

Physical Separation Processes and EBS Water Chemistry – A Modeling Study

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I. INTRODUCTION

Presence and composition of water are major factors controlling corrosion and leaching processes within the Engineered Barrier System (EBS) at Yucca Mountain. Wetting of the EBS occurs when drips fall from the drift ceiling, from capillary condensation, and condensation promoted by soluble salts and dust [1]. Water dripping or seeping into the repository may evaporate leaving deposits of precipitated salts on the drift rock/air interface and EBS materials, particularly during early time periods when temperatures and temperature gradients are highest [2]. A second evaporation period occurs later in time, after waste packages have failed. Corrosion products and rock fall can insulate portions of the waste, leading to significant localized temperature gradients (with associated gradients in relative humidity) even at low heat generation rates. The local temperature gradients provide a driving force for smaller scale evaporation and condensation cells.

An important consideration is that, in general, water within the EBS is not necessarily stagnant during the evaporation process. Rather, evaporation occurs while the water is moving, potentially leading to precipitation of minerals in bands as wetted areas transition into dry areas. That is, water movement during evaporation may cause a physical separation of ions in the original source waters.

Moreover, as temperatures cool over time, salts deposited on the drift ceilings, walls, and EBS materials will rehydrate [3]. If the original salts are physically separated, the rehydrated system will not reverse the original evaporation sequence. Many of the original ions will now be separated in space, leading to solutions with a simpler much more but

more varied range of compositions. The wide variety of chemical environments caused by physical separation of ions may influence on corrosion of the drip shield, Alloy-22, support materials, and cladding [3]. Chemical environments may also influence radionuclide solubility [3]. The large range of chemical compositions that may be present on rewetting of precipitated salts subsequent to physical separation is currently uninvestigated and not considered in performance assessment models. The purpose of the work presented is to examine the range of water chemistry to be expected within the EBS as a result of physical separation of ions.

II. EVAPORATION AND WETTING OF THE ENGINEERED BARRIER SYSTEM

Evaporation of water from a wetted area may be approximated by the following equation.

$$\text{Evaporation} = \text{Wetted Area} * \text{Mass Transfer Coefficient} \\ (Pv_{EBS} - Pv_{drift}) \quad (1)$$

Where Pv_{EBS} is the vapor pressure of water at the location of interest in the EBS as influenced by temperature, capillary pressure, and dissolved constituents; and Pv_{drift} is the water vapor pressure in the drift air [1]. The equation illustrates that the evaporation rate is a function of the wetted area. This allows for a wetted area to grow until either evaporation matches the drip rate, or excess water exits the system. Evaporation and dripping often occur at equal rates since the evaporation rate increases with wetted area size until it matches drip rate. The Supplemental Science and Performance Analysis [3] erroneously implies that this case is rare. Within the wetted area, the extent of evaporative concentration will increase as one moves from the drip location out-

ward. This will result in physical separation of salts as the least soluble salts are deposited near the drip location and the more soluble salts are deposited near the edges of the wetted area. The drip rate and evaporation rate are likely to influence the precipitates formed on the EBS, the amounts precipitated, and the spatial separation of minerals.

The physical separation just described for the case of dripping will occur more commonly on the drift walls and ceiling as water evaporates while subject to movement by capillary suction. Heterogeneities in the rock will cause evaporation along flow gradients, again leading to physical separation of ions based upon solubility. Minerals formed in the rock around the repository can rehydrate in the future producing highly concentrated brines and may contact the waste container in this form through dripping after the thermal pulse or as dust fall.

Sanford and Wood [4] describe the evolution of brines and mineral deposition in open evaporite basins. They found that these processes are dependent on the a "leakage ratio", which is defined as the ratio of basin water input to water output. Water inputs into a basin such as a lake basin may include precipitation and stream flow; and outputs may include evaporation and seepage. They found that in hydrologically open evaporite basins moderately and even highly soluble minerals could precipitate in significant quantities given a low leakage ratio [4]. The leakage ratio is important in allowing highly soluble minerals to precipitate. A large leakage ratio precipitates only less soluble minerals in significant quantities [4]. In the context of Yucca Mountain these findings suggest that, as the leakage ratio decreases with distance away from the location of the drip, highly or moderately soluble minerals may precipitate.

