MOL.20051021.0151

DT# 45228
QA:NA
8/3/05

Evaluation of the Corrosivity of Dust Deposited on Waste Packages at Yucca Mountain, Nevada

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ABSTRACT

Potentially corrosive brines can form during post-closure by deliquescence of salt minerals in dust deposited on the surface of waste packages at Yucca Mountain during operations and the pre-closure ventilation period. Although thermodynamic modeling and experimental studies of brine deliquescence indicates that brines are likely to form, they will be nitrate-rich and non-corrosive. Processes that modify the brines following deliquescence are beneficial with respect to inhibition of corrosion. For example, acid degassing (HCl, HNO_3) could dry out brines, but kinetic limitations are likely to limit the effect to increasing their passivity by raising the pH and increasing the NO_3/Cl ratio.

Predicted dust quantities and maximum brine volumes on the waste package surface are small, and physical isolation of salt minerals in the dust may inhibit formation of eutectic brines and decrease brine volumes. If brines do contact the WP surface, small droplet volumes and layer thicknesses do not support development of diffusive gradients necessary for formation on separate anodic-cathodic zones required for localized corrosion. Finally, should localized corrosion initiate, corrosion product buildup will stifle corrosion, by limiting oxygen access to the metal surface, by capillary retention of brine in corrosion product porosity, or by consumption of brine components (Cl^-).

INTRODUCTION:

Small amounts of dust will be deposited on the surfaces of waste packages in drifts at Yucca Mountain during the operational and the preclosure ventilation periods. Salts present in the dust will deliquesce as the waste packages cool and relative humidity in the drifts increases. In this paper, we evaluate the potential for brines formed by dust deliquescence to initiate and sustain localized corrosion that could result in failure of the waste package outer barrier. Multiple arguments are used to show that waste package failure due to dust deliquescence-induced localized or crevice corrosion of the outer barrier (Alloy 22) is insignificant with respect to repository performance.

Measured atmospheric and underground dust compositions are the basis of thermodynamic modeling and experimental studies to evaluate the likelihood of brine formation and persistence, the volume of brines that may form, and the relative corrosivity of the initial deliquescent brines and of brines modified by processes on the waste package surface. In addition, we evaluate several mechanisms that could inhibit or stifle localized corrosion should it initiate.

Arguments are developed using a logical framework approach, similar to that developed by other authors [1], evaluating the potential importance of localized corrosion by high-temperature

deliquescent brines. We expand upon that approach, considering a wider range of dust and brine compositions, conditions, and arguments.

METHODS

The potential for waste package failure due to localized corrosion caused by dust deliquescence was evaluated using a logical framework approach. In order for dust deliquescence to cause failure of the waste package, each of the following propositions must be affirmative:

1) *Can multiple-salt deliquescent brines form at elevated temperature?* Salt assemblages expected to control deliquescence of the dust have been identified through thermodynamic modeling of the soluble components in dust samples from the underground and at the surface. Thermodynamic speciation and reaction-path calculations were done with the software code EQ3/6, with a thermodynamic database including Pitzer parameters. This database is a compilation of published dissociation constants and Pitzer parameters and was carefully vetted; solubility constants were recalculated if necessary to maintain internal consistency. This Pitzer database has been validated for temperatures up to 140°C (with some limitations) by comparison with published laboratory data and field studies. Then, experimental deliquescence studies using the identified salt assemblages were carried out [2,3] and the results of those experiments are discussed in this report.
2) *If brines form at elevated temperature, will they persist?* After deliquescence, several processes can alter deliquescent brines on the waste package surface. The effects of acid degassing and reaction with low-solubility dust minerals have been evaluated using thermodynamic modeling; both processes may lead to brine dryout. In addition, the relative rate of acid removal by degassing has been evaluated parametrically, using mass balance calculations based on YMP design parameters and thermal-hydrological modeling estimates of gas flow in the drift, and assuming well-mixed conditions in the drift atmosphere.
3) *If deliquescent brines persist, are they corrosive?* The relative corrosivity of predicted initial deliquescent brine compositions is evaluated by comparison with experimental data on corrosion of Alloy 22. The effects of acid degassing and reactions with silicate minerals on persistent brines have been examined using EQ3/6 thermodynamic calculations, and the resulting brine compositions evaluated with respect to Alloy 22 corrosivity.
4) *If deliquescent brines are potentially corrosive, will they initiate localized corrosion?* To provide an estimate of dust mass deposited on the waste packages, in-drift transport and deposition of airborne particulates during the ventilation stage was modeled. Potential deliquescent brine volumes were calculated using EQ3/6, using regional atmospheric dust compositions. Tunnel dust porosity was characterized by epoxy impregnation and image processing, and the capillary response of the dust was determined. Then, scale limitations on corrosion processes in thin brine layers and small droplets were investigated by parametrically examining diffusion of oxygen, varying in such inputs as viscosity, brine film thickness, and salting out factor.
5) *Once initiated, will localized corrosion penetrate the waste package outer barrier?* Processes that could limit penetration by localized corrosion include cathodic limitation due to precipitation of corrosion products, and consumption of the limited available brine by physical or chemical sequestration in the corrosion products. YMP experimental data supporting stifling of crevice corrosion of Alloy 22 are presented. A parametric study of physical sequestration of brine in corrosion product porosity or fluid inclusions has been

performed. Finally, the consumption of brine components, especially chloride, by incorporation into corrosion products, is evaluated, based on EQ3/6 thermodynamic modeling and limited experimental results.

RESULTS

Can multi-salt deliquescent brines form at elevated temperatures? Yes

The conditions under which brines may form by dust deliquescence have been evaluated using both thermodynamic simulations and experimental testing. Geochemical modeling has been used to determine the salt assemblages in the dust that are likely to control the deliquescent behavior, and to estimate the conditions under which deliquescence occurs. Experimental testing of those assemblages has provided direct information on the deliquescence behavior of these salts.

Two sets of data provide inputs to these calculations. The first set consists of measured dust and dust leachate compositions for tunnel dust samples collected from the Yucca Mountain underground facility. The tunnel dust samples consist mostly of crushed rhyolite, generated by excavation and other support activities underground, and contain only a small amount (typically < 0.5% by weight) of total soluble salts. However, tunnel dusts are probably not representative of dust that will be deposited during the pre-closure ventilation period, which will be atmospheric dusts and aerosols, with a greater soluble salt content (generally 10 to 15%) [5], and very different composition [6]. The composition of atmospheric dusts is evaluated using rain-out data collected by the National Atmospheric Deposition Program at a Nevada sampling site, which reflects contributions of both atmospheric aerosols and windblown dust.

Brines formed by dust deliquescence are determined by simulating evaporation of dust leachate compositions to a eutectic brine composition using EQ3/6 and the Pitzer-based thermodynamic database developed for the Yucca Mountain Project. Three major salt assemblages have been identified as controlling the deliquescence RH for tunnel dust:

- Assemblage A: $NaCl–KNO_3$
- Assemblage B: $NaCl–KNO_3–NaNO_3$
- Assemblage C: $NaCl–KNO_3–NaNO_3–Ca(NO_3)_2$.

Experimental work has been performed with these salt assemblages to evaluate the potential for deliquescence at high temperature and low relative humidity [2,3]. Assemblage A boiled at 134°C, a temperature relatively close to that predicted using geochemical modeling. However, boiling-point and short-term resistivity experiments suggest that Assemblage B will deliquesce at temperatures in excess of 190°C, much higher than predicted. By inference, assemblage C, of which Assemblage B is a subset, must also deliquesce at temperatures greater than 190°C.

