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**KEY WORDS: Reduction Capacity, Reduction
Potential, Redox, Slag, Saltstone, Grout**

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

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ABSTRACT

The formula for saltstone includes ~25 wt% slag to create a reducing environment for mitigating the subsurface transport of a number of radionuclides, including technetium-99. Based on laboratory measurements and mass balance calculations, it was estimated that the Z-Area saltstone waste form will maintain a reducing environment for more than a thousand years and likely for more than 10,000 years. The calculations were very sensitive to infiltration flow rate, underscoring the importance of the proposed moisture barrier for mitigating contaminant transport. Laboratory measurements indicated that the slag used in the formulation of the saltstone has an exceptionally high reduction capacity. Furthermore, measurements of a subsurface SRS sediment indicated that it also had a significant reduction capacity, albeit almost an order of magnitude less than that of the slag. Approximately 78% of the reduction capacity in the disposal system came from the saltstone, 14% from the geological materials in the overlying moisture barrier, and 9% from the vault made from reducing grout.

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LIST OF ACRONYMS AND ABBREVIATIONS

ACRONYMS

SRS Savannah River Site

ABBREVIATIONS

e^-	electron
η_x	porosity of material x
ρ_x	density of x
D_x	Length of x
f_x	weight fraction of x in saltstone
kg	kilogram
L	liter
m	meter
meq $e^- L^{-1}$	milli electron equivalents
mL	milliliter
mV	millivolts
O_x	electron equivalents of oxidizing agent x
R_x	electron equivalents of reducing agent x
t	time
yr	year

1.0 INTRODUCTION

The nominal blend composition of saltstone is 3 wt% lime source, 25 wt% fly ash, 25% 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).

1.1 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 consumption of oxidation of the slag by dissolved oxygen (O₂) in infiltrating rainwater.

2.0 APPROACH

An electron-equivalent mass balance was conducted to calculate the duration that the Z-Area Saltstone Disposal Facility would remain reducing (Figure 1). 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 2.0-1.



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 that 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 Eq. 2.0-2.

$$O_{infiltrating\ groundwater} + O_{salt\ solution} = R_{soil} + R_{slag} \quad (\text{Eq. 2.0-2})$$

where

$O_{infiltrating\ groundwater}$	=	electron equivalents of oxidizing agent from infiltrating groundwater, $\text{meq } e^- \text{ m}^{-2}$,
$O_{salt\ solution}$	=	electron equivalents of oxidizing agent from salt solution, $\text{meq } e^- \text{ m}^{-2}$,
R_{soil}	=	electron equivalents of reducing agent from soil, $\text{meq } e^- \text{ m}^{-2}$, and
R_{slag}	=	electron equivalents of reducing agent from slag, $\text{meq } e^- \text{ m}^{-2}$.

The important assumption made for these calculations are presented in Table 1.

Table 1. Important Assumption

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. 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 lines 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 slightly more negative, hence the measurement underestimates the reduction capacity of the saltstone and native soil.

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 $2.65\text{E-}4\text{ M}$, 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) (Table 2). The amount of oxygenated groundwater that came into contact with the saltstone was estimated using infiltration rate and porosity (Eq. 2.0-3).

$$O_{\text{infiltrating groundwater}} = C_{\text{infiltrating groundwater}} \times 1000 \times i_{\text{saltstone}} + \eta_{\text{saltstone}} + t \quad (\text{Eq. 2.0-3})$$

where

$O_{\text{infiltrating groundwater}}$	=	electron equivalents of oxidizing agent from infiltrating groundwater, $\text{meq } e^- \text{ m}^{-2}$,
$C_{\text{infiltrating groundwater}}$	=	oxidant concentration in groundwater, $\text{meq } e^- \text{ L}^{-1}$,
1000	=	conversion factor, L m^{-3} ,
$i_{\text{saltstone}}$	=	saltstone infiltration rate, m yr^{-1} ,
$\eta_{\text{saltstone}}$	=	saltstone porosity, $\text{m}^3 \text{ m}^{-3}$, 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 $<0.001\text{ wt}\%$. The details for calculating the total concentration of oxidizing agents is presented in Table 3 and the mass balance equation is presented in Eq. 2.0-4.