Physical separation has two end points, the single cell mixing tank assumption and infinite cell mixing tank assumption, that bound the range of physical separation possible. A single cell mixing tank allows for no physical separation of minerals and evenly precipitates minerals on the EBS. The highest degree of physical separation is described by the infinite cell mixing tank, where each infinitely small cell is independent and physically separate from the cell next to it. The two assumptions account for the range of physical separation of minerals that is possible in the real world.

Wetted areas that remain in equilibrium with evaporation will have a very low leakage ratio and both high and low solubility minerals will precipitate. This case is well modeled by the infinite cell assumption. Drips with wetted areas where evaporation rates are far less than drip rates will be expected to have a higher leakage ratio, where excess water runs off the EBS. This should, in general, allow only low solubility minerals such as calcite, gypsum and fluorite to precipitate. This situation is not modeled in this paper, in

comparison to other dripping cases it presents little corrosion risk. Drips that have a wetted area with high evaporation rates compared to drip rates are expected to produce a relatively mixed composition of minerals due to a small wetted area size. The single cell mixing tank accounts for mineral formation in this manner.

The importance of physical separation appears as the repository cools and relative humidity rises. Hygroscopic salts on the drift walls, ceiling, and the EBS components pull moisture out of the air, potentially leading to the wetting of metal surfaces and dripping of salt solutions from the drift ceiling. Prior physical separation of salts now translates into different aqueous chemical environments. A portion of these environments are simulated in this work.

At this point in time we do not have a rigorous quantitative method for determining degree of separation to be expected from dripping scenarios. We only note that the single cell mixing tank will not always occur and cannot provide the sole basis for prediction of waste package chemistry.

III. MODEL DESCRIPTION

We have developed a model that predicts EBS water chemistry using both limiting assumptions. Actual water compositions will vary at each location and likely be somewhere between the two endpoints. The model developed is numerically simpler, but conceptually more complex than current Project simulations. The current DOE model EQ3/6 employs the Pitzer method for calculating the thermodynamics of high ionic strength solutions. The model we developed is consistent with chemical divides as illustrated by Eugster and Hardie [5]. The principle of chemical divides sets the evolutionary path of brine and the precipitates formed from the starting concentration of aqueous ions. This model takes the starting water chemistry and concentrates the solution in steps, as starting waters are increased in concentration, the precipitation of supersaturated minerals occurs. The temperature, solubility, and activity coefficients are assumed to remain constant and precipitates are not allowed to back react with the solution. Saturation indices are held at unity whenever a solid phase is present or predicted to occur. This leaves a record of the mass of each ion precipitated at each evaporation step. The model is iterative and begins by concentrating the solution by a factor, then checks for saturation of the mineral suite, precipitates saturated minerals, records ion concentrations in solution and precipitated, and iterates to concentration.

Output data collected from the model is analyzed to under the two degrees of separation. The single cell mixing tank, the method employed by DOE, presents no physical separation of minerals. This assumption describes an environment wherein minerals precipitate evenly across the wetted area. This is much like water dripping into a heated beaker that is continuously stirred, as the concentration of ions

in the beaker increases, minerals form, and are evenly distributed on the bottom of the beaker. Rewetting is predicted as an exact reversal of this process for the single cell mixing tank model. The assumption of infinite cell mixing tanks accounts for the physical separation of minerals as they precipitate. In this case the water is no longer mixed as precipitates form and the wetted area shrinks. Low solubility minerals like calcium carbonate, would form close to the drip location (or water source) and high solubility minerals, like soda-niter and niter, would form near the wetted area fringe. The wetted area would result in the banding of minerals. The physical separation of minerals can be seen everyday in rings that form on the sidewalk after a puddle of water evaporates. The infinite cell mixing tank area rehydrates as a series of physically separated, infinitely small, independent cells. The range of physical separation enclosed by the two assumptions encompasses possible microenvironments that may influence localized corrosion. Model results represent a first estimate of the range of chemical environments anticipated to occur on drift walls, ceilings, on and inside waste containers, and support structures.

IV. RESULTS

The minerals precipitated from the model and solubility constants are as shown in Table 1 Minerals precipitated by this model are based on the work presented in “Evaporative chemical evolution of natural waters at Yucca Mountain, Nevada” [6].

Table 1: Minerals considered with solubility constants.

