

**Comments Regarding In-Drift Chemistry Related to
Corrosion of Containment Barriers at the
Candidate Spent Fuel and HLW Repository at
Yucca Mountain, Nevada**

1010941

Comments Regarding In-Drift Chemistry Related to Corrosion of Containment Barriers at the Candidate Spent Fuel and HLW Repository at Yucca Mountain, Nevada

1010941

Technical Update, May 2004

EPRI Project Manager

J. Kessler

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

Monitor Scientific, LLC
Integrity Corrosion Consulting Ltd.
Hydrochem Systems Corp.
EPRI, Inc.

This is an EPRI Technical Update report. A Technical Update report is intended as an informal report of continuing research, a meeting, or a topical study. It is not a final EPRI technical report.

ORDERING INFORMATION

Requests for copies of this report should be directed to EPRI Orders and Conferences, 1355 Willow Way, Suite 278, Concord, CA 94520. Toll-free number: 800.313.3774, press 2, or internally x5379; voice: 925.609.9169; fax: 925.609.1310.

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. ELECTRIFY THE WORLD is a service mark of the Electric Power Research Institute, Inc.

Copyright © 2004 Electric Power Research Institute, Inc. All rights reserved.

CITATIONS

This document was prepared by

Monitor Scientific LLC
3900 S. Wadsworth Blvd.
Suite 555
Denver CO 80235

Principal Investigators

Apted, Michael J.
Arthur, Randolph

Integrity Consulting Ltd.
6732 Silverview Dr.
Calgary, Alberta,
Canada T3B 3K8

Principal Investigator
King, Fraser

Hydrochem Systems Corp.
P. O. Box 17090
Golden, CO 80402

Principal Investigator
Langmuir, Donald

EPRI, Inc.
3412 Hillveiw Ave
Palo Alto, CA 94304 >

Project Manager
Kessler, John

This document describes research sponsored by EPRI.

The publication is a corporate document that should be cited in the literature in the following manner:

Comments Regarding In-Drift Chemistry Related to Corrosion of Containment Barriers at the Candidate Spent Fuel and HLW Repository at Yucca Mountain, Nevada, EPRI, Palo Alto, CA, 2004. 1010941.

ABSTRACT

The Nuclear Waste Technical Review Board (NWTRB) has postulated a scenario for the formation of a deliquescent divalent cation-chloride brine that they believe could lead to earlier than expected penetration of nuclear waste packages at a repository at Yucca Mountain, and thereby compromise compliance with established regulatory criteria. The present report documents the results of an independent technical analysis of this scenario carried out on behalf of EPRI.

The analysis has specifically examined and responded to a series of decision points in the NWTRB's scenario. These decision points are cast in the form of the following questions:

- can a pure divalent-cation chloride brine (e.g., CaCl_2 or MgCl_2) form via deliquescence involving deposited dust on the waste package surface?;
- if such a brine could form, would it be stable?;
- if the brine is stable and persists, will chemical conditions (e.g., pH, nitrate/chloride ratio, rate of O_2 supply) necessary for initiation of localized corrosion be maintained?;
- if localized corrosion is initiated, will penetrations propagate through the entire wall-thickness of the waste package?; and
- if there is localized failure of the waste package, will this cause the regulatory safety standard to be exceeded?

If, and only if, *all* of these questions can be answered affirmatively would NWTRB's scenario result in potential non-compliance with established regulatory criteria.

Multiple lines of evidence using credible, and even highly conservative and bounding, assumptions have been used to address the above questions. The results of these analyses indicate that the respective answers to these questions are as follows:

- such pure divalent-cation chloride brines will not form;
- such brines will not be stable if formed;
- such brines, if they are stable, will not lead to initiation of localized corrosion;
- localized corrosion, if it initiates, cannot be sustained;
- penetration through the container of the waste package will likely not occur, even if localized corrosion is sustained, and lastly;
- early, localized penetration of waste packages would not compromise the ability of a repository at Yucca Mountain to comply with established regulatory criteria.

Thus, not one of the required assumptions and conjectures regarding the NWTRB's deliquescent scenario is supported. It is EPRI's judgment that further concern about this issue is without foundation or merit.

ACKNOWLEDGEMENTS

We would like to gratefully acknowledge the efforts of:

Authors:

MJ Apted

RC Arthur

D Langmuir

F King

J Kessler

Editors:

L Nelson

P Salter

CONTENTS

1 PURPOSE	1-1
2 BACKGROUND	2-1
3 CHEMICAL SYSTEM OF THE REPOSITORY DRIFT	3-1
4 DELIQUESCENCE DURING THE TRANSITION INTERVAL	4-1
4.1 Formation of Deliquescent Brines	4-1
4.2 Neutralization Capacity of ESF Dust and Wind-Blown Dust	4-6
4.3 Stability of Deliquescent Brines	4-9
4.3.1 Brine stability in isolated microenvironments.....	4-11
4.3.2 Brine stability in the in-drift chemical system.....	4-17
5 LOCALIZED CORROSION OF ALLOY-22	5-1
5.1 Inhibition of Localized Corrosion of Alloy 22 Based on Composition of Deliquescent Solution.....	5-1
5.2 Inhibition of Localized Corrosion of Alloy 22 Based on Properties of Dust Deposits as Crevice Formers	5-2
5.3 Stifling of Localized Penetration.....	5-9
5.4 Overall Assessment of the Localized Corrosion of Waste Packages Due to Deliquescence	5-11
6 IMPACT OF EARLY WASTE PACKAGE FAILURE ON SAFETY COMPLIANCE	6-1
7 REFLUX DURING LOW-TEMPERATURE INTERVAL	7-1
7.1 Source Waters, Chemical Divides and Brine Types	7-1
7.2 Modeling the Behavior of Corrosion-Relevant Species During Brine Formation	7-2
7.3 Experimental Data on Refluxing.....	7-3
7.4 Mass Balance, Distribution and Chemistry of Acid Gases in Drifts	7-6
7.5 Conclusions on State of Nevada Corrosion Studies.....	7-8
8 REVIEW OF NWTRB ANALYSIS	8-1
8.1 Stability of Deliquescent Brines.....	8-2
8.2 Corrosion Behavior of the Waste Package and Drip Shield.....	8-6
8.3 Total System Performance Assessment	8-8
9 SUMMARY	9-1
10 REFERENCES	10-1