$$O_{\text{salt solution}} = C_{\text{salt solution}} \times 1000 \times 1/\rho_{\text{salt solution}} \times f_{\text{salt solution}} \times \rho_{\text{saltstone}} \times D_{\text{saltstone}} \quad (\text{Eq. 2.0-4})$$

where

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

The reduction capacity of the geological materials above the vaults, R_{soil} , was calculated using Eq. 2.0-5. 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 opposed 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 3.0 Laboratory Measurements of Reduction Potential.

$$R_{soil} = C_{soil} \times \rho_{soil} \times D_{soil} \quad (\text{Eq. 2.0-5})$$

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 3.0 Laboratory Measurements of Reduction Potential).

$$R_{slag} = C_{slag} \times \rho_{saltstone} \times f_{slag} \times D_{saltstone} \quad (\text{Eq. 2.0-6})$$

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.

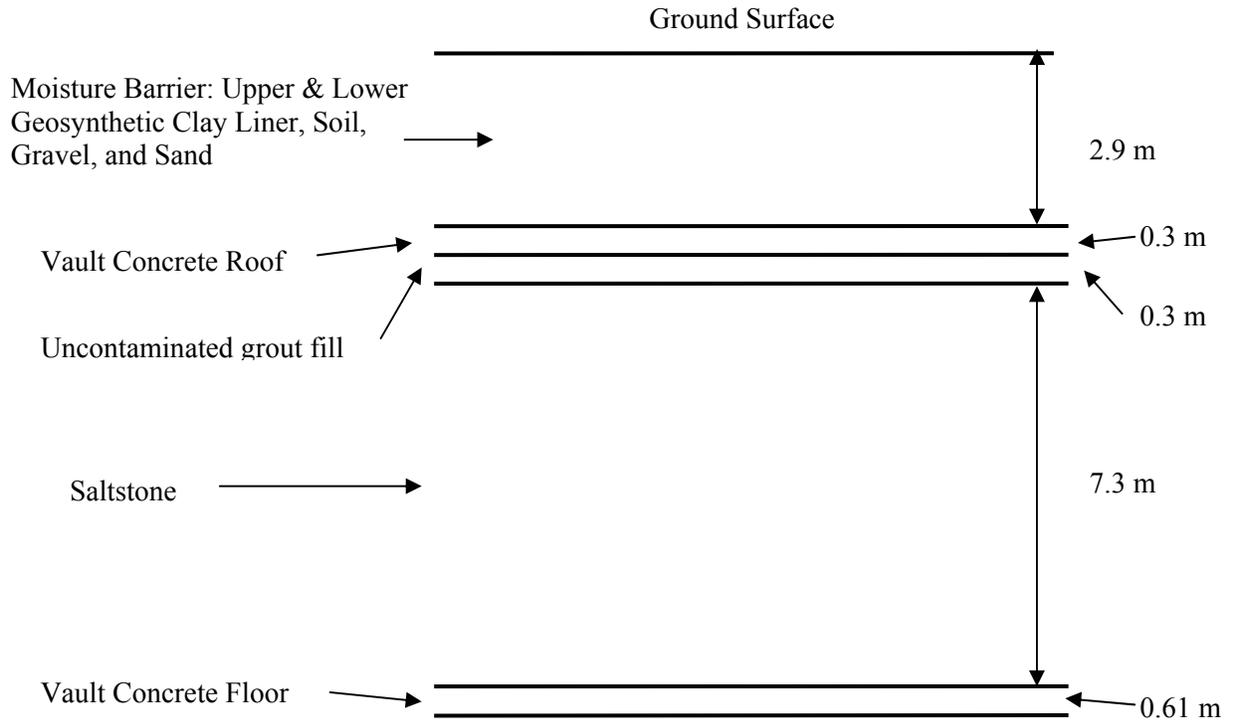


Figure 1. Schematic Representation of the Modeled Saltstone System

Table 2. Input Values Used to Calculate Duration that Saltstone Maintains a Reducing Subsurface Environment