Mineral	Formula	Log K (25°C)
Calcite	CaCO ₃	-9.316
Niter	KNO ₃	-0.00971
Soda-Niter	NaNO ₃	1.094
Magnesite	MgCO ₃	-9.202
Sylvite	KCl	0.912
Gypsum	CaSO ₄	-4.58
Fluorite	CaF ₂	-10.6
Thenardite	Na ₂ SO ₄	-0.273
Halite	NaCl	1.57

These minerals account for the major precipitates found in the experiment with the exclusion of trona where precipitation may be kinetically inhibited. The model initially predicted that large amounts of trona would precipitate, and effectively remove all of the HCO₃⁻ from solution. This is believed to be inaccurate because it does not match results from Rosenberg’s experiment and was removed from the model for this reason. The solubility constants were calculated from Gibb’s free energy of formation [7]. Each mole of carbonate species which precipitates forms one mole of carbonic acid which is lost through degassing. H₂CO₃ is assumed to be in equilibrium with atmospheric CO₂. A variety

of starting water compositions are plausible as listed in Table 2.

For each starting water compositions input to the model, the water composition during rewetting is predicted for the single mixing tank and infinite series of mixing tanks endpoints. The infinite cell mixing tank model predicts a much wider range of water chemistry that will form in microenvironments or bands on the drift ceiling, drip shield, container wall, and inside failed containers.

IV.A. J-13 Well Water

J-13 well water is a HCO₃⁻-CO₃²⁻-Na⁺ water type and is a commonly used proxy for perched water at Yucca Mountain. The probability that perched water will contact the EBS is unknown. It is the focus of this study because it was recently used in the repository performance assessment and for long-term laboratory corrosion testing on EBS (6). In corro-

Table 2: Initial water composition.

Constituent (mg/l)	Precipitation [8]	J-13 [6]	UZ-14 PTn [6]	UZ-14 TSw [9]
Ca ²⁺	0.78	5.8	65.0	43.0
Mg ²⁺	0.10	2.1	12.0	3.70
Na ⁺	0.55	45.2	9.00	67.0
K ⁺	0.20	5.2	0.01	N/A
SiO ₂	0.17	10.4	46.0	35.0
Cl ⁻	0.35	7.2	77.0	88.0
SO ₄ ²⁻	0.96	18.5	79.0	19.0
NO ₃ ⁻	1.55	7.9	12.0	16.0
HCO ₃ ⁻	1.22	105	66.0	170
F ⁻	0.02	2.3	N/A	N/A

[8] (Meijer, 2001) [6] (Rosenberg et al., 2001) [9] (O.C.R.W.M., 2000)

sion testing of Alloy 22 a few anions are crucial in corrosion rates. Localized corrosion occurs in conditions where the molar ratio of chloride to nitrate plus sulfate exceeds 5 to 1 [10]. This ratio will be referred to as the critical anion ratio. The critical chloride to nitrate plus sulfate ratio is a focal point in the analysis.

Simulation results for J-13 water anions are shown in Figure 1. The anion fractions in the figure represent rehydration of salts deposited with the infinite series of mixing tanks assumption.

Under the single mixing tank assumption the anions shown in Figure 1 would rehydrate as one cell. Under this condition the critical anion ratio is never exceeded. Employing the infinite cell mixing tank assumption each step in the evaporation process would rehydrate independently. Anions displayed in Figure 1 rehydrated under the infinite cell assumption produces several spatially separated brines. The end of the evaporation sequence near the wetted area fringe is of the most concern. The composition of the brine near the wetted area fringe is rich in chloride. Despite the large

amount of chloride the critical anion ratio is not exceeded, and does not present an elevated corrosion potential. The results presented for J-13 water under the infinite cell assumption match the conservative estimate for the chloride to nitrate plus sulfate that DOE used in corrosion testing of Alloy 22 [11]. This ratio is three to one for chloride and nitrate respectively. The minerals precipitated from J-13 never exceed the critical anion ratio under either physical separation scenario, which affirms the corrosion testing performed by DOE using J-13 well water. All of the Halite precipitation is accompanied with a significant amount of Soda-Niter (Figure 1) which will mitigate the corrosion risk in that band of minerals.

The single cell mixing tank is created by high evaporation rates and fast mineral formation, which would be typical in the repository during the period of high heat loading after waste emplacement. The diversity presented by the drip scenarios is not very significant for J-13 water because in all cases the critical anion ratio is not exceeded.

