C: DESIGN CHECK INSTRUCTIONS AND REVIEW

Design Check Instructions to Robert Hiergesell (Geo-Modeling Group)

Perform a design check for the report, *Estimated Duration of the Subsurface Reducing Environment Produced by the Z-Area Saltstone Disposal Facility (U), WSRC-RP-2003-00362, Rev. 2*, following the general guidance provided in WSRC-IM-2002-00011, Rev.1.

Specific instructions for this design check are as follows:

1. Check the overall modeling approach to judge if it is reasonable.
2. Check to ensure that the INPUTS are correct for the following:
    a. Dimensions of the Saltstone shown in Figure 1 and Figure 2 are accurately transcribed into the PORFLOW™ input files.
    b. Material and transport properties as shown in Table 2 are accurately transcribed into the PORFLOW™ input files.
3. Check to ensure that the OUTPUTS are correct for the following:
    a. Spot check mass balance information produced by PORFLOW™ simulations.
    b. Check that Figure 5 and Figure 6 correctly represent the output data.

Design Check Instructions to Kim Powell (Waste Processing Technology Group)

Perform a design check for the report, *Estimated Duration of the Subsurface Reducing Environment Produced by the Z-Area Saltstone Disposal Facility (U), WSRC-RP-2003-00362, Rev. 2*, following the general guidance provided in WSRC-IM-2002-00011, Rev.1.

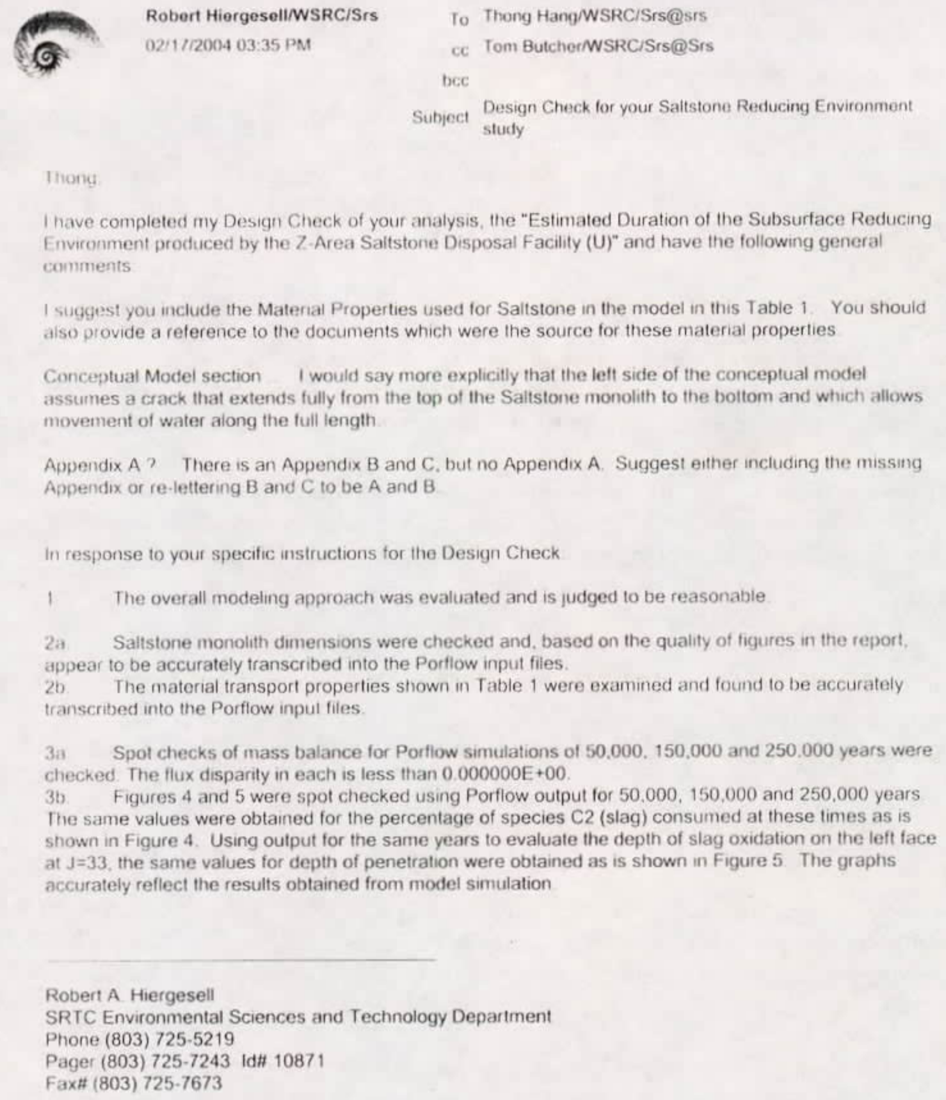
Specific instructions for this design check are as follows:

1. Check the scientific logic, especially with the description of the models and the assumptions.
2. Check that the calculations are in fact conservative, where we state they are.
3. Check grammar, clarity, data presentation, and appropriate use of graphics.
4. Check interpretation and conclusions are supported by data
5. Be aware that we have asked Robert Hiergessell to conduct the following design check to supplement your design check.