	Parameter (symbol; units)	Value	Comments/Source
Grout	Grout height, vault and saltstone 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 · m ⁻³)	1.70E+03	WSRC-RP-92-1360; p. 2-56
	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 2; "Reduction Capacity v1.xls"
Water	Infiltration rate - grout/saltstone ($i_{saltstone}$; m · yr ⁻¹)	40	Dependent variable; WSRC-RP-92-1360; p. 2-72
	Infiltration rate - soil (i_{soil} ; m · yr ⁻¹)	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	Conservative average of several materials
	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 · 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)	2.92E+00	WSRC-RP-92-1360; p. 2-71
	Soil Reduction Capacity (C_{soil} ; meq e ⁻ · [kg soil] ⁻¹)	5.10E+00	Measured, see Figure 2; "Reduction Capacity v1.xls"
	Soil Density (ρ_{soil} ; kg · 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 3. Calculations for Estimating Oxidation Capacity of Salt Solution

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 ₂ CrO ₄	3.06E-03	3000	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	2000	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 from ITP & ETF (Table 2.3-3 in WSRC-RP-92-1360; page 2-41)

^(b) Skipped any salt solution ingredients that had a concentrations >1e-4 molar.

3.0 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. Following is a detailed description of the procedure adapted from Lee and Batchelor (2003).

3.1 Materials

1. Z-100 Slag: Provided by Chris Langton, who in turn got it directly from Saltstone Silos.
2. Glovebag
3. 1000-mL 10 mM NaHCO₃: Add 0.84 g NaHCO₃ (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 NaHCO₃: Place 1.000 g of K₂CrO₄ (F.W. = 194.2) in a 100-mL volumetric flask and then bring up to volume with 10 mM NaHCO₃.
5. 100-mL 1 M H₂SO₄: Add 50-mL water to 100-mL volumetric flask. Then add 5.58 mL of concentrated H₂SO₄ 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. Na₂SO₄: Pre-weigh 6 aliquots into weighing boats containing 0.142 g of Na₂SO₄
8. 9 50-mL centrifuge tubes
9. Minilysimeter sediment, a sandy loam soil described in Hawkins (1982).

3.2 Method

1. Label 9 tared 50-mL centrifuge tubes as described in Table 4.
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 4.
3. Place tubes, solutions #3, #4, #5, and #6, six 0.142-g Na₂SO₄ aliquots, and litmas paper into glovebag for 2 days before proceeding to next step. After one day in the glovebag stir things up to help O₂ gas diffuse out of solids and liquids.
4. Add 10 mL of the 51.5-mM Cr(VI) in 10-mM NaHCO₃ solution to each tube.
5. Adjust the pH of each tube to 7 ± 1 by adding NaOH or H₂SO₄.
6. Shake by hand every ~3 hours for 1 day.
7. Add 0.142-g Na₂SO₄ 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 4, centrifuge, and pass through a 0.45- μ m filter.
10. Send to ADS for Cr analysis by ICP-ES.

Table 4. Sample Descriptions and Weights Used to Measure Reduction Capacity (Example)

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			

4.0 RESULTS

Laboratory measurements of the reducing capacity of an SRS sediment and slag are presented in Figure 2. These values indicate that the slag has a very high reducing capacity. Furthermore, it shows that our soils 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 in line with the values reported in Figure 2. Also shown in Figure 2 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. 2.0-1). 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. (2003) 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 Figure 2.

At this writing, the infiltration rates to be used for the various layers at the disposal site (Figure 1) have not been finalized. So to calculate the reducing lifespan of the saltstone system, infiltration rate was used as a dependent variable (Figure 3). Figure 3 shows that the reducing lifespan, if limited by the infiltration rate of the intact saltstone vault ($2.54\text{E-}07$ 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 4). Thus, relatively little reducing capacity is gained by including slag in the vault cement. The data presented in Figure 3 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 3 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 $\text{meq e}^- \text{L}^{-1}$ 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.