LIST OF FIGURES

Figure 2 . 1 Schematic Diagram of Temperature-Time Evolution for the Drift Environment of the High-Temperature Operating Mode (HTOM) Concept for a Repository at Yucca Mountain (from Boyle, 2003).	2-2
Figure 3 . 1 Time Dependence of the Ranges of Waste Package Surface Temperature and Drift Relative Humidity in the Yucca Mountain Repository.	3-1
Figure 3 . 2 Schematic Illustration of Equilibrium Chemical System for Emplacement Drifts. Blue region indicates water in drift walls and red region indicates possible brine formed on waste package surface. Other terms are as defined in text.	3-2
Figure 4 . 1 Anion Percent Values in Soluble Salts in ESF Dust.....	4-2
Figure 4 . 2 Anion Percent Values in Soluble Salts in Wind-blown Dust from Near Yucca Mountain.....	4-4
Figure 4 . 3 Triangular plot of percent concentrations of chloride, nitrate and sulfate in the soluble salts of ESF dust (▼), wind-blown dust (▲) and in precipitation (3 points). Also shown are regions of the diagram in which the anion concentrations are corrosive and non-corrosive. The data are from Table 4.1.	4-5
Figure 4 . 4 Weigh Percent Minerals in ESF Dust.....	4-7
Figure 4 . 5 Weight Percent Minerals in Wind-Blown Dust	4-7
Figure 4 . 6 Calculated variations in m_{H^+} , $p_{H_2O(g)}$ and $p_{HCl(g)}$ attending the incremental addition of $CaCl_2 \bullet 2H_2O$ to an aqueous solution at 146°C, 1 bar. A saturated solution is attained after addition of 28.5 moles of $CaCl_2 \bullet 2H_2O$. This solution is chemically equivalent to a deliquescent brine equilibrated with the salt and a gas phase.	4-13
Figure 4 . 7 Diagram illustrating the effects of calcite dissolution on the equilibrium m_{H^+} and $p_{HCl(g)}$ of a $CaCl_2 \bullet 2H_2O$ deliquescent brine at 146°C, 1 bar.	4-14
Figure 4 . 8 Diagram illustrating the effects of albite dissolution and precipitation of a Na-beidellite reaction product on the equilibrium pH of a $CaCl_2 \bullet 2H_2O$ deliquescent brine at 146°C, 1 bar.....	4-15
Figure 4 . 9 Calculated variations in $(NO_3^- + SO_4^{2-})/Cl^-$ molar ratio during reaction of a $CaCl_2$ brine with soda niter ($NaNO_3$) and thenardite (Na_2SO_4) at 146°C, 1 bar. The dashed line indicates the lower threshold value for inhibition of Alloy 22 corrosion by the total concentration of $NO_3^- + SO_4^{2-}$	4-16
Figure 4 . 10 Diagram illustrating the effects of buffering by albite + Na-beidellite + kaolinite (\pm halite) on m_{H^+} as $HCl(g)$ is added to condensate at 96°C, 1 bar.	4-21
Figure 5 . 1 Comparison of Nitrate / Chloride Molar Concentration Ratios in Dust and Precipitation Samples Relevant to the Yucca Mountain Repository with those Found to Inhibit the Localized Corrosion of Alloy 22. 5-2	
Figure 5 . 2 Comparison of Repassivation Potentials for Pitting of Planar Samples and Crevice Corrosion of Creviced Samples (after Dunn et al., 1996). Data shown for Alloy 825 in deaerated dilute groundwater solution at 95°C.....	5-4
Figure 5 . 3 Schematic Illustration of the Conceptual Model for the Formation of a Thin Deliquescent Liquid Film Under a Permeable Dust Deposit or Precipitated Salt Film. (Note that a continuous surface water film is assumed here for simplicity. In reality, the water film is likely to be discontinuous along the surface. This would not change the conclusions from the simplified conceptual model).....	5-4
Figure 5 . 4 Dependence of the Porosity and Tortuosity Factor of Compacted Montmorillonite on Dry Density (Oscarson et al., 1992).	5-6
Figure 5 . 5 Temperature Dependence of the Concentration of Dissolved Oxygen in Water in Contact with Air at a Pressure of 101.325 kPa (after Battino et al. 1983).	5-7
Figure 5 . 6 Predicted Rate of Oxygen Consumption due to Passive Corrosion and of Oxygen Replenishment by Diffusion Through Surface Water Films of Different Thicknesses as a Function of Temperature (porosity 0.5, tortuosity factor 0.2).	5-8
Figure 5 . 7 Predicted Ratio of the Interfacial Oxygen Concentration Under a Dust Deposit to that on the Exposed Surface of the Waste Package Based on the Data in Figure 5.6.	5-10
Figure 5 . 8 Comparison of the Time Dependence of the Penetration due to Localized Corrosion for Two Values of the Exponent n for Power-law Growth and the Wall Thickness of the Alloy 22 Waste Package.	5-12
Figure 6 . 1 IMARC 8.0 analysis with 108 branches, with the initial failure fraction of waste packages set equal to unity.	6-1
Figure 6 . 2 MARC 8.0 analysis with 108 branches, with the initial failure fraction of waste packages and drip shields set equal to unity.	6-2

Figure 7 . 1 Some possible paths for the evaporation of natural waters, modified from Hardie and Eugster (1970) as given by Drever (1997).7-1
Figure 7 . 2 Schematic diagram of experimental apparatus used in the distillation experiments (Stahle, 2003).....7-4

LIST OF TABLES

Table 4 . 1 Mole Percent of Ions in Soluble Salts in Wind-Blown Dust and ESF Dust and in Precipitation from Near Yucca Mountain, and Anion Chloride Ratios.	4-2
Table 4 . 2 Average Mineral Composition of ESF Dust and Wind-Blown Dust	4-3
Table 4 . 3 (a) Example Acid-Base Mineral Reactions that Will Neutralize Acid Gases	4-8
Table 4 . 4 Neutralization Capacity of ESF Dust (Topopah Spring Tuff) For Potential Acidity.	4-9
Table 4 . 5 Neutralization Capacity of Wind-Blown Dust for Potential Acidity	4-10
Table 4 . 6 The acid-neutralization capacity of wind-blown and ESF dusts compared to the potential acidity arising from salts in those dusts.	4-10
Table 4 . 7 Condensate chemistry (solute concentrations in mol kg ⁻¹ , $p_{\text{CO}_2(g)}$ in bars).....	4-18
Table 4 . 8 Thermodynamic data for HCl(g) at 25°C and 1 bar. Parameters a , b and c are coefficients that can be used with the Maier-Kelley equation to calculate isobaric heat capacities as a function of temperature, <i>i.e.</i> , $C_p = a + bT + cT^2$	4-19
Table 4 . 9 Comparison of modeling results on the formation and stability of CaCl ₂ deliquescent brines at 146°C. ...	4-20
Table 7 . 1 Relative Ratios of Surface Areas for Components within Emplacement Drift.	7-7
Table A . 1 Weight percent minerals in wind-blown dust excluding organic matter (see text—Chapter 4.2).....	A-1

1

PURPOSE

The purpose of this report is to provide the Nuclear Waste Technical Review Board (NWTRB) with an in-depth, independent analysis sponsored by the Electric Power Research Institute (EPRI) with respect to the potential development of corrosive brines, and their impact on safety, during the post-dry-out period of a planned repository at Yucca Mountain. The NWTRB has previously submitted (NWTRB, 2003a) its own report on this topic to the US Department of Energy (USDOE). That NWTRB report raised concerns regarding the possible formation of divalent chloride (Mg-Ca-Cl) brines at temperatures above the ambient boiling point of water, with speculation that such brines could lead to earlier-than-anticipated failure of nuclear waste packages. In their report, the NWTRB stated:

“Thus, the Board believes that under conditions associated with the DOE’s current high-temperature repository design, widespread corrosion of the waste packages is likely to be initiated during the thermal pulse. Once started, such corrosion is likely to propagate rapidly even after conditions necessary for initiation are no longer present. The result would be perforation caused by localized corrosion of the waste packages, with possible release of radionuclides....the Board believes that the implications of the Board’s conclusions for repository system performance could be substantial.”

Related to the last comment of this quote, in an earlier NWTRB letter on the topic to the USDOE, dated, October 21, 2003 (NWTRB, 2003b), the Board also states:

“The Board believes that total system performance assessment should not be used to dismiss these corrosion concerns.”

EPRI-sponsored independent analysis of this topic encompasses a similar review of physicochemical processes as in the NWTRB’s November 25, 2003 (NWTRB, 2003a) report, but reaches significantly different conclusions. The formation of such corrosive brines is not likely, and furthermore, if such brines were to form, it is extremely unlikely that they could persist, or that through-going penetrations to the containers of waste packages would occur as a result of them. In this regard, EPRI is in accord with the minority report by Dr. Corradini included in the NWTRB’s November 25, 2003 report (NWTRB, 2003a).

This report also addresses the key question of public safety, ‘Will long-term isolation of nuclear waste be assured?’ even if such a highly improbable set of assumptions and conjectures regarding brine formation and localized corrosion were to occur, independent calculations by EPRI’s contractors robustly indicate the clear answer is “yes”, long-term safe isolation would still be assured, even for the NWTRB’s speculative scenario.

The following sections present EPRI’s analysis (conducted by EPRI contractors). Portions of this report were published as a 2003 year-end report (EPRI, 2003), and additional work reported here has been conducted in the intervening months. EPRI’s systematic approach starts with a review of fundamental thermodynamics and data, and extends through an examination of deliquescence, localized corrosion, and issues with experimental simulations of such processes. Total system

performance assessment calculations conducted by EPRI-sponsored contractors are also reported here that show compliance with regulatory safety criteria even for the unexpected early failure of both containers and drip shields arising from the speculative formation of deliquescent brines. In addition, a concluding section compares and contrasts the NWTRB's analysis with EPRI's, to identify key areas of agreement or disagreement. It is hoped that such a comparison can be used constructively to efficiently and effectively resolve any conflicting views.

2

BACKGROUND

The containment and isolation strategy of the Department of Energy's (DOE) Yucca Mountain Project (YMP) was described and defended in a series of technical presentations to the US Nuclear Waste Technical Review Board (NWTRB) in May, 2003 (Boyle, 2003; Bodvarsson, 2003; Peters, 2003; Farmer, 2003). This strategy, broadly illustrated in Figure 2.1 taken from these presentations, divided the performance of the repository into three intervals:

- *Dry-out interval*: initial isolation by a vapor barrier imposed by dry-out arising from above-boiling rock temperature (Bodvarsson, 2003);
- *Transition interval*: once rock above drift cools to boiling point, diversion of possible limited, benign seepage waters by capillary action of unsaturated drift and Ti-drip shield, (Peters, 2003),
- *Low-temperature interval*: temperature at drift wall is well below boiling point, limited, benign seepage water may enter drift, and temperature at waste package surface is below a threshold temperature for crevice corrosion (Farmer, 2003; Cragnolino, 2003).