> Perform a design check for the report, *Estimated Duration of the Subsurface Reducing Environment Produced by the Z-Area Saltstone Disposal Facility (U), WSRC-RP-2003-00362, Rev. 2*, following the general guidance provided in WSRC-IM-2002-00011, Rev.1.
>
> Specific instructions for this design check are as follows:
>
> 1. Check the overall modeling approach to judge if it is reasonable.
> 2. Check to ensure that the INPUTS are correct for the following:

    a. Dimensions of the Saltstone shown in Figure 1 and Figure 2 are accurately transcribed into the PORFLOW™ input files.
    b. Material and transport properties as shown in Table 2 - 3 are accurately transcribed into the PORFLOW™ input files.
3. Check to ensure that the OUTPUTS are correct for the following:
    a. Spot check mass balance information produced by PORFLOW™ simulations.
    b. Check that Figure 5 and Figure 6 correctly represent the output data.

Bob Hiergesell's Design Check



Robert Hiergesell/WSRC/Srs
02/17/2004 03:35 PM

To Thong Hang/WSRC/Srs@srs
cc Tom Butcher/WSRC/Srs@Srs
bcc
Subject Design Check for your Saltstone Reducing Environment study

Thong:

I have completed my Design Check of your analysis, the "Estimated Duration of the Subsurface Reducing Environment produced by the Z-Area Saltstone Disposal Facility (U)" and have the following general comments.

I suggest you include the Material Properties used for Saltstone in the model in this Table 1. You should also provide a reference to the documents which were the source for these material properties.

Conceptual Model section ... I would say more explicitly that the left side of the conceptual model assumes a crack that extends fully from the top of the Saltstone monolith to the bottom and which allows movement of water along the full length.

Appendix A ? There is an Appendix B and C, but no Appendix A. Suggest either including the missing Appendix or re-lettering B and C to be A and B.

In response to your specific instructions for the Design Check:

1. The overall modeling approach was evaluated and is judged to be reasonable.

2a. Saltstone monolith dimensions were checked and, based on the quality of figures in the report, appear to be accurately transcribed into the Porflow input files.
2b. The material transport properties shown in Table 1 were examined and found to be accurately transcribed into the Porflow input files.

3a. Spot checks of mass balance for Porflow simulations of 50,000, 150,000 and 250,000 years were checked. The flux disparity in each is less than 0.000000E+00.
3b. Figures 4 and 5 were spot checked using Porflow output for 50,000, 150,000 and 250,000 years. The same values were obtained for the percentage of species C2 (slag) consumed at these times as is shown in Figure 4. Using output for the same years to evaluate the depth of slag oxidation on the left face at J=33, the same values for depth of penetration were obtained as is shown in Figure 5. The graphs accurately reflect the results obtained from model simulation.

Robert A. Hiergesell
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Fax# (803) 725-7673

Kim Powell's Design Check

Kim Powell/WSRC/Srs

02/20/2004 08:43 PM

To:	Daniel Kaplan/WSRC/Srs@Srs
cc	Tom Butcher/WSRC/Srs@Srs
Subject:	Review of WSRC-RP-2003-00362 Rev 2

Dan,

I have completed the review of your document WSRC-RP-2003-00362 Rev 2 "Estimated Duration of the Subsurface Reducing Environment Produced by the Z-area Saltstone Disposal Facility." I address the specific design check instructions below with a number of recommendations following.

1. Scientific logic is clear as are the descriptions of the models and assumptions. In the description of the assumptions, the use of the terminology "one crack down the center" and "Simulations start at the time when cracks are formed in the saltstone" in Section 3.3 is confusing.

2. Calculations appear to be reasonably conservative.

3. Grammar, data presentation and graphics are addressed in the recommendations below.

4. Conclusions follow well from the data presented and are further reinforced by additional supporting references.

Recommendations:

1. Clarify that model input for Slag reduction capacity in Table 2 (9.25 E-3 meq/g solid)) is based on 25% Slag in the solid matrix. Slag reduction capacity in Table 3 (37 meq/kg slag) is based on 100% slag. I would suggest taking Slag out of the name in Reduction Capacity in Table 2 since this is a matrix (that happens to contain 25% slag) rather than slag alone.