Mineral formation is not limited to the EBS. Minerals will form in the desiccated zone of the host geologic horizon, and on the walls and ceiling of the drift. Minerals formed on the ceiling and in the desiccated zone can be rehydrated in the future when the repository cools and infiltration penetrates the drift. Minerals formed on the ceiling and walls have the possibility of falling off and settling on the EBS. Physically separated minerals are likely to have relatively pure compositions and on rehydration could produce solutions with high chloride concentrations.

IV.B. Model Comparison with Experimental Results

A good method to judge the accuracy of this model is comparison with laboratory experimental results conducted

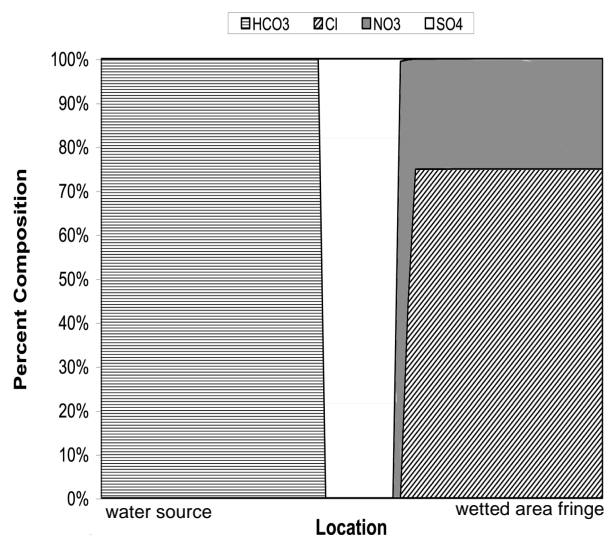


Figure 1: Anion ratio (in percent composition) with respect to location of the drip.

by Rosenberg et al. [6]. Ratios of aqueous concentration over initial concentrations were recorded at 100 and 1000 times concentration for all aqueous ions as synthetic J-13 water was concentrated in the laboratory. This laboratory study found that calcite precipitated very quickly, effectively removing calcium from the solution. The precipitation of calcite changes the aqueous concentrations of HCO₃⁻ and Ca²⁺. Halite precipitation does not occur until the solution is above 1000 times concentration, thus chloride should be a conservative tracer in the solution. This allows for the comparison of data from the model and analytical solution for two non-conservative species, Ca²⁺ and HCO₃⁻, and a conservative ion, Cl⁻.

Figure 2 shows that model predictions for chloride concentrations match the laboratory results, showing a high degree of accuracy in the prediction of chloride behavior. HCO₃⁻ concentrations predicted are close to the analytical results. The HCO₃⁻ concentration is predicted within a factor of two. Model predictions for calcium remove calcium more aggressively than the analytical solution and don't display a rebound of calcium at 1000 times concentration. This may be attributed to the kinetics of calcite precipitation. The principle of chemical divides, on which the model is based, states that once a mineral is supersaturated, the amount precipitated is set by the ion with the lowest aqueous concentration [5]. In the model calcite remains supersaturated once it precipitates and subsequent concentration of the solution removes any increase in calcium through calcite precipitation, although the first precipitation contains almost all of the mass of calcium present in solution. The model predicts calcium concentrations within an order of magnitude at 100 times concentration. The level of accuracy in this numerically simple model is exceptional given that EQ 3/6 predicts chloride concentrations within a factor of 2 and all other ions by not less than a factor of 10 [3].

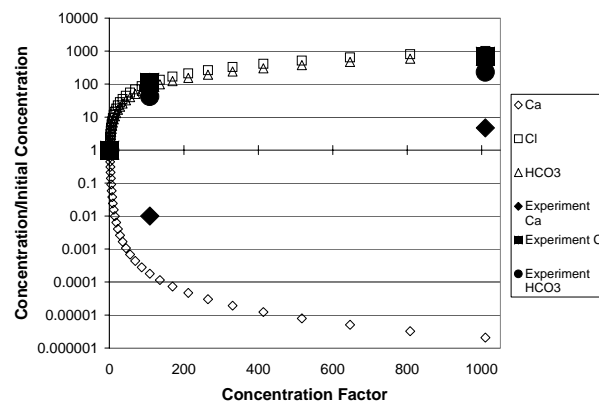


Figure 2: Modeled and laboratory measured normalized concentrations vs. the concentration factor for conservative and non-conservative ions.