With respect to possible development of solutions on the surface of the waste packages leading to aggressive modes of localized corrosion, two separate, alternative scenarios have been proposed. The first is possible brine formation from the deliquescent behavior of dust that is assumed to settle onto the surface of waste packages (see NWTRB, 2003a). In the extreme, pure deliquescent brines of divalent-cation chlorides, such as $MgCl_2$ and $CaCl_2$, are speculated to form at temperatures as high as 150-160°C during the "transition interval." Such brines are further speculated to lead to localized corrosion of the Alloy 22 outer shell of the waste package. This deliquescence concern was raised by the NWTRB to the Department of Energy (NWTRB, 2003). A second concern, raised from a number of experiments conducted by researchers supported by the State of Nevada¹, is the postulated development of an acidic environment on waste package surfaces during a reflux-boiling/evaporation of various simulated repository waters and salts that might occur during the low-temperature interval.

In response to these issues being raised, EPRI initiated an independent investigation of both of these proposed scenarios during 2003. The approach adopted by EPRI was to first develop a physicochemical system description based on thermodynamic principles and boundary conditions for the emplacement drifts of a repository at Yucca Mountain. A series of questions were posed as part of this investigation:

¹ The experiments are discussed in a paper (No. 3693) presented at the conference "Corrosion 2003" by A. L. Pulvirenti, K. M. Needham, A. Adel-Hadadi, E. J. Bishop, A. Barkat, C. R. Marks and J. A. Gorman. The paper is titled "*Corrosion Behavior of Alloy 22 Under Conditions of Dynamic Groundwater Composition*". The results are also discussed in two recent presentations:

"*Continuing Investigations of Local Environments on Waste Container Surfaces*" (presented by R. Staehle at the Nuclear Waste Technical Review Board Meeting of January 28, 2003), and

"*Near-Field Environments and Corrosion*" (presented by D. L. Shettel at the March 26, 2003 meeting of the Advisory Committee on Nuclear Waste).

These references are referred to as Pulvirenti *et al.* (2003), Staehle (2003) and Shettel (2003), respectively, in this report.

- Can a pure CaCl_2 (or MgCl_2) brine form via deliquescence involving deposited dust on the container surface?
- If the brine forms, is it stable and will it persist?
- If the brine is stable, will chemical conditions (*e.g.*, pH, nitrate / chloride ratio, rate of O_2 supply) within the brine necessary for initiation of localized corrosion be maintained?
- If localized corrosion is initiated, will penetrations propagate through the entire wall-thickness of the container?
- If there is localized failure of the waste package, will this lead to exceeding the regulatory safety standard?

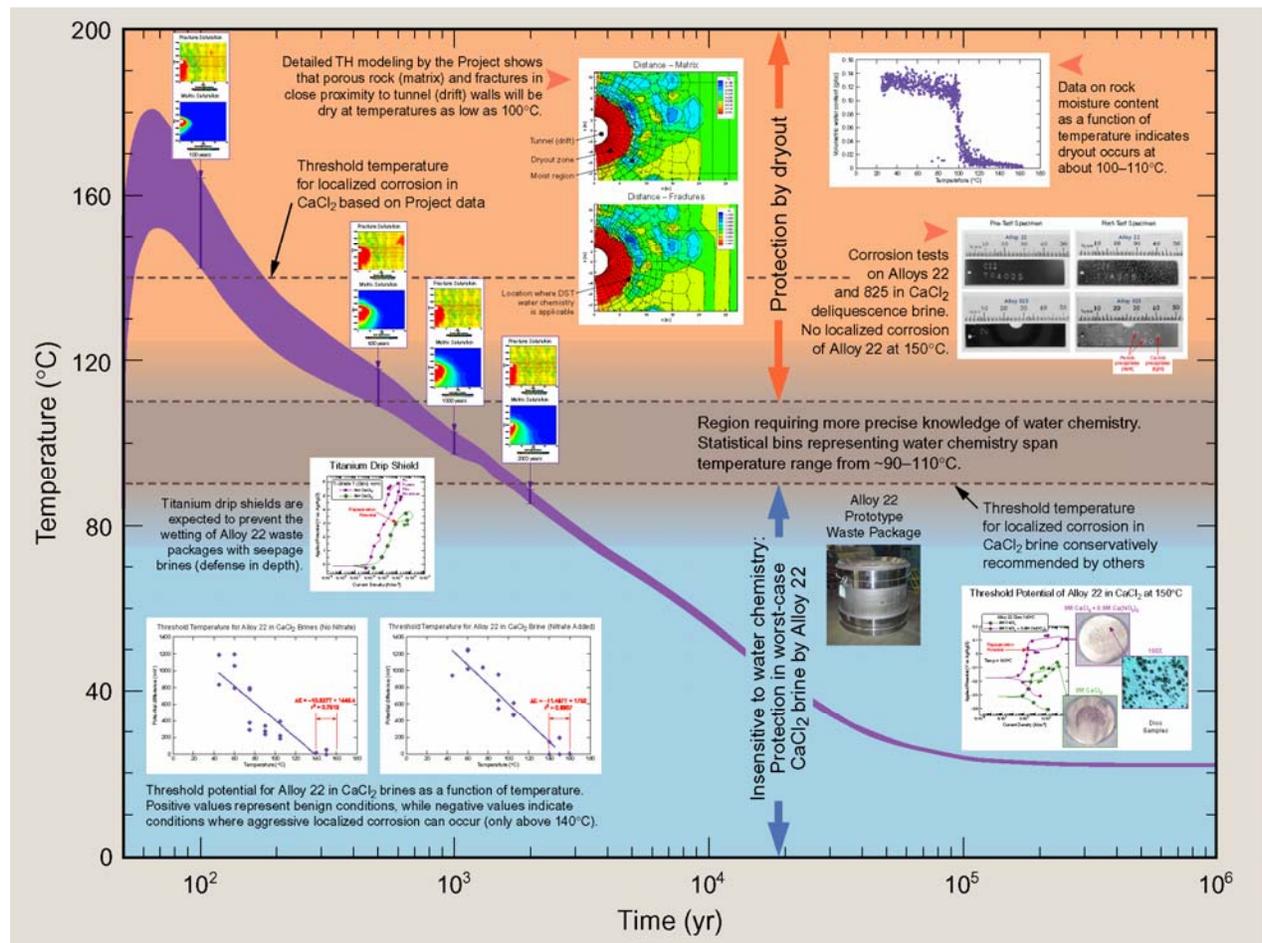


Figure 2. 1
Schematic Diagram of Temperature-Time Evolution for the Drift Environment of the High-Temperature Operating Mode (HTOM) Concept for a Repository at Yucca Mountain (from Boyle, 2003).

This report presents and summarizes the results of the analyses that have been conducted to address these questions.

In addition, EPRI has been active in obtaining and developing supplemental data in key areas. One such area is the collection of new information on possible wind-borne dust and deliquescent brine formation. The new EPRI data further affirms the previous conclusions of the YMP on this topic.

A second continuing study area is improving modeling capabilities with respect to the formation and thermodynamic stability of concentrated brine solutions. As specified by safety regulations (see NRC, 2003), such modeling capabilities will be necessary to extend understanding of in-drift geochemical processes, and to defensibly critique the corrosion tests that have recently been conducted by the State of Nevada. Results of these geochemistry analyses are reported here.

3

CHEMICAL SYSTEM OF THE REPOSITORY DRIFT

The ambient conditions within the emplacement drift for a repository at Yucca Mountain will evolve because of a combination of excavation effects and radiogenic heating from emplaced nuclear waste packages (*e.g.*, Bodvarsson, 2003). As shown in Figures 2.1 (previous chapter) and 3.1, there will be a period of prograde heating followed by a much longer period of retrograde cooling. At any point in time, temperatures will radially decrease from the centerline of the waste package outward into the open drift and surrounding tuff host rock. Modifications to this temperature profile will arise from convective movement of both air in the drift (*e.g.*, Danko and Bahrami, 2003; 2004) and water in the partially saturated tuff. Relative humidity (see Figure 3.1), chemical potentials and stress states will adjust over time and space, largely in response to the temperature evolution shown in Figures 2.1 and 3.1.