If brines form at elevated temperature, will they persist? Sometimes

Deliquescent brines predicted using thermodynamic modeling to form on the waste package surface are initially pH-neutral, highly concentrated nitrate and chloride solutions, and will be modified by loss of acid gas species and reactions with silicate minerals in the dust.

Aqueous acid species are present in steady-state concentrations, and form by protonation of the conjugate acids (e.g., Cl^-, NO_3^-, and SO_4^{2-}). There is an equilibrium between the aqueous acid species and the partial pressure of the acid species in the gas phase above the solution; lower

pH and higher concentrations of the conjugate acid in solution correspond to higher partial pressures of that acid gas. The dissociation reactions for both $HNO_{3(aq)}$ and $HCl_{(aq)}$ are strongly temperature-dependent, such that elevated temperatures result in higher equilibrium partial pressures of acid gas in the atmosphere above the solution. HCl has a lower mass than HNO_3 and degasses more readily; at any given set of conditions, the ratio of Cl to NO_3 in the gas phase will be higher than that in the aqueous phase.

Degassing of acid gases, in the absence of a buffering reaction, will deplete H^+ from solution, increasing the pH of the remaining solution and lowering the equilibrium partial pressure of the acid gas, thus limiting further degassing. Chemical reactions that buffer the pH at neutral or acid values will mitigate the effects of acid loss and keep the equilibrium partial pressures of acid gases high.

In experimental studies performed in support of YMP has shown that calcium chloride brines rapidly undergo loss of acid gasses at elevated temperature, precipitating a non-deliquescent calcium chloride hydroxide phase and drying out [8]. Degassing continues in these brines because precipitation of the calcium chloride hydroxide phase consumes hydroxide, buffering the pH to near-neutral values and keeping acid gas partial pressures high.

Experimental work with monovalent salt systems has not resulted in dryout, and such brines are not observed to dry out in natural environments. Thermodynamic modeling calculations have been performed to evaluate the effects of acid degassing on these brine systems at constant pCO_2, constant relative humidity, and constant temperature (conditions approximating those on the waste package for extended periods of time). Degassing in these brines causes an increase in pH until sodium or potassium carbonate precipitates, at which point the solution composition becomes invariant, the pH is buffered to values of 10–10.5, and further degassing results in brine dryout (Figure 1). However, at these pH values, partial pressures of acid gasses are very low (although still higher than predicted in-drift background concentrations). Modeling of acid gas removal using predicted air flow rates in the drifts after closure indicate that complete degassing and dryout is unlikely for the Assemblage A and B monovalent salt assemblages. The calcium-bearing Assemblage C is buffered to near-neutral pH by precipitation of calcite, maintaining high acid gas partial pressures; hence, it may degas sufficiently to dry out.

Deliquescent brine reactions with low-solubility minerals in the dust were modeled using EQ3/6. Reactions modify brine compositions, buffering the pH to near-neutral values, removing Ca and Mg, and changing the Na:K ratio. In many cases, the net result is evolution of the brine to a less deliquescent salt assemblage, resulting in dryout.

If brines persist, will they be corrosive? No

The compositional factors affecting the corrosivity of aqueous solutions with respect to Alloy 22 have been determined experimentally using simple one- and two-component salt solutions and more complex synthetic groundwaters, and a predictive model developed [9]. Initiation of localized corrosion is a function of temperature and electrolyte composition, including chloride and nitrate ion molal concentrations, nitrate:chloride ratio, and pH.

Initial brines formed by deliquescence are predicted to be near-neutral pH, nitrate-rich, and chloride-poor, and within the temperature limits of applicability of the thermodynamic modeling and of the localized corrosion model, are benign, due to high nitrate concentrations that inhibit localized corrosion. At higher temperatures, thermodynamic principles dictate that eutectic brine compositions can only be more nitrate-rich. Thus, initial deliquescent brines are noncorrosive.

