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Estimation of Eh and pH Transitions in Pore Fluids During Aging of Saltstone and Disposal Unit Concrete

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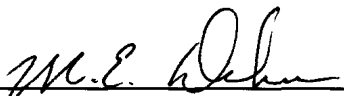
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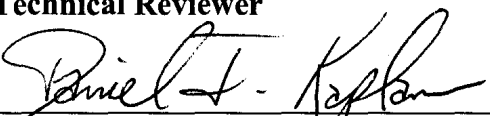
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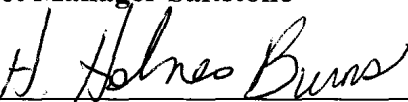
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Summary

Transport behavior of radionuclides out of the Saltstone disposal units depends on redox conditions (Eh) and pH of pore fluids. As Saltstone ages these parameters change and it is imperative to know how and when they change to develop models of radionuclide release from the Saltstone disposal units. Calculations of pore fluid Eh and pH in Saltstone and disposal unit concrete were done using The Geochemist's Workbench® and mineralogies calculated from the cement formulations. Calculations for Saltstone were done for three different infiltrating fluid compositions – unreacted groundwater, groundwater reacted with unaged concrete, and groundwater reacted with aged concrete. Eh and pH transitions for the concrete were calculated for reaction with groundwater. The calculations considered only the case of advective flow where each pore volume of fluid that enters the solid material displaces the existing fluid and equilibrates with the solid materials. A summary table of the Eh and pH transitions is presented below.

Case	Eh Transition		pH Transition	
	Pore Volume	Value Range (V)	Pore Volume	Value Range
Saltstone/fluid=GW (no fluid contact with concrete)	2734	-0.45 to +0.66	2274	11.0 to 9.5
Saltstone/fluid=GW+calcite (concrete oxidized Region III)	2775	-0.45 to +0.61	2558	11.0 to 10.3
Saltstone/fluid=CW+CSH (concrete oxidized (Region II)	2806	-0.45 to +0.56	10422 (extrapolated)	11.0 to ?
Concrete/fluid=GW	3230	-0.46 to +0.57	4206 (extrapolated)	11.0 to ?

Introduction

Chemical degradation of reducing Saltstone and disposal unit concrete controls the chemical composition of the pore fluids passing through the Saltstone, and ultimately influences the release of contaminants from the waste form. Simulations were done using The Geochemist's Workbench® (Bethke, 2005) to estimate the chemical degradation of the reducing cementitious materials. The simulations presented here estimate chemical changes as a function of a number of pore volumes of infiltrate that react with concrete minerals. This information provides step changes in Eh and pH of pore fluids in Saltstone and concrete with the number of pore volumes of reacting fluid passing through these forms. The simulations do not consider physical degradation, such as fracturing, though physical degradation may ultimately affect the rate of chemical degradation by influencing the rate at which porewater passes through the cementitious materials.

Methods

Simulations were run in a "flush" mode. This mimics column experiments where for each pore volume of infiltrate that enters the column an equal volume of reacted infiltrate exits and is analyzed. Figure 1 shows a schematic of the flush mode. Each pore volume of fluid equilibrates with cementitious minerals. All transport of dissolved ions was assumed to be the result of advective flow of the infiltrating fluid. In this conceptual model, the initial Saltstone and concrete pore fluids are flushed out with the first pore volume of infiltrate. Thus, issues with high ionic strengths and calculation of activity coefficients by the extended Debye-Hückel method were ignored.

Three cases were run for Saltstone and one case for concrete. Saltstone is encased in concrete so it was assumed that the origin of the infiltrate into Saltstone was groundwater with or without interaction with the concrete. The first case represents a situation where a "fast flow" path is created through the concrete and unreacted groundwater directly contacts Saltstone. For the second case infiltrate, groundwater was equilibrated with an oxidized concrete in Region III of Bradbury and Sarott (1995). For the third case infiltrate, groundwater was equilibrated with an oxidized concrete in Bradbury and Sarott (1995) Region II. The Saltstone cases are listed in Table 1. For the concrete, the infiltrate was groundwater.