Defining the effective “chemical system” of the drift is of crucial importance in proper evaluation of alternative corrosion scenarios. This chemical system imposes important controls and bounds on the chemical compositions of aqueous and gaseous phases within the emplacement drift, including the waste package surface. The chemical system definition also sets important constraints on any proposed test intended to realistically simulate chemical processes for the repository.

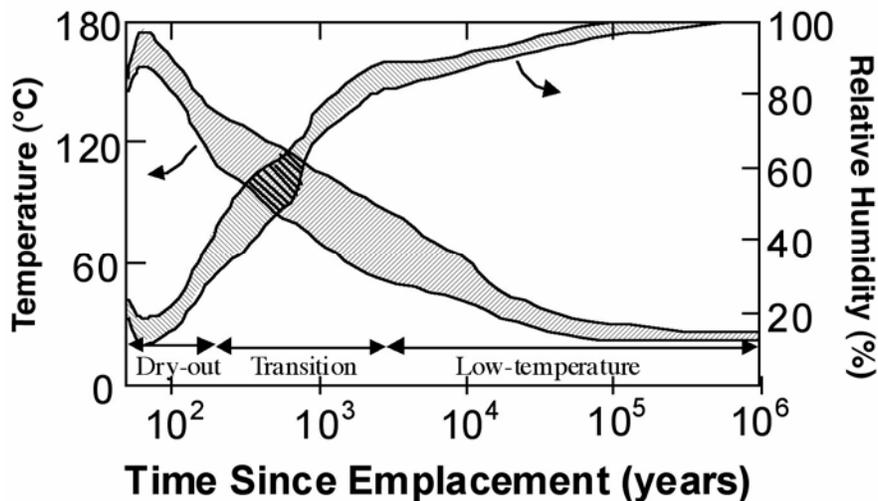


Figure 3 . 1
Time Dependence of the Ranges of Waste Package Surface Temperature and Drift Relative Humidity in the Yucca Mountain Repository.

Figure 3.2 shows a simple schematic picture of the chemical system for an emplacement drift. The key components and phases include:

- waste package surface,
- drip shield surface (excluded from Figure 3.2 for clarity),

- solution and dust solids on the waste package surface,
- air environment of open drift,
- water and gas in pores and fractures of the tuff host rock , and
- minerals comprising the tuff matrix.

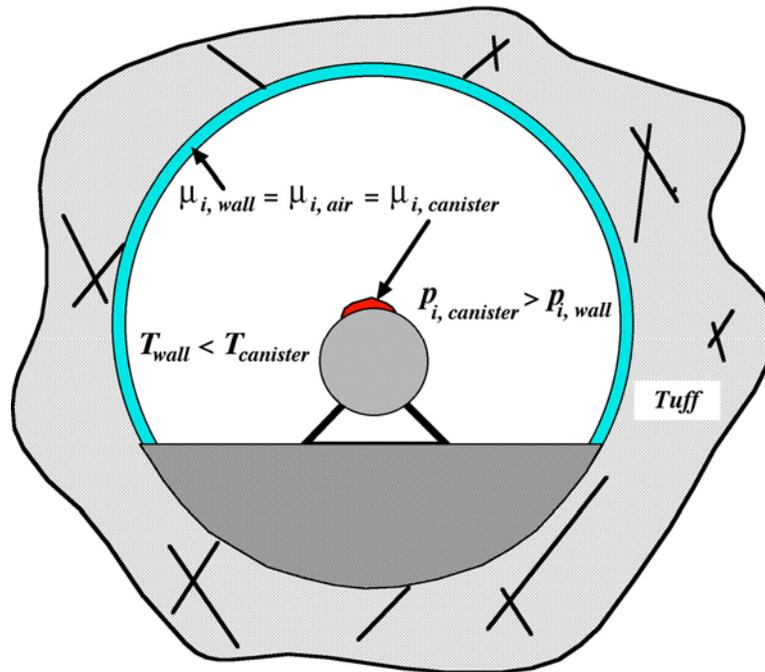


Figure 3 . 2
Schematic Illustration of Equilibrium Chemical System for Emplacement Drifts. Blue region indicates water in drift walls and red region indicates possible brine formed on waste package surface. Other terms are as defined in text.

The status of reactions involving volatile (gas) species at two distinct locations (with brine solution on waste package surface and dilute pore water in the drift wall) is determined by comparing the fugacities or partial pressures of the gases.² For an isothermal situation, an equilibrium condition exists when the chemical potential of the gas species is equivalent at both locations. Because the temperature is also the same at both locations, the partial pressure of the gas must also be equivalent. Thus, there would be no thermodynamic driving force to move the gas from one location to the other.

If a temperature gradient exists, however, then the effects of the differences in temperature on partial pressures must be compared. The chemical potential of the *i*-th volatile species at absolute temperature *T* is given by:

² The partial pressures for volatile acid-gas species will be extremely small, less than 10^{-10} bars, compared to a total system pressure of ~ 1 bar. The slight differences between fugacities and partial pressures are not relevant in this low-pressure environment (*e.g.*, Wood and Fraser, 1976).

$$\mu_i(T) = \mu_i^o(T) + RT \ln p_i \quad (3.1)$$

where $\mu_i^o(T)$ is the standard chemical potential at temperature T , R is the gas constant (8.3143 J/K-mol), and p_i is the partial pressure of the gas. As the in-drift chemical system strives to attain equilibrium, the chemical potential of a volatile species at the waste package surface, in the “air” of the drifts, and in the water in the drift walls will tend to equalize. As a limiting condition, it can be assumed that

$$\mu_{i,canister} = \mu_{i,air} = \mu_{i,wall} \quad (3.2)$$

A key point is that the “air” in the drifts acts as a continuous contacting medium that allows the waters in the two different locations (brine on the surface of the waste package or drip shield and drift-wall water) to be in chemical communication, hence to approach equilibrium, with each other for volatile species³.

The two waters, however, are always at different temperatures, call them T_c for the solution on the waste package, and T_w for the water in the fractures and pores of the drift wall. Given the constraint implied by Equation 3.2:

$$\mu_i^o(T_c) + RT_c \ln p_{i,c} = \mu_i^o(T_w) + RT_w \ln p_{i,w} \quad (3.3)$$

where $p_{i,c}$ is the pressure of the i -th gas in the solution on the waste package and $p_{i,w}$ is its corresponding pressure in the water in the drift wall. This sets up a bounding non-isothermal steady-state condition in which the volatile species [*e.g.*, HCl(*g*)] will move through a connecting gas phase from a region of high partial pressure to a region of lower partial pressure.

If temperatures at the two locations are known, as well as the pressure of a gas species at one location, the equilibrium value of the partial pressure at another location can be calculated by rearranging Equation 3.3, *i.e.*

$$\ln p_{i,c} = \frac{T_w}{T_c} \ln p_{i,w} + \frac{(\mu_i^o(T_w) - \mu_i^o(T_c))}{RT_c} \quad (3.4)$$

³ It might be speculated that a brine or solution phase forming on the container surface of waste packages or the surface of the drip shield might not be in chemical communication with the rest of the drift system, perhaps because of (a) occlusion of a brine within a deep crevice, or (b) the capping of a brine by an impermeable, gas-tight “crust”. In the former speculative case, brine formation (hence, brine stability) is needed to possibly induce formation of deep crevices in the container. Geometrical ‘crevices’, occurring at the intersection of the container with its emplacement pedestal, will require sufficient opening for dust (the postulated chloride source for deliquescent brines) and water vapor to enter. This condition for brine formation would reasonably indicate that any brine phase would have a free surface exposed to air, and hence would be in chemical communication with the entire drift system. With respect to speculative formation of an impermeable crust, such a phase would have to be not only water-tight, but also air-tight, trapping volatile species escaping the brine. There is no direct evidence that such gas-tight crusts form on containers, nor measurements of composition and affirmation of impermeability of such speculative crusts, cited in NWTRB (2003a). However, the impact of brine formation within speculative closed-system crevices or crusts can and has been examined by EPRI, with initial results provided in Section 4.3 of this report.

The applicability of this equilibrium requires that transport of the gas between the two locations be rapid. Given the distances between the drift wall and the waste packages, and that both convection and diffusion of the air in the drift are relatively fast processes, the use of this equation is justified.