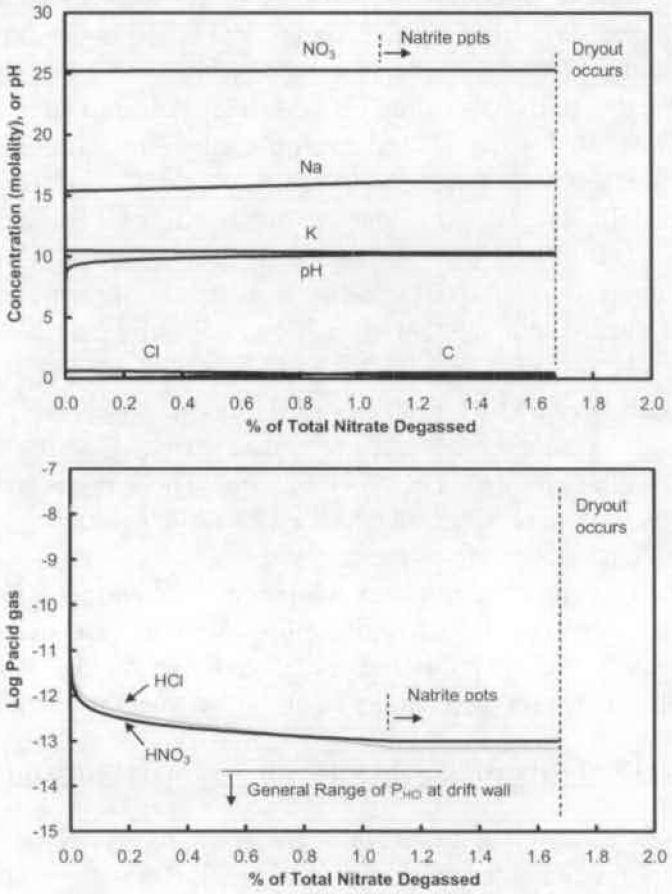

Figure 1. Evolution of the NaCl–KNO_3–$NaNO_3$ Salt Assemblage ("B") at 100°C and $10^{-3.5}$ bar pCO_2, as HCl and HNO_3 Degas in a Swept-Away Gas Boundary Condition.

As discussed in the last section, thermodynamic modeling of acid degassing indicates that the effects of degassing are beneficial with respect to corrosion. Even small amounts of degassing result in large increases in pH, to values near 10 for Assemblages A and B, and to near-neutral values for Assemblage C. In addition, acid degassing results in an increase in the nitrate:chloride ratio in the remaining brine. Reactions with silicates in the dust buffer the pH to near-neutral values and potentially lead to dryout, but otherwise have little effect on the corrosivity of the brine. Thus, initial deliquescent brines are benign, and will not evolve into corrosive brines due to processes occurring on the waste package surface.

<u>If potentially corrosive brines form, will they initiate localized corrosion? No</u>

If corrosive brines do somehow develop, scale limitations due to limited brine volumes will inhibit initiation of localized corrosion. Reasonable bounding estimates of the dust brine volume begin with estimates of the quantity of dust that will be deposited on the WP surface during the pre-closure ventilation period. Using air-quality airborne particulate size and amount measurements, drift and WP design parameters, and the nominal ventilation period and airflow volume, dust deposition is modeled. A dry dust deposition model and deposition velocities from published scientific literature [4], are used to determine that the typical quantity of dust deposited

in 50 years of ventilation on the leading waste package (that closest to the ventilation inlet), is 22 mg/cm^2. These values were verified using a second model based on an exponential decay of the deposition rate with distance [10].