Table 1: Saltstone degradation cases simulated.

Saltstone Case Number	Reacting Fluid
1	GW
2	GW equilibrated with Calcite
3	GW equilibrated with CSH ($\text{CaSiH}_2\text{O}_{4\text{amorphous}}$)

The infiltrate compositions were calculated for each simulation using The Geochemist's Workbench (Bethke, 2005). For the first Saltstone case, groundwater in equilibrium with atmospheric oxygen was reacted directly with Saltstone. For the second Saltstone case, groundwater in equilibrium with atmospheric oxygen was reacted with calcite. For the third Saltstone case, groundwater in equilibrium with atmospheric oxygen was reacted with the cementitious gel phase CSH. The groundwater composition in all simulations was from an analysis of a sample from a water table monitoring well in the vicinity of the Saltstone facility

reported in Strom and Kaback (1992). Table 2 shows the key constituents in the compositions of the infiltrating solutions in each of the three Saltstone simulations and the concrete simulation.

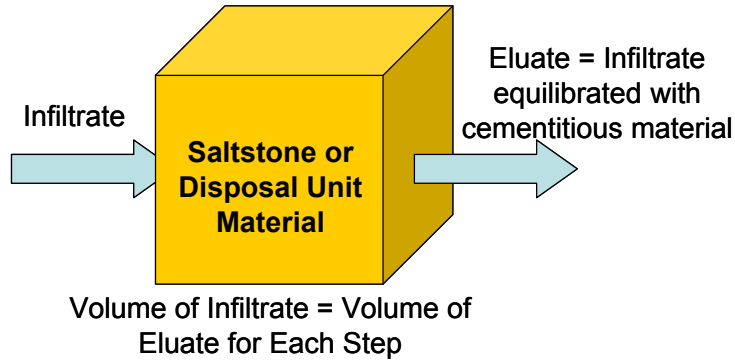


Figure 1: Schematic of flush mode simulations.

Table 2: Key constituents in the composition of infiltrating solutions for each simulation.

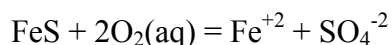
Constituent	Groundwater (GW)	GW + CSH	GW + Calcite
pH	5.4	11.1	8.3
Ca (moles/liter)	6.2×10^{-5}	2.9×10^{-3}	4.5×10^{-4}
Na (moles/liter)	4.2×10^{-5}	4.2×10^{-5}	4.2×10^{-5}
Cl (moles/liter)	9.4×10^{-5}	1.3×10^{-4} *	1.32×10^{-4} *
Dissolved CO ₂ (moles/liter)	9.8×10^{-5}	7.0×10^{-6}	7.6×10^{-5}
Dissolved O ₂ (moles/liter)	2.5×10^{-4}	2.5×10^{-4}	2.5×10^{-4}

* -- chloride concentrations are adjusted to achieve charge balance

Derivation of Saltstone and concrete mineralogy is a fundamental basis for the simulations presented here. There are no quantitative measurements of these mineralogies, but there are chemical analyses of the components that make up the cementitious forms. The formulas reported in Dixon et al. (2008) for the Saltstone and the concrete (Mix 2) were used in the simulations. Chemical analyses for the components in Saltstone reported in Harbour et al. (2006) were used in these mineralogy calculations. For mineralogy calculations of concrete, chemical compositions from Harbour et al. (2006) were used for fly ash and slag, silica fume was assumed to be 100% SiO₂, and the composition of Type V cement was obtained from Tennis (1999).