The standard state chemical potential for any given volatile phase decreases (becomes more negative) with increasing temperature (Helgeson *et al.*, 1978):

$$\mu_i^o(T_c) < \mu_i^o(T_w) \quad (3.5)$$

and

$$\frac{T_w}{T_c} < 1 \quad (3.6)$$

Therefore, the partial pressure of a volatile species at the hotter solution at the waste package surface will always be higher than the equilibrium partial pressure for the same species at the cooler water in the drift wall. This gradient in pressure (hence, gradient in concentration) will act to move volatile species from the solution on the waste package into the water of the drift wall. Such movement will occur, independent of any other transfer mechanism such as advection, if either the partial pressure of the volatile species increases at the solution on the surface of the waste package, or decreases at the water within the drift wall. This principle, arising from the realistic definition of the operative chemical system of an emplacement drift, applies during both the transition and the low-temperature intervals.

4

DELIQUESCENT DURING THE TRANSITION INTERVAL

During the transition interval of the thermal pulse under the nominal conditions for the high-temperature operating mode (HTOM), temperatures within the drift always exceed the boiling point of water. Importantly, seepage of porewaters into the drifts cannot occur during this period because such porewater is completely vaporized before it enters the drift. Aqueous solutions that could come into contact with the drip shield and waste packages are, therefore, limited to solutions that could form from the absorption of water vapor by deliquescent salts. Such salts may be part of the mineralogy of dust that is entrained by circulating air in the drifts and possibly deposited on the surface of the waste packages. Pure deliquescent salts (if they can exist in this system) may form concentrated brines at temperatures considerably higher than the ambient boiling point; on the order of 140-160°C for divalent chlorides such as $MgCl_2$ and $CaCl_2$. Such brines are potentially aggressive, promoting both general and localized corrosion of Alloy 22 waste packages (NWTRB, 2003a).

To address the subject of deliquescence within the repository, EPRI has convened independent experts to examine the various data, assumptions, and modeling related to possible formation, stability, persistence, corrosion implications, and safety compliance impacts of deliquescent solutions on waste packages. The following sections review these topics.

4.1 Formation of Deliquescent Brines

The possible formation of high-temperature deliquescent brines depends on the mineralogy of dust that will be deposited on waste package surfaces as a result of air circulation in the drifts. This is because the deliquescence relative humidity of a mixture of salts is always less than that of any pure salt in the mixture (*e.g.*, Wexler and Seinfeld., 1991; Ge *et al.*, 1998). Thus, given the inverse relation between relative humidity and temperature shown in Figure 3.1 (see previous chapter), the brine that first forms as the temperature at the surface of a waste package cools during the transition interval will be the deliquescent brine of a mixture of salts contained in the dusts coating this surface. The composition of the brine will be determined by the compositions of the individual salts comprising the mixture.

Peterman *et al.* (2003) studied the composition of soluble salts in dust currently in the exploratory studies facility (ESF). They found that calcium and sodium were the major cations, and sulfate and nitrate the dominant anions. The decreasing molar abundance of soluble anions was, on average, in order: SO_4^{2-} (42%) > NO_3^- (33%) > Cl^- (25%) (see Table 4.1 and Figure 4.1). Soluble salts comprise only 0.3% of the ESF dust on average. Peterman *et al.* (2003) note that at least 95% of the dust is made up of Topopah Spring Tuff particles derived from tunnel operations. Assuming for simplicity that the Topopah Spring Tuff makes up the remaining 99.7% of the dust, the mineral composition of the ESF dust is given in Table 4.2, which is based on Dobson *et al.* (2003). Table 4.2 shows that the ESF dust is made up of about 59% aluminosilicate minerals, and 41% silica polymorphs (tridymite, cristobalite and quartz).

Table 4 . 1
Mole Percent of Ions in Soluble Salts in Wind-Blown Dust and ESF Dust and in Precipitation from Near Yucca Mountain, and Anion Chloride Ratios.

Source	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻ /Cl ⁻ Ratio	(NO ₃ ⁻ +SO ₄ ²⁻)/Cl ⁻ Ratio
(1) Salts in wind-blown dust (USGS, Reheis, 2003; Izbicki, 2003)	60	10	26	4	65	25	10	6.50	9.00
(2) Precipitation chemistry maps, 1997, 2002 (NADP ⁴)	60	10	25	5	66	23	11	6.00	8.09
(3) Red Rock Canyon precip (Site NV-00), 1997-2002 (NADP ⁴)	68	12	18	3	69	20	11	6.27	8.09
(4) Death Valley precip.(Site CA-95), 2000-2002 (NADP ⁴)	54	7	37	3	63	19	18	3.50	4.56
(5) Salts in dust from ESF (USGS, Peterman <i>et al.</i> , 2003)	40	4	42	14	33	42	25	1.32	3.00

Italicized values for cations in wind-blown dust have been estimated by averaging the values from sources (1) through (4). Ammonia in precipitation has been ignored.

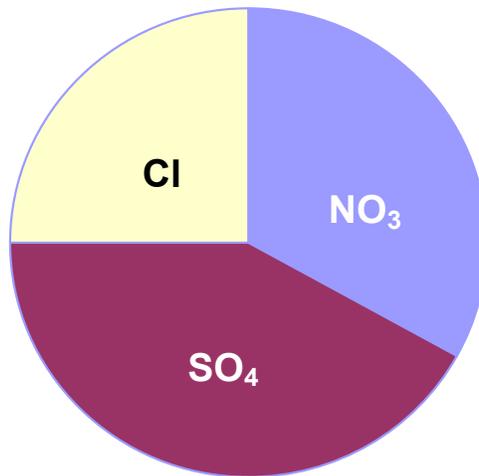


Figure 4 . 1
Anion Percent Values in Soluble Salts in ESF Dust

Pure divalent-cation (Ca²⁺, Mg²⁺) chloride deliquescent brines could not possibly form from the soluble salts in ESF dust without separation of the salts. Furthermore, the presence of competing non-chloride anions increases the maximum temperature of any possible deliquescent brine that might form. Starting with the soluble salt as found in actual dust compositions observed by Peterman *et al.* (2003), Peters (2003) shows geochemical modeling results using the EQ3/6 software package that indicate that among the endpoint brines, none would form predominately

Table 4 . 2
Average Mineral Composition of ESF Dust and Wind-Blown Dust

	<u>Mineral</u>	<u>ESF Dust</u>	<u>Wind-Blown Dust</u>
		<u>Wt %</u>	<u>Wt%</u>
Basic Minerals	K-spar	31.7	10.5
	Albite	23.9	5.7
	Oligoclase		12.1
	Anorthite	0.8	
	Kaolinite		4.2
	Montmorillonite		6.6
	Smectites	2.1	
	Illite + muscovite	0.3	8.9
	Biotite		5.4
	Goethite		1.4
	Calcite		6.6
	Dolomite		1.2
	Sum	58.9	62.5
Inert Minerals	Tridymite	4.4	
	Cristobalite	23.7	
	Quartz	12.7	26.3
	Rutile		0.4
	Gypsum		1.1
	Sum	40.9	27.7
	Soluble Salts	0.3	9.6

Ca-Cl brines. To confirm the robustness of this analysis, the full range of possible dust compositions must be identified. EPRI-sponsored contractors have been collecting additional data on dust compositions, in response to the acknowledgement by Peterman *et al.* (2003) that on the longer time scale (1000's years), "ambient atmospheric dust may become important after the repository is closed." For example, Reheis *et al.* (1999; 2002) and Reheis (2003) have sampled wind-blown ambient dust at a network of stations in southern California and Nevada since 1985. Izbicki (2003) chemically analyzed the anion concentrations of soluble salts in the dust sampled by Reheis (2003) from localities near Yucca Mountain. Reheis (personal communication, 2003) believes that these samples are representative of present and future dust that might enter into the repository. In 16 samples obtained during the period 2001-2003, the average molar anion concentrations of soluble salts decreased in the general order NO_3^- (65%) > SO_4^{2-} (25%) > Cl^- (10%) (Table 4.1 and Figure 4.2). The concentrations of soluble cations have not been determined in the wind-blown dust. However, evidence shown in Table 4.1 indicates that the soluble cations in wind-blown dust can be estimated from the chemistry of precipitation. Listed in Table 4.1 are mole percent concentrations of cations and anions in precipitation sampled near Yucca Mountain based on precipitation chemistry maps drawn using data from the National Atmospheric Deposition Program (NADP⁴) given by Langmuir (1997) and/or available on the

WEB⁴. Also shown in Table 4.1 are mole percent concentrations of the ions in precipitation collected at NADP sites at Red Rock Canyon which is 76 miles southeast of Yucca Mountain, and Death Valley, which is 33 miles west-southwest of Yucca Mountain. The strong similarity of the anion concentrations in wind-blown dust and precipitation indicates that average cation values in precipitation may be used to estimate mole percent cation values in wind-blown dust, which has been done in Table 4.1.