V. SUMMARY AND RECOMMENDATIONS

Physical separation of dissolved constituents is caused by evaporation from moving water and differential solubility. Separated salts may form directly on the EBS materials or drop from the drift ceiling. Rehydration of the separated salts leads to a wide range of aqueous solutions contacting the EBS materials.

A simplified model was developed to assess likely aqueous environments. Model results match well with Yucca Mountain Project water chemistry projections [6]. When J-13 is used as a source water the predicted chloride to non-aggressive anion ratios does not create a situation promoting localized corrosion of Alloy-22. Pore and rain water present a greater range of microenvironments in rehydration but are the subject of on going work.

Laboratory corrosion tests and performance assessment models may need to be expanded to incorporate the expected range of chemical compositions that are likely to occur within the EBS given varying water compositions and degrees of physical separation.

VI. ACKNOWLEDGEMENTS

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more varied range of compositions. The wide variety of chemical environments caused by physical separation of ions may influence on corrosion of the drip shield, Alloy-22, support materials, and cladding [3]. Chemical environments may also influence radionuclide solubility [3]. The large range of chemical compositions that may be present on rewetting of precipitated salts subsequent to physical separation is currently uninvestigated and not considered in performance assessment models. The purpose of the work presented is to examine the range of water chemistry to be expected within the EBS as a result of physical separation of ions.

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IV. RESULTS

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sion testing of Alloy 22 a few anions are crucial in corrosion rates. Localized corrosion occurs in conditions where the molar ratio of chloride to nitrate plus sulfate exceeds 5 to 1 [10]. This ratio will be referred to as the critical anion ratio. The critical chloride to nitrate plus sulfate ratio is a focal point in the analysis.

Simulation results for J-13 water anions are shown in Figure 1. The anion fractions in the figure represent rehydration of salts deposited with the infinite series of mixing tanks assumption.

Under the single mixing tank assumption the anions shown in Figure 1 would rehydrate as one cell. Under this condition the critical anion ratio is never exceeded. Employing the infinite cell mixing tank assumption each step in the evaporation process would rehydrate independently. Anions displayed in Figure 1 rehydrated under the infinite cell assumption produces several spatially separated brines. The end of the evaporation sequence near the wetted area fringe is of the most concern. The composition of the brine near the wetted area fringe is rich in chloride. Despite the large

amount of chloride the critical anion ratio is not exceeded, and does not present an elevated corrosion potential. The results presented for J-13 water under the infinite cell assumption match the conservative estimate for the chloride to nitrate plus sulfate that DOE used in corrosion testing of Alloy 22 [11]. This ratio is three to one for chloride and nitrate respectively. The minerals precipitated from J-13 never exceed the critical anion ratio under either physical separation scenario, which affirms the corrosion testing performed by DOE using J-13 well water. All of the Halite precipitation is accompanied with a significant amount of Soda-Niter (Figure 1) which will mitigate the corrosion risk in that band of minerals.

The single cell mixing tank is created by high evaporation rates and fast mineral formation, which would be typical in the repository during the period of high heat loading after waste emplacement. The diversity presented by the drip scenarios is not very significant for J-13 water because in all cases the critical anion ratio is not exceeded.

Mineral formation is not limited to the EBS. Minerals will form in the desiccated zone of the host geologic horizon, and on the walls and ceiling of the drift. Minerals formed on the ceiling and in the desiccated zone can be rehydrated in the future when the repository cools and infiltration penetrates the drift. Minerals formed on the ceiling and walls have the possibility of falling off and settling on the EBS. Physically separated minerals are likely to have relatively pure compositions and on rehydration could produce solutions with high chloride concentrations.