2. No experimental data is currently reported for the measurement of Cr in the reduction capacity experiments to verify the calculation of slag and soil reduction capacity. As a further design check, I would recommend including the experimental data set along with the calculation used. Data for the control solution was measured as well but not reported.

3. Figure 1: in diagram make location of crack evident.

4. Error bars on Figure 3 are inconsistent.

5. Table 4. a) rather than *Calculations for Estimating* Oxidation capacity of Salt Solution...I would suggest Estimation of Oxidation Capacity of Salt Solution based on Oxidizing Constituents (or ingredients). Should be "Used in equation 2" not equation 3. Footnote b) should read <1E-04 molesL-1).

6. One standard format for scientific notation to be used throughout the document would add clarity. Tables 1, 3 and 4 use different variations such as 1E1 verses 1E01 verses 1E+01. Table 4 mixes

Scientific and standard where it would be clearer to use Scientific throughout (eg 2.00E+00 instead of 2 in one column and 3000 instead of 3E+3 in the next).

7. Equation 4: R for rate is confusing because R is used for reducing capacity in eq 2 and 3 and for reducing agent in eq1

8. Table 1: I must be missing something...for the k=0(no reaction)... time for consumption is the shortest...20yr?

9. Redox potential measurements: Are these measurements v. SHE? Discussion of Redox potential and capacity in the laboratory measurements section is somewhat confusing since red potential values were not used in the model nor to calculate capacity. Perhaps breaking into separate paragraphs.

10. 4.2 Method: #3 spelling of litmus

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12.0 APPENDIX D: SLAG REDUCTION CAPACITY CALCULATIONS

Slag and Sediment Reduction Capacity Calculations

File = Kaplan Results 3-31-03.xls **WSRC-NB-2002-00093 pg 142**

Concentration in original sample in mg/L (ppm) - Raw Data

ADS#	193302	193303	193304	193305	193306	193307	193308	193309	193310
	slag	slag	slag	control	control	control	soil	soil	soil
Cr	2630	2580	2560	2680	2680	2680	2610	2690	2620

ID	Description	Tube Tare Wt (g)	Tube + Solid wt (g)	Tube + slag + liquid (g)	Solid Added (g)	Liquid Added (g)	Total Cr (ppm)	Total Cr (M)	Cr(VI) (M) **	CrO4-2 (mol/tube)	Reduction Capacity for Cr(VI) (ueq/g)***	**** Avg. Red. Cap. For Cr(VI) (microeq/g)
21	Slag, Rep 1	11.909	12.906	22.896	0.997	9.99	2630	0.050577	0.050557	0.0005051	38.8	30.9
22	Slag, Rep. 2	11.855	12.854	23.173	0.999	10.319	2580	0.049615	0.049595	0.0005118	18.6	
23	Slag, Rep. 3	11.88	12.879	23.166	0.999	10.287	2560	0.049231	0.049211	0.0005062	35.2	
24	Control (just liquid), Rep1	11.914	11.914	21.982	0	10.068	2680	0.051538	0.051518	0.0005187		
25	Control (just liquid), Rep. 2	11.886	11.886	21.969	0	10.083	2680	0.051538	0.051518	0.0005195		
26	Control (just liquid), Rep. 3	11.929	11.929	21.94	0	10.011	2680	0.051538	0.051518	0.0005158		
27	Mini-lysimeter, Rep 1	11.811	12.786	22.813	0.975	10.027	2610	0.050192	0.050172	0.0005031	45.8	39.3
28	Mini-lysimeter, Rep 2	11.805	12.768	22.753	0.963	9.985	2690	0.051731	0.051711	0.0005163	5.1	
29	Mini-lysimeter, Rep 3	11.79	12.786	22.628	0.996	9.842	2620	0.050385	0.050365	0.0004957	67.1	

** Approximately 2e-6 molar Cr(III) exists in pH 8 solution in contact with Cr(OH)3(s), Cr(VI) = Cr total - Cr(III) (Eary and Rai, 1987).
Test was conducted at pH 8, solution Cr(III) concentrations varied 2.5e-6 to 2.0e-6 between pH 6.3 and 10.1 (least soluble).

*** equiv = electron equivalents

**** By way of comparison, Lee and Batchelor (2003), reported a fine loamy sand [Alfisol; 10 - 15% clay, 1.2 mg/g Fe(II)]) of 6 ueq/g, pyrite had 32 ueq/g Red. Cap. for Cr(VI).

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Other Authors T. Hang		Key Words (list 3) Reduction Capacity, Reduction Potential, Redox, Slag, Grout		

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