According to data published by Reheis and Kihl (1995), the wind-blown dusts sampled near Yucca Mountain had an average soluble salt content of about 10% and carbonate content of 11%. About 75% of the dust was present as silicate and alumino-silicate minerals. EPRI consultants obtained, x-ray diffraction patterns for five samples of wind-blown dust sampled near Yucca Mountain between 1986 and 1989 from Dr. Marith Reheis⁵. Taking into account the x-ray data, along with published elemental oxide analyses and the content of soluble salts, carbonate and sulfate in the dust⁶, Dr. Maynard Slaughter⁷ has performed a quantitative mineralogical analysis of the five samples. His detailed results are summarized in Appendix A Table A.1. The average mineralogical composition of the wind-blown dust, based on the five samples, is given in Table 4.2. The tabulated data show that the dust is comprised of about 28% feldspar minerals, 25% clay and mica minerals, 8% Ca and Mg carbonates, and 9.6% soluble salts. The mineral amounts given in Table 4.2 will be assumed in subsequent calculations involving acid gas neutralization by wind-blown dust.

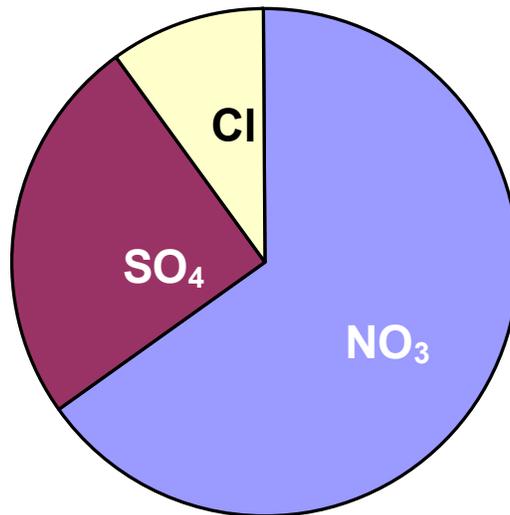


Figure 4 . 2
Anion Percent Values in Soluble Salts in Wind-blown Dust from Near Yucca Mountain.

⁴ <http://nadp.sws.uiuc.edu/sites/ntnmap.asp>

⁵ U.S. Geological Survey, Denver, CO

⁶ This information is available at the web sites <http://geochange.er.usgs.gov/pub/dust/Derived/dos/labdust.xls> and <http://geochange.er.usgs.gov/pub/dust/Derived/dos/dustloc.xls>

⁷ Crystal Research Laboratories, Greeley, CO

Shown in Table 4.1 are $\text{NO}_3^-/\text{Cl}^-$ and $(\text{NO}_3^- + \text{SO}_4^{2-})/\text{Cl}^-$ ratios of the soluble salts in wind-blown dust and in dust from the ESF. Dunn and Brossia (2002) and Hall and Walton (2003) note that the critical threshold molar $(\text{NO}_3^- + \text{SO}_4^{2-})/\text{Cl}^-$ ratio is 0.2 at 95°C. Only below this value can localized corrosion of welded Alloy 22 occur. Cragnolino (2003) indicates that the critical $\text{NO}_3^-/\text{Cl}^-$ ratio (in a sulfate-free system) is 0.2 for welded Alloy 22, and 0.12 for mill-annealed Alloy 22. The $\text{NO}_3^-/\text{Cl}^-$ and $(\text{NO}_3^- + \text{SO}_4^{2-})/\text{Cl}^-$ ratios of salts in wind-blown dust are 6.5 and 9.0, respectively, and 1.3 and 3.0 respectively in ESF dust. These ratios are much greater than the threshold values below which corrosion may occur. Mole percent concentrations of nitrate, sulfate and chloride in precipitation, and in the salts in wind-blown dust and ESF dust are plotted in Figure 4.3. Also shown is the line that defines conditions where the molar $(\text{NO}_3^- + \text{SO}_4^{2-})/\text{Cl}^-$ ratio exceeds or is less than 0.2; the threshold value below which welded Alloy 22 may corrode at 95°C. Clearly, the high nitrate and sulfate, and low chloride content of the salts in ESF dust and wind-blown dust make these salts non-corrosive towards Alloy 22.

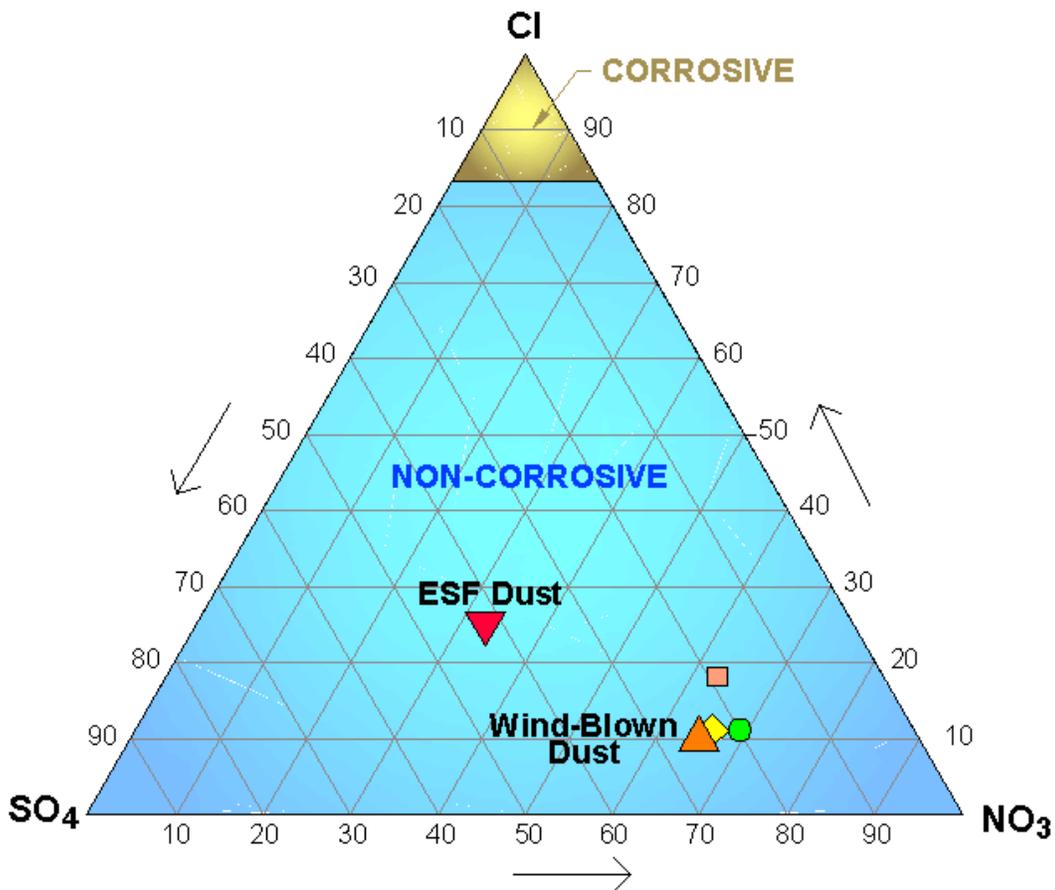


Figure 4 . 3
Triangular plot of percent concentrations of chloride, nitrate and sulfate in the soluble salts of ESF dust (▼), wind-blown dust (▲) and in precipitation (3 points). Also shown are regions of the diagram in which the anion concentrations are corrosive and non-corrosive. The data are from Table 4.1.

Based on a review of this new information by EPRI's experts, these data further confirm the results and interpretations of Peters (2003), and indicate that the possible formation of $\text{Ca}^{2+}\text{-Cl}^-$

dominated deliquescent solutions at high temperature is even less probable than presumed by Peters (2003). Taken together, the data from Peterman *et al.* (2003), Reheis *et al.* (2002) and Izbicki (2003) confirm that corrosive calcium (or magnesium) chloride brines, as conjectured by the NWTRB (2003A), will not form or will be extremely rare (on a probability basis) during the transition interval. Furthermore, any non-divalent-cation chloride deliquescent brine that did form during the transition interval would form at a much lower temperature than that possible for pure calcium (or magnesium) chloride brines.