The volume of brine due to the deposited dust has been determined by using the soluble salt content found in local dust (10.5 wt% [5]) and a soluble salt compositions measured for regional dust [5]. The dust samples are high in ammonium salts, about 50% by weight. Because these will decompose prior to deliquescence, the dust salt compositions were recalculated without these components prior EQ3/6 Pitzer evaluate the quantity of deliquescent brine that would form. The brine volume is a function of relative humidity, but varies little with temperature, up to the model limits of 140°C. Results indicate that at an RH of 45%, the maximum sustainable value within the repository at 120°C, only about 0.07 μL of brine exist per mg of dust. Therefore, the leading waste package can have up to 1.5 $\mu L/cm^2$ of deliquesced brine at 120°C, or 0.15 Liters per typical waste package. Assuming the dust is evenly distributed on the waste package, this corresponds to a film with thickness of less than 0.02 mm. These predicted brine volumes are so small that it is likely they will be retained by capillarity within the dust, thus limiting contact with the WP surface and aqueous phase connectivity.

Initiation of localized corrosion requires development of chemically distinct anodic and cathodic regions, connected by a continuous brine film. A parametric analysis of diffusion in the thin films and small droplets of brine predicted to contact the waste package indicates that the necessary diffusive gradients for oxygen, chloride, and other species cannot be maintained.

Once initiated, will localized corrosion penetrate the waste package outer barrier? No

Crevice corrosion occurs within shielded or occluded regions on a metal surface [12]. Within this region, a volume of stagnant liquid must form; the crevice geometry must be wide enough to permit liquid entry but narrow enough to maintain the stagnant. Crevice corrosion initiation involves: 1) local depletion of oxygen in the crevice; 2) formation of an anodic region, where electrons are produced (the crevice), and cathodic regions, where electrons are consumed (typically outside the crevice); 3) metal dissolution within the crevice; and 4) hydrolysis of dissolved metal ions and the accompanying acidification of the creviced region [12]. Metal ion hydrolysis also leads to a charge imbalance within the crevice and migration of anions such as chloride into the creviced region. Oxygen depletion within the crevice coupled with metal dissolution leads to an excess of positive charge in the crevice solution, which is balanced by migration of chloride ions [12]. It is this build-up of chloride ions which leads to breakdown of the passive film and crevice corrosion initiation.

Progress of crevice or localized corrosion requires precipitation of solid phases in the cathodic region, which for fine crevices would then impede the transport processes necessary for the corrosion cell to function. Any decrease of the cathodic area available to support the dissolution reaction (e.g., from solid precipitates) would lead to cathodic limitation of the crevice corrosion process. Any blockage of the gas-phase pathway for replenishment of reactants would similarly impede corrosion progress. Both of these effects would lead to slowing, or stifling, of the corrosion process.

Experimental evidence for stifling under immersed conditions is available from constant potential experiments with artificially creviced samples, conducted in a variety of electrolytes at exposure temperatures between 80°C and 155°C. The data consist of measurements of current versus exposure time for specimens held at constant potentials (usually slightly above the repassivation potential for the material under the exposure conditions used). The data from these