The phase in the slag responsible for its reducing properties was assumed to be pyrrhotite with a stoichiometric formula of FeS. Pyrrhotite is a high temperature highly reduced phase potentially formed under conditions expected during the formation of blast furnace slag and has been identified in various smelting slags (Zainoun et al., 2003; Muszer, 2006; Gupta et al., 2007). The amount of pyrrhotite in the slag was assigned based on Saltstone reducing capacity

measurements by Kaplan et al. (2008). They measured reduction capacities of 0.82 meq/g for Saltstone and 0.24 meq/g for concrete. Based on the oxidation reaction of pyrrhotite:



there are 8000 meq of electrons transferred per mole of pyrrhotite or 91 meq/g FeS. From this and the measured reducing capacities of Saltstone and concrete the amount of pyrrhotite assumed to account for the reducing capacities was estimated.

To estimate Saltstone and mineralogy, a normative calculation was done that assigned chemical constituents from the calculated bulk compositions to specific mineral phases. All sulfur was assigned to gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$], remaining calcium was assigned to CSH [$\text{CaSiO}_3 \cdot \text{H}_2\text{O}$], all magnesium was assigned to hydrotalcite [$\text{Mg}_4\text{Al}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$], all Fe_2O_3 was assigned to hematite [Fe_2O_3], remaining aluminum was assigned to kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] or gibbsite [$\text{Al}(\text{OH})_3$], and remaining silica was assigned to quartz. Pyrrhotite was estimated as discussed above. In the simulations using The Geochemist's Workbench®, hematite and gypsum were considered part of the inert fraction. The resulting mineralogical composition used in The Geochemist's Workbench® simulations is shown in Table 3.

Table 3: Mineralogical composition of Saltstone and Disposal Unit concrete used in The Geochemist's Workbench simulations.

Mineral	Formula	Saltstone (g/m ³)	Concrete (g/m ³)
CSH	$\text{CaSiO}_3 \cdot \text{H}_2\text{O}$	415239	328288
Hydrotalcite	$\text{Mg}_4\text{Al}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	139830	8821
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	259543	-
Gibbsite	$\text{Al}(\text{OH})_3$	-	11127
Quartz	SiO_2	59441	25315
Pyrrhotite	FeS	11378	5570
Inert		69469	1577232

Thermodynamic data for several cement phases were entered into a database provided with The Geochemist's Workbench®. The dissolution reactions for these, the log of the equilibrium constants for these reactions, and the references from which these data were derived are listed in Table 4. CSH has a variable formula and thus a variable dissolution reaction and free energy of dissolution. For these calculations, the CSH dissolution model of Berner (1992) as presented by Park and Batchelor (2002) was used. In this model, CSH is considered as a non-ideal mixture of two solid phases, the identity of which, and their respective dissolution constants, depend on the Ca/Si ratio of the CSH. Here the Ca/Si ratio was assumed to be low, $\text{Ca/Si} = 0.5$, because of the low amount of portlandite relative to fly ash and slag used in the cementitious forms. This Ca/Si ratio is at the low end of possible CSH compositions, but the results of these simulations are not particularly sensitive to Ca/Si ratios up to a ratio of 1.

Table 4: Thermodynamic data entered into database of The Geochemist's Workbench®.

Cement Phase	Dissolution Reaction	log K	Reference
CSH*	$\text{CaSiO}_3 \cdot \text{H}_2\text{O} + 2\text{H}^+ = \text{Ca}^{+2} + \text{SiO}_{2(\text{aq})} + 2\text{H}_2\text{O}$	15.15	Park and Batchelor (2002)
Hydrotalcite	$\text{Mg}_4\text{Al}_2\text{O}_7 \cdot 10\text{H}_2\text{O} + 14\text{H}^+ = 4\text{Mg}^{+2} + 2\text{Al}^{+3} + 17\text{H}_2\text{O}$	73.78	Bennett et al. (1992)
C4AH13	$\text{Ca}_4\text{Al}_2\text{O}_7 \cdot 13\text{H}_2\text{O} + 14\text{H}^+ = 4\text{Ca}^{+2} + 2\text{Al}^{+3} + 20\text{H}_2\text{O}$	100.77	Reardon (1990)
Ca-carboaluminate	$\text{Ca}_2\text{Al}_2\text{O}_4\text{CO}_3 \cdot 11\text{H}_2\text{O} + 9\text{H}^+ = 2\text{Ca}^{+2} + 2\text{Al}^{+3} + \text{HCO}_3^- + 15\text{H}_2\text{O}$	34.76	Reardon (1990)
Ettringite	$\text{Ca}_6\text{Al}_2\text{O}_6(\text{SO}_4)_3 \cdot 32\text{H}_2\text{O} + 12\text{H}^+ = 6\text{Ca}^{+2} + 2\text{Al}^{+3} + 3\text{SO}_4^{-2} + 38\text{H}_2\text{O}$	57.15	Reardon (1990)