4.2 Neutralization Capacity of ESF Dust and Wind-Blown Dust

In Section 3 of this report it is emphasized that the total repository system must be considered in any analysis of the behavior of possible deliquescent brines. In particular, the supposition that acid solutions can develop on the container surface of waste packages or drip shields (see Chapter 7 of this report) and fate of possible acid gases needs to be examined in the context of the full repository system. Tests purporting to demonstrate formation of acid solutions on surfaces of containers and drip shields (Pulvirenti *et al.* (2003), Staehle (2003) and Shettel (2003) apparently have not considered the ubiquitous presence of basic minerals in the dust itself, and the presence of the same basic minerals in the walls of the drift. The analyses of this section address how these volumetrically dominant basic minerals will neutralize any acid gases produced by the breakdown of deliquescent salts developed on the dust.

As noted in Section 4.1, soluble salts represent a small fraction of the dust that might coat a waste package. (See Figures 4.4 & 4.5). The dust is made up of basic minerals, inert minerals (not affected by pH), and smaller amounts of soluble salts. Basic minerals, which predominate in the dust, are those that react with and tend to neutralize any contacting acidity. Shown in Table

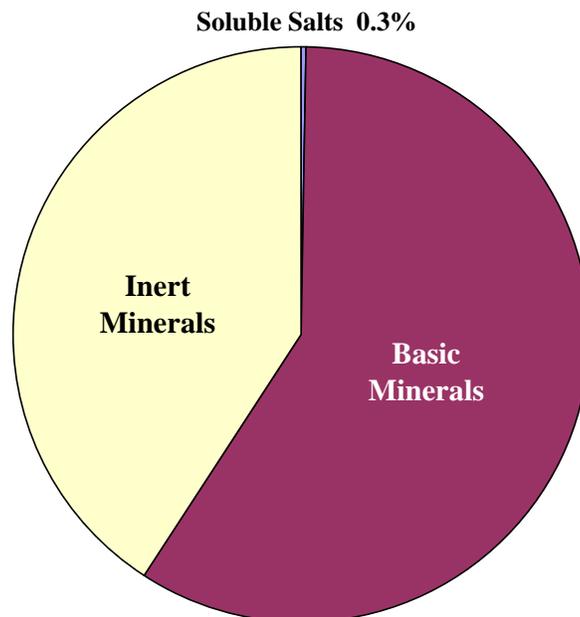


Figure 4 . 4
Weigh Percent Minerals in ESF Dust

4.3(a) are such reactions for example minerals present in dust. The same reactions describe the chemical weathering of these minerals in soils. The pH at which these minerals will buffer any solution in contact with them can be computed as long as the mineral is present. For the three feldspar minerals in Table 4.3(a), the pH is buffered at about 6.5-6.8, for calcite the buffered pH is 8.3. The presence of basic minerals will tend to prevent pH values from becoming more acid than approximately pH 4-5 as long as the minerals are present in excess of the available acidity.

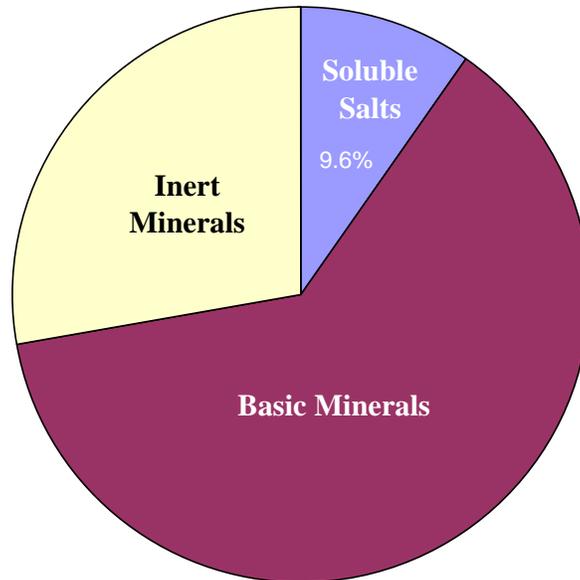


Figure 4 . 5
Weight Percent Minerals in Wind-Blown Dust

Basic minerals dominate in the repository, particularly in the walls of the drift. In fact even in the dust itself, these minerals will easily neutralize any possible acidity that might be produced by acid gases from deliquescent salts. Shown in Tables 4.4 and 4.5 is the neutralization capacity of basic minerals in the ESF dust and wind-blown dust. This capacity has been computed based on the weight percent of dust minerals and on balanced mineral-acid weathering reactions such as those given in Table 4.3(a). Tables 4.4 and 4.5 show that the basic minerals in a kilogram of ESF dust and wind-blown dust can consume 9.0 and 12.0 moles of protons, respectively.

If it is very conservatively assumed that all of the chloride and nitrate in the soluble salts in dust can occur as HCl and HNO₃, the resultant total acidity can be computed. This acidity is compared to the neutralization capacity of the dust in Table 4.6. The comparison shows that neutralization of all of the acid gases that might be produced by wind-blown dust would consume only 7.3% of the basic minerals in that dust. The same calculation for ESF dust indicates that considerably less than 1% of that dust would be consumed by any acidity produced by its deliquescent salts.

These calculations indicate that any acid species produced by the breakdown of deliquescent salts that reach the surface of a waste package will be neutralized by basic minerals in the dust, which are ubiquitous and dominate among dust particles.

Table 4 . 3
(a) Example Acid-Base Mineral Reactions that Will Neutralize Acid Gases

1)	$\text{KAlSi}_3\text{O}_8 + 4\text{H}^+ + 4\text{H}_2\text{O} \rightarrow \text{K}^+ + \text{Al}^{3+} + 3\text{H}_4\text{SiO}_4^0$
	K-spar
2)	$\text{NaAlSi}_3\text{O}_8 + 4\text{H}^+ + 4\text{H}_2\text{O} \rightarrow \text{Na}^+ + \text{Al}^{3+} + 3\text{H}_4\text{SiO}_4^0$
	Albite
3)	$\text{CaAl}_2\text{Si}_2\text{O}_8 + 8\text{H}^+ \rightarrow \text{Ca}^{2+} + 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4^0$
	Anorthite
4)	$\text{Ca}_{.167}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 + 7.32\text{H}^+ + 2.68\text{H}_2\text{O} \rightarrow$
	Ca-smectite $0.167\text{Ca}^{2+} + 2.33\text{Al}^{3+} + 3.67\text{H}_4\text{SiO}_4^0$
5)	$\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$
	Calcite

(b) Equilibrium pH Values for some Major Minerals in the Topopah Spring Tuff and/ or in Windblown Dust at 25°C and Atmospheric CO₂ Pressure.

Mineral	Formula	Equilibrium pH
K-feldspar	KAlSi_3O_8	6.5
Albite	$\text{NaAlSi}_3\text{O}_8$	6.8
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	6.8
Calcite	CaCO_3	8.3

This evaluation has not even considered the vastly greater neutralization capacity of basic minerals in the Topopah Spring Tuff in the drift walls. Their amount in the drift walls will exceed their amount in dust on the waste packages by orders of magnitude. For example, assuming a reactive skin at the drift walls that is 2 mm thick (see discussion in Section 7.4), a 1-meter longitudinal section of the drift walls (drift diameter 5.5 m) contains 900 kg of rock which can neutralize more than 8000 moles of acidity⁸. This neutralization capacity and its relevance to the issue of brine stability and the fate of volatile acid gas species, is discussed below in Section 4.3.

⁸ The neutralization capacity of the Topopah Spring Tuff (ESF dust) is summarized in Table 4.4.

**Table 4 . 4
Neutralization Capacity of ESF Dust (Topopah Spring Tuff) For Potential Acidity.**

Mineral	Wt.% in dust	Moles Mineral per kg dust	Moles Protons consumed per mole mineral	Moles Protons that can be neutralized by 1 kg dust
K-spar	31.7	1.14	4.00	4.57
Albite	23.9	0.91	4.00	3.65
Anorthite	0.85	0.03	8.00	0.24
Ca-smectite	0.74	0.02	7.32	0.15
Na-smectite	0.32	0.01	7.32	0.06
Mg-smectite	0.74	0.02	7.32	0.15
K-smectite	0.32	0.01	7.32	0.06
Illite	0.29	0.01	8.00	0.06
Tridymite	4.41	0.74	0.00	0.00
Cristobalite	23.7	3.96	0.00	0.00
Quartz	12.7	2.12	0.00	0.00
Soluble Salts	0.3			
Neutralization Capacity/kg dust				8.94 moles

4.3 Stability of Deliquescent Brines

EPRI contractors, as well as YMP, have evaluated whether any deliquescent brines that could form on waste package surfaces would be stable and aggressive with respect to localized corrosion of Alloy 22. EPRI-sponsored contractor work in this area addresses the following questions:

- would such brines be stable in hypothetical “microenvironments”, which may be isolated from the in-drift chemical system?, and
- would such brines be stable in the in-drift chemical system?