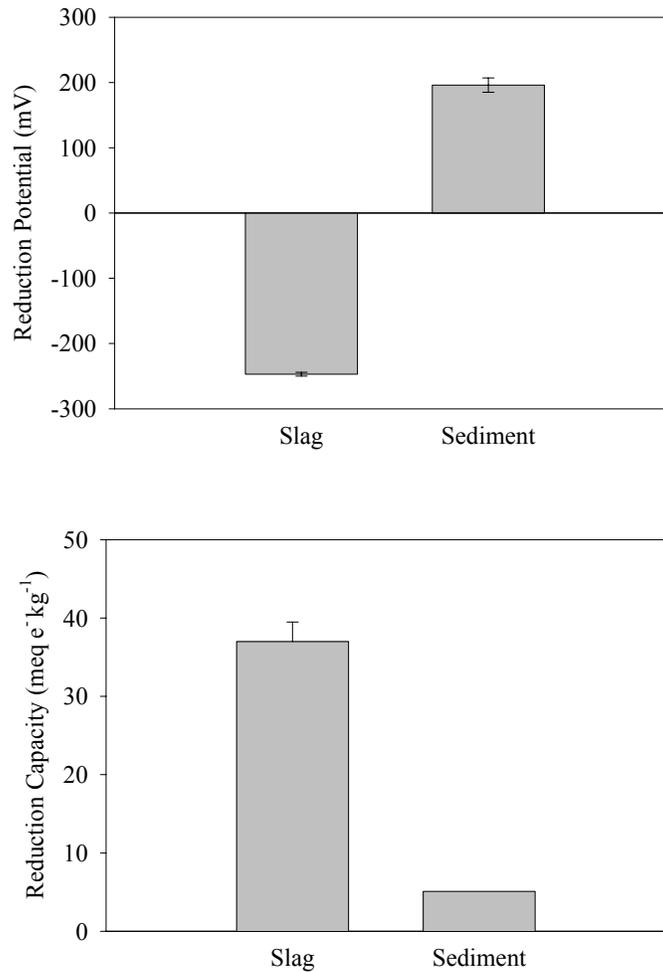


Figure 2. Reduction Potential and Reduction Capacity of an SRS Subsurface Sediment and the Slag Used to Make Saltstone