* -- see explanation in text

Results

Saltstone

The Saltstone simulations were run to 4000 pore volumes. All of the Eh transitions took place before 4000 pore volumes (Figure 2). The pH transitions for Saltstone cases 1 and 2 also occurred within the 4000 pore volumes (Figure 3), but the case 3 simulation terminated before 4000 pore volumes and the pH transition did not occur. The pH transition for Saltstone case 3 was estimated by assuming that the transition occurs when the mass of CSH is completely reacted. The results of cases 1 and 2 suggest this is a reasonable assumption. Figure 4 shows all three cases for comparison. Extrapolation of the case 3 curve gives a pH transition at 10,422 pore volumes of fluid reacted. The number of pore volumes of reacted fluid for the Eh transitions are close for all three Saltstone cases because the dissolved oxygen concentration in the reacting fluids is the same. The pH transitions are different for the three cases because the pH of the reacting fluid is different.

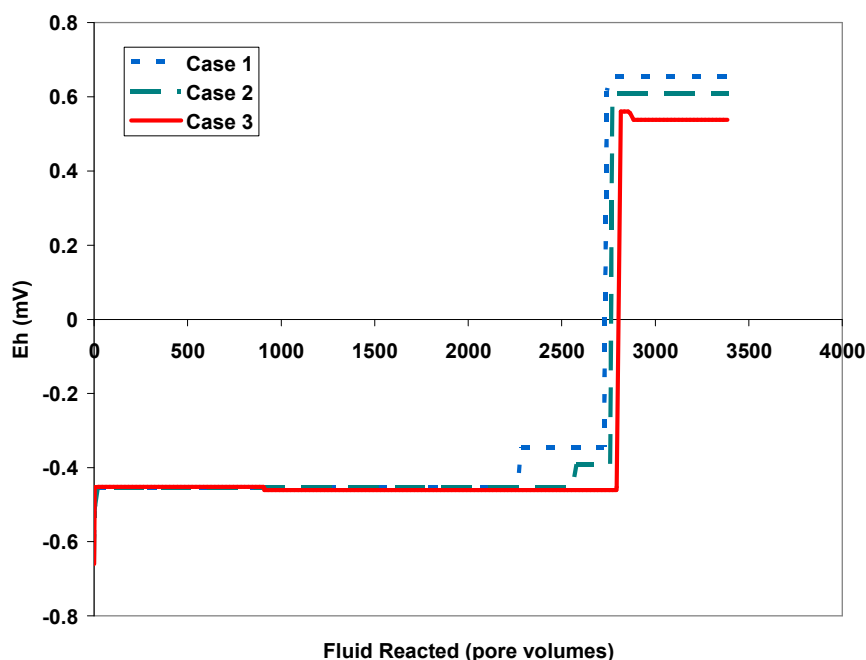


Figure 2: Curves of Eh vs. pore volumes of fluid reacted for the Saltstone simulations.