IV.B. Model Comparison with Experimental Results

A good method to judge the accuracy of this model is comparison with laboratory experimental results conducted

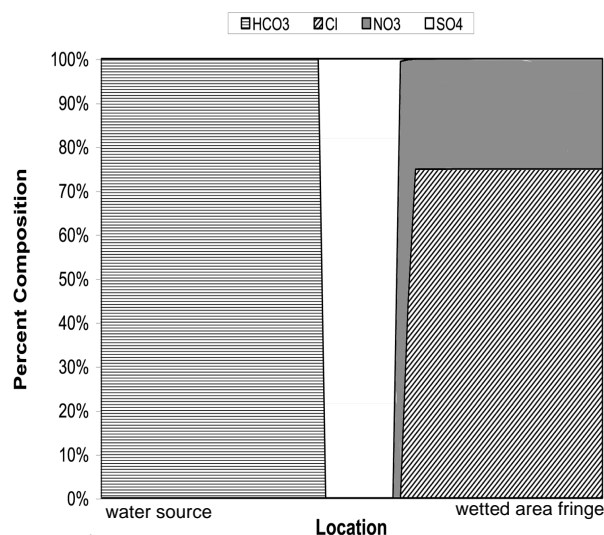


Figure 1: Anion ratio (in percent composition) with respect to location of the drip.

by Rosenberg et al. [6]. Ratios of aqueous concentration over initial concentrations were recorded at 100 and 1000 times concentration for all aqueous ions as synthetic J-13 water was concentrated in the laboratory. This laboratory study found that calcite precipitated very quickly, effectively removing calcium from the solution. The precipitation of calcite changes the aqueous concentrations of HCO₃⁻ and Ca²⁺. Halite precipitation does not occur until the solution is above 1000 times concentration, thus chloride should be a conservative tracer in the solution. This allows for the comparison of data from the model and analytical solution for two non-conservative species, Ca²⁺ and HCO₃⁻, and a conservative ion, Cl⁻.

Figure 2 shows that model predictions for chloride concentrations match the laboratory results, showing a high degree of accuracy in the prediction of chloride behavior. HCO₃⁻ concentrations predicted are close to the analytical results. The HCO₃⁻ concentration is predicted within a factor of two. Model predictions for calcium remove calcium more aggressively than the analytical solution and don't display a rebound of calcium at 1000 times concentration. This may be attributed to the kinetics of calcite precipitation. The principle of chemical divides, on which the model is based, states that once a mineral is supersaturated, the amount precipitated is set by the ion with the lowest aqueous concentration [5]. In the model calcite remains supersaturated once it precipitates and subsequent concentration of the solution removes any increase in calcium through calcite precipitation, although the first precipitation contains almost all of the mass of calcium present in solution. The model predicts calcium concentrations within an order of magnitude at 100 times concentration. The level of accuracy in this numerically simple model is exceptional given that EQ 3/6 predicts chloride concentrations within a factor of 2 and all other ions by not less than a factor of 10 [3].

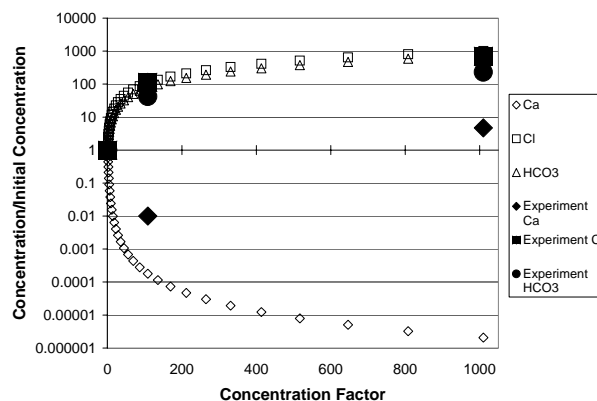


Figure 2: Modeled and laboratory measured normalized concentrations vs. the concentration factor for conservative and non-conservative ions.

V. SUMMARY AND RECOMMENDATIONS

Physical separation of dissolved constituents is caused by evaporation from moving water and differential solubility. Separated salts may form directly on the EBS materials or drop from the drift ceiling. Rehydration of the separated salts leads to a wide range of aqueous solutions contacting the EBS materials.

A simplified model was developed to assess likely aqueous environments. Model results match well with Yucca Mountain Project water chemistry projections [6]. When J-13 is used as a source water the predicted chloride to non-aggressive anion ratios does not create a situation promoting localized corrosion of Alloy-22. Pore and rain water present a greater range of microenvironments in rehydration but are the subject of on going work.

Laboratory corrosion tests and performance assessment models may need to be expanded to incorporate the expected range of chemical compositions that are likely to occur within the EBS given varying water compositions and degrees of physical separation.

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