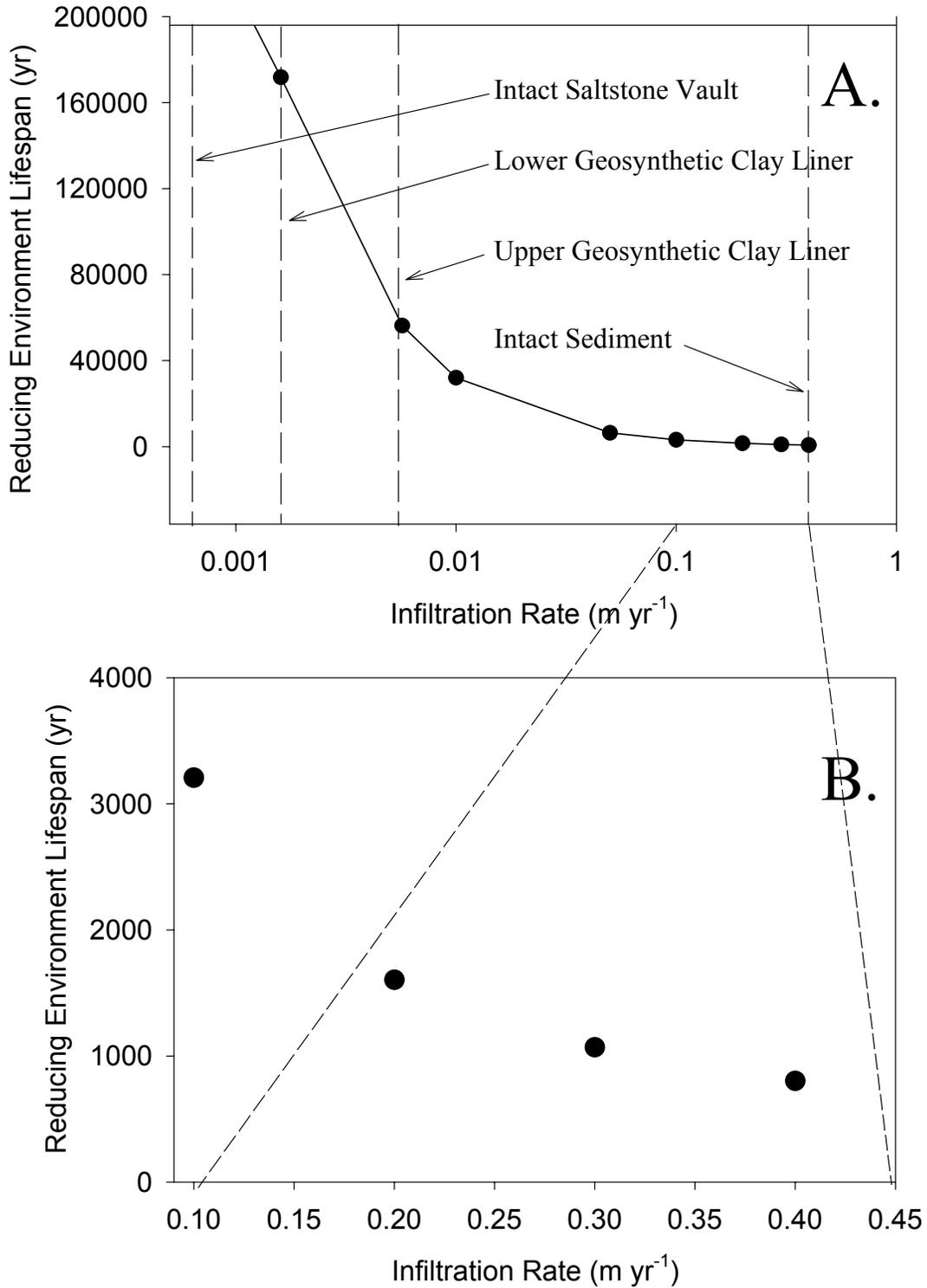


Figure 3. Infiltration Rate Versus Years Until System Becomes Oxidized: (A) Identifies the Infiltration Rates of the Intact Saltstone Vault, Lower Geosynthetic Clay Liner, Upper Geosynthetic Clay Liner, and Intact Sediment; (B) Close up of the Data.

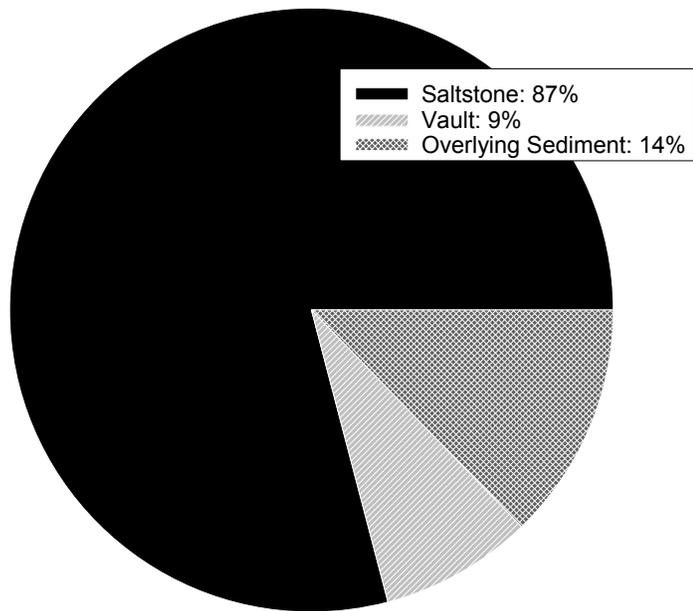


Figure 4. Mass Balance of Reduction Capacity in the Saltstone Disposal Facility

5.0 ACKNOWLEDGEMENTS

The laboratory work was conducted by Cathy Coffey (WSRC). Steve Serkiz conducted a time consuming in depth review of the assumptions and calculations.

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