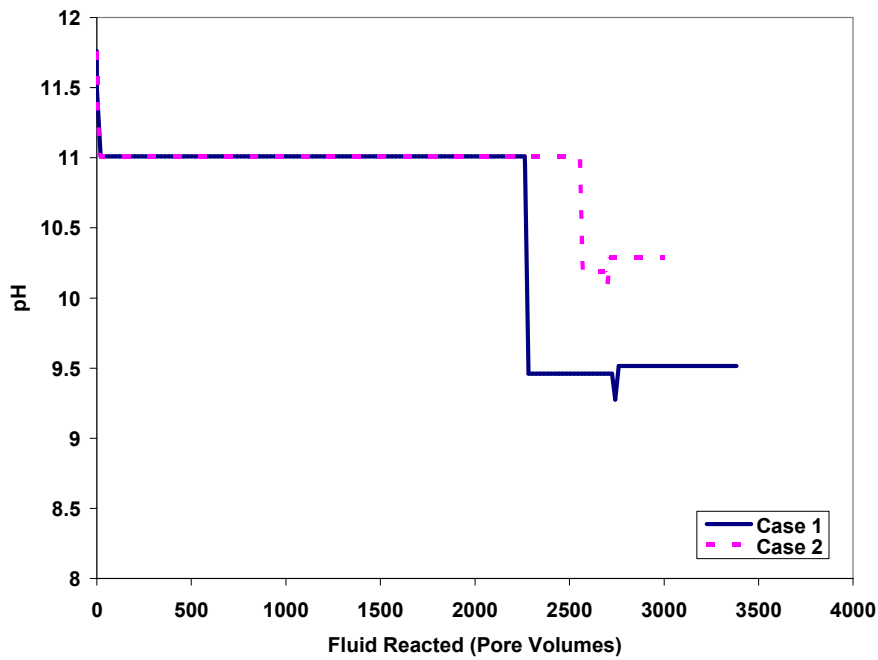


Figure 3: Curves of pH vs. pore volumes of fluid reacted for Saltstone simulations Case 1 and Case 2.

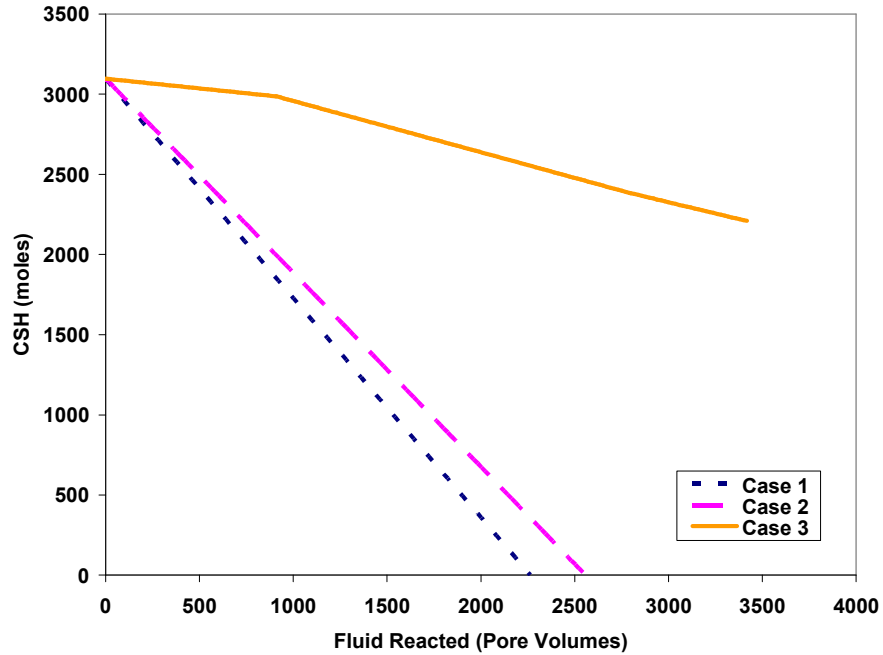


Figure 4: CSH dissolution curve used to extrapolate Case 3 pH transition.

Disposal Unit Concrete

The Eh-pH transition simulation for concrete was set to run for 4000 pore volumes but terminated prior this. The Eh transition occurred before termination (Figure 5), but the pH transition did not. The pH transition was estimated using the CSH dissolution curve (Figure 6), assuming transition occurs when CSH is completely depleted. It was estimated that the pH transition occurs at 4206 pore volumes of fluid reacted.