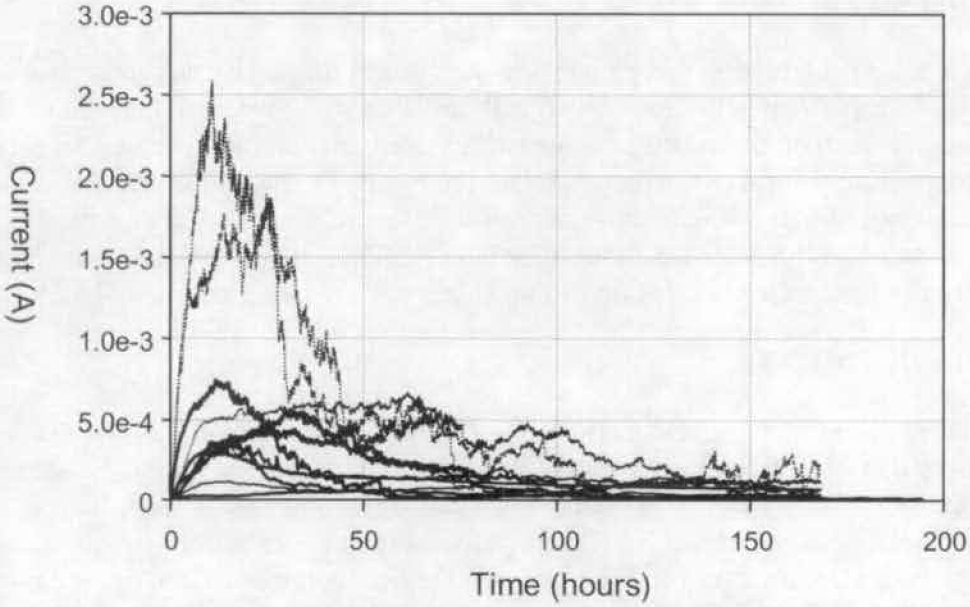

Figure 2. Plot of Current versus Time during Constant Potential Testing of As-Welded Alloy 22 Prism Crevice Assembly Specimens. From [9].

tests are plotted in Figure 2. After crevice corrosion initiates (the initial increase of the current density to a peak seen in the figure), the current density decreases to passive levels with increasing exposure time, indicating that crevice corrosion has stifled.

In the unsaturated environment of the waste package surface, additional stifling mechanisms could occur. Porous corrosion products deposited in the cathodic region of the corrosion cell will have a capillary response that could retain the aqueous phase. The result would be gradual incorporation of brine in the physical structure of the corrosion products. This effect was examined parametrically, by assuming various pit geometries and estimating the required porosity to physically sequester all of the brine available over the surface area corresponding to the top of the pit. The results show that, for a range of penetration geometries, corrosion product liquid saturations would have to be less than 1% to allow penetration of the 2 cm thick outer barrier. Although the porosity of Alloy 22 corrosion products has not been measured, they would have to be nearly nonporous for this sequestering mechanism not to be effective.

Deliquescent brine components, especially chloride, may also be sequestered chemically, by structural incorporation into corrosion phases. One potential sink that has been identified by X-ray diffraction in YMP experimental studies is a layered double hydroxide (LDH) phase. Although chemical analyses are not available, this phase is likely to be Ni:Cr LDH (Alloy 22 contains ~ 50 % Ni and 22.5% Cr, and lesser amounts of Mo, Fe, W, and Co). LDH materials are commonly observed products of metal corrosion, and are anion exchangers that will sequester anions in the brine. Thermodynamic modeling of the stability of this phase in the experimental system in which was observed, and in predicted deliquescent brine compositions, indicates that it is metastable with respect to Eskolaite (Cr_2O_3), and $NiCr_2O_4$, though it may persist for very long times. Exchange into LDH phases, if present, will raise the nitrate–chloride ratio in the remaining brine, because chloride is preferred over nitrate in the interlayer anion exchange site. Because of the limited available brine volumes, only a small amount of chemical sequestration is necessary for brine dryout and cessation of corrosion to occur.

CONCLUSIONS

The arguments presented in this paper show that brines formed by deliquescence of tunnel and atmospheric dust compositions are chemically passive with respect to corrosion. Processes that act to modify them on the waste package surface are beneficial with respect to corrosivity. Should corrosive brines form, scale factors related to brine volume will inhibit initiation of localized corrosion. Finally, should corrosion initiate, several processes will act to limit or stifle it before penetration of the outer waste package barrier. Thus, the overall consequence of dust deliquescence on the localized corrosion of the waste package outer barrier will be insignificant.

ACKNOWLEDGEMENTS

The authors would like to thank Carlos Jove-Colon and Yifeng Wang of Sandia National Laboratories; Susan Carroll, and Henry Shaw of Lawrence Livermore National Laboratories; Yvonne Tsang of Lawrence Berkeley National Laboratories; and Kevin Mon, James Kam, John Case and Bruce Kirstein of Bechtel SAIC Company for their contributions to this study. David Sassani of the U.S. Department of Energy, provided review comments. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. This work is supported by the Yucca Mountain Site Characterization Project.

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