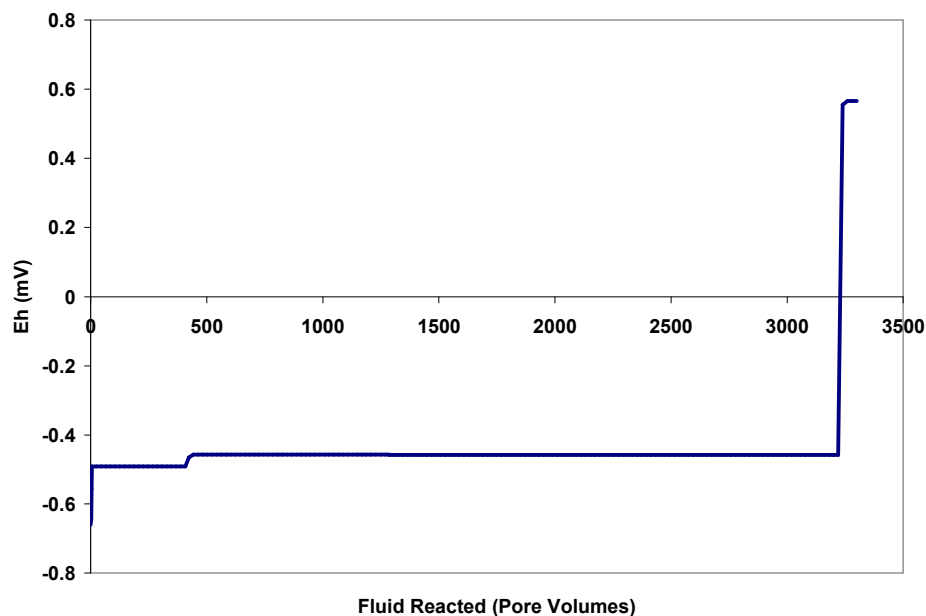


Figure 5: Eh transition curve for concrete.

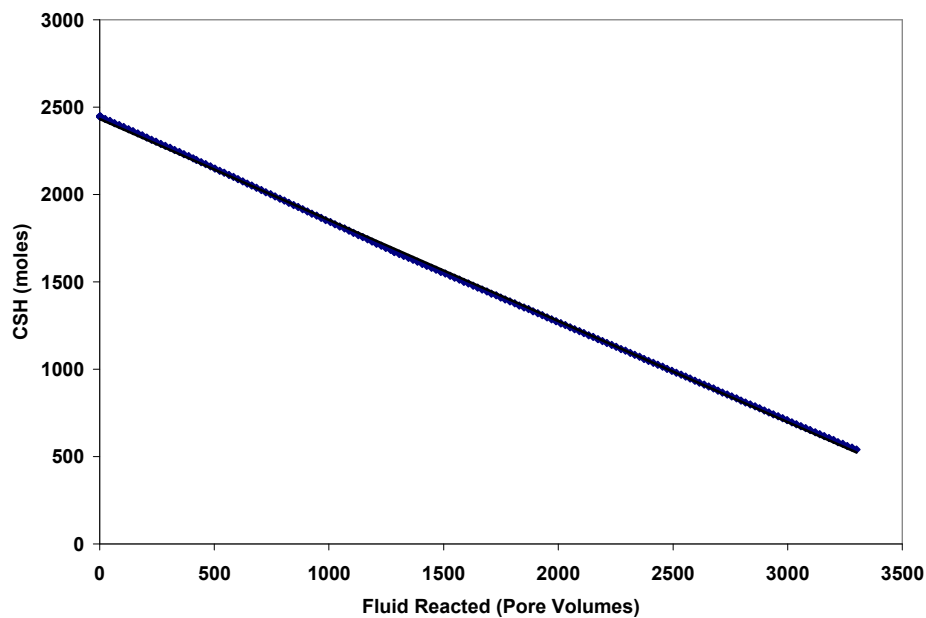


Figure 6: CSH dissolution curve for concrete.

Summary of Eh-pH Transitions

The Eh-pH transitions calculated by The Geochemist's Workbench® simulations are summarized in Table 5.

Table 5: Eh and pH transitions for Saltstone and Disposal Unit concrete.

Case	Eh Transition		pH Transition	
	Pore Volume	Value Range (V)	Pore Volume	Value Range
Saltstone/fluid=GW (no fluid contact with concrete)	2734	-0.45 to +0.66	2274	11.0 to 9.5
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Concrete 2/fluid=GW	3230	-0.46 to +0.57	4206 (extrapolated)	11.0 to ?

To illustrate how changes in concrete and Saltstone formulations effect the Eh-pH transitions, similar calculations were made using the Vault 1 and 4 concrete formulations (Phifer et al., 2006) for the case where unreacted groundwater is the infiltrating fluid (Case 1). These are shown in Table 5. The lower number of pore volumes of infiltrating fluid required to achieve the Eh-ph transitions reflects a lower mass of pyrrhotite and CSH in the calculated mineralogies of the Vault 1 and 4 concrete formulation relative to the Vault 2 concrete formulation.

Table 6: Eh and pH transitions for Vaults 1 and 4 Saltstone and Concrete.

Vault 1 and 4 Case	Pore Volumes (Eh transition)	Pore Volumes (pH transition)
Saltstone/fluid=GW	2360	1739
Vault Concrete/fluid=GW	2994	3660 (extrapolated)

Uncertainty

This analysis is a relatively simple approach to understanding the timing of chemical degradation of the cementitious forms that make up the Saltstone disposal units. There are many complexities that this analysis cannot address. Some of these are briefly discussed below.

1. The mass of minerals available for reaction. This analysis assumes that 100% of the minerals in the Saltstone are available for reaction with infiltrating fluid. If this is not true, because of fracturing or occlusion of portions of the cementitious materials from infiltrating fluid, the number of pore volumes required to reach Eh and pH transitions will be decreased. It should also be noted that if a portion of cementitious materials remains isolated from infiltrating fluid, then the inventory of radionuclides associated with that

portion also remains isolated and only mobile through diffusion. Together these processes would tend to smear the transition over a wider duration, as oppose to occurring essentially over a single pore volume.

2. The effect of Saltstone pore fluid. Saltstone pore fluid is a highly alkaline, high ionic strength fluid with high nitrate concentrations. At some point in the aging of the Saltstone disposal units, when fluid contact is made between the Saltstone and concrete, a diffusion gradient will be established such that hydroxyl ions and nitrate will tend to diffuse into the concrete. The hydroxyls will tend to counter acidification of the cementitious forms and delay pH transformations. The nitrate, though typically not a highly reactive oxidant, may tend to oxidize slag, accelerating the Eh transitions.
3. The effects of other degradation processes. Other degradation processes occur in concrete such as sulfate attack and alkali attack that are not addressed here. It is unknown what the effects of these on Eh and pH transitions would be.
4. The bias introduced by assuming step changes in Eh and pH. The changes in Eh and pH as the cementitious forms age are unlikely to be step changes. For example, CSH dissolves incongruently, so its formula changes as it reacts. The result is a change in the amount of acid that CSH can neutralize as it ages – not a step change in pH. Other minerals also contribute to the pH change and will result in a transition curve rather than a step change. Heterogeneity in the distribution of slag may also result in an Eh transition curve rather than a step change.

In light of these uncertainties, establishing a distribution of Eh and pH transitions by any statistically or scientifically rigorous method is beyond the scope of this analysis. In the absence of any rigorous basis, it is recommended, using professional judgment, that the distribution of Eh and pH transitions used in modeling sensitivity be $\pm 50\%$ of the pore volumes. For example, when the infiltrating fluid is unreacted groundwater the pH transition distribution would be about 2300 ± 1150 pore volumes and the Eh transition distribution would be about 2800 ± 1400 .

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