Progress toward resolving these questions is summarized below in Sections 4.3.1 and 4.3.2, respectively.

The results are based in part on numerical geochemical models, which were evaluated using version 8.0 of the EQ3/6 geochemical modeling software package and a supporting thermodynamic database (data0.ypf; version 1.0) that is compatible with the Pitzer formalism for calculation of activity coefficients in concentrated brines at temperatures between 0° and up to 250°C (OCRWM, 2003). The models consider CaCl₂-type brines exclusively because such solutions are generally regarded as being potentially the most aggressive with respect to localized corrosion of Alloy 22 (*e.g.*, Peters, 2003). Results and conclusions are generally applicable to other types of deliquescent brines as well, because the chemical behavior of most of the anionic constituents of these solutions (*i.e.*, Cl⁻, F⁻, and NO₃⁻) is similar insofar as they tend to

react with H^+ to form potentially significant concentrations of volatile acid-gas species [*i.e.*, $HCl(aq)$, $HF(aq)$ and $HNO_3(aq)$].

Table 4 . 5
Neutralization Capacity of Wind-Blown Dust for Potential Acidity

Mineral	Average Wt.%in Dust	Moles Mineral per kg Dust	Moles Protons consumed per mole mineral	Moles Protons that can be neutralized by 1 kg dust
Albite	5.7	0.22	4.00	0.87
Sanidine	10.5	0.38	4.00	1.50
Oligoclase	12.1	0.46	4.80	2.20
Biotite	5.4	0.12	12.00	1.38
Illite-muscovite	6.9	0.17	12.00	2.08
Illite	2.0	0.05	8.00	0.42
Montmorillonite	6.6	0.19	6.60	1.29
Kaolinite	4.2	0.16	6.00	0.97
Goethite	1.4	0.16	3.00	0.47
Calcite	6.6	0.66	1.00	0.66
Dolomite	1.2	0.06	2.00	0.13
Quartz	26.3	4.38	0.00	0.00
Rutile	0.4	0.05	0.00	0.00
Gypsum	1.1	0.06	0.00	0.00
Soluble Salts	9.6			

Neutralization Capacity/kg dust 11.97 moles

Table 4 . 6
The acid-neutralization capacity of wind-blown and ESF dusts compared to the potential acidity arising from salts in those dusts.

	Soluble Salts Wt%	Basic Minerals Wt%	H^+ Neutr.Capacity of Basic Minerals (mol/kg dust)	Acidity if all ($NO_3^- + Cl^-$) were ($HNO_3 + HCl$)	Mol% Basic Minerals Consumed to Neutralize this Acidity
Wind-Blown Dust	9.6	62.6	12.0	0.88	7.3
ESF Dust	0.3	58.9	9.0	0.012	0.13

It is important to emphasize that the models discussed below are based on the so-called Mesmer pH scale (Wolery, 1992). When using this scale it is assumed that the activity coefficient of H^+ is equal to unity at any temperature. Calculated pH values are thus numerically equal to the

negative logarithm of the molality of H^+ (m_{H^+}). This scale is adopted by EPRI because the alternative pH scale in EQ3/6 (NBS scale) is based on an extended form of the Debye-Hückel equation (Wolery, 1992) that is not applicable to concentrated electrolyte solutions. It can be noted in this regard that attempts to measure the pH of concentrated brines using conventional combination electrodes are severely complicated by the fact that liquid-junction potentials obtained with a brine sample differ significantly from those obtained with dilute calibration solutions. It is difficult to account for these differences quantitatively, and measurement results are thus likely to be highly ambiguous and therefore unreliable. Alternative approaches that have been proposed to measure the acidity of concentrated brines involve the use of ion-selective electrodes in place of standard reference electrodes (*e.g.* Knauss *et al.*, 1990; 1991), or direct measurement of H^+ concentration (Mesmer, 1991). Corresponding parameters that provide a quantitative measure of acidity include the partial pressures of acid gases [*e.g.*, $p_{HCl(g)}$, $p_{HF(g)}$, etc.] and m_{H^+} . These parameters are thus of primary interest in the models discussed below.

4.3.1 Brine stability in isolated microenvironments

The NWTRB (2003a) has postulated that small areas on the surfaces of waste packages could be effectively isolated from contact with the in-drift chemical system. It has been asserted that microenvironments could exist, for example, in crevices or under hypothetical mineral crusts that are assumed to be completely impermeable to transport of gases and aqueous solutes. Although the NWTRB (2003a) provides no references to evidence that such conditions can and do form under realistic repository conditions, the question arises, if such conditions are assumed to exist, whether deliquescent brines would be stable under such closed-system conditions.

An evaluation of this question requires several assumptions. First, it is assumed that the pressure inside such a closed system would be equal to the total atmospheric pressure in the surrounding drift. This is a reasonable assumption because it is unlikely that a significant difference in pressure could be sustained between the closed system and drift by mineral crusts (or by other means). The system is also assumed to consist of a $CaCl_2$ salt, its deliquescent brine and a gas phase. The relevant salt, at the temperatures of interest during the thermal pulse, is $CaCl_2 \bullet 2H_2O$. The higher hydrates, antarcticite ($CaCl_2 \bullet 6H_2O$) and $CaCl_2 \bullet 4H_2O$, are stable only at temperatures less than about $45^\circ C$ (as can be inferred from the thermodynamic data for these salts in data0.ypf, as cited above).

To be stable under such closed-system conditions, the brine must simultaneously equilibrate with its salt and with the gas phase. Brine stability thus depends in part on the partial pressure of the acid-gas species $HCl(g)$ [$p_{HCl(g)}$] and on the equilibrium vapor pressure of H_2O [$p_{H_2O(g)}$]. The former parameter is controlled by total dissolved Cl^- , pH and temperature. The latter parameter is related to brine composition by:

$$p_{H_2O(g)} = a_w p_{H_2O(g),sat} \quad (4.3.1.1)$$

where a_w stands for the activity of H_2O in the brine and $p_{H_2O(g),sat}$ refers to the vapor pressure of pure water at the same temperature.

It is important to note that the brine will not be stable if its equilibrium vapor pressure exceeds the total pressure inside the microenvironment's closed system. If such were the case, the resultant disequilibrium condition would stimulate a continuous, irreversible loss of H_2O from

the brine, resulting eventually in complete dry out. Thus, a key constraint on brine stability is that $p_{\text{H}_2\text{O}(g)}$ cannot exceed 1 bar. As noted above, this pressure is assumed because it is roughly equivalent to the total, atmospheric pressure in drifts at Yucca Mountain.

The equilibrium composition of brine and gas in the closed-system discussed above can be estimated using EQ3/6 to simulate a reaction path involving the incremental addition of $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$ to a 1 kg reference mass of $\text{H}_2\text{O}(l)$ until equilibrium between the brine, salt and gas phase is attained. Following this procedure, a trial-and-error approach can then be used to deduce the temperature at which a stable brine would result while satisfying the constraint $p_{\text{H}_2\text{O}(g)} \approx 1$ bar. This reaction path differs from the process of deliquescence, which involves absorption of a sufficient mass of water vapor at the deliquescence relative humidity to form a discrete liquid phase. The end result of both reaction paths is identical, however, a saturated solution equilibrated with $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$ and the coexisting gas phase. It is important to emphasize that no external influence on the chemistry of the gas phase is considered in these calculations. The composition of the gas is thus controlled only by brine chemistry and temperature and is not influenced by external constraints imposed by the in-drift chemical system. The effects of these external constraints are considered in Section 4.3.2.

Key results of the EQ3/6 simulations are shown in Figure 4.6, where m_{H^+} , $p_{\text{H}_2\text{O}(g)}$ and $p_{\text{HCl}(g)}$ are plotted versus the number of moles of $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$ added to the liquid phase. Using the trial-and-error approach discussed above, it was found that the constraint $p_{\text{H}_2\text{O}(g)} \approx 1$ bar is satisfied when $T \leq 146^\circ\text{C}$. The results shown in the figure thus refer to the maximum temperature at which a deliquescent CaCl_2 -type brine could conceivably exist in microenvironments on waste-package surfaces. As can be seen, equilibrium is attained under such conditions after ≈ 28.5 moles of the salt are dissolved, at which point $p_{\text{HCl}(g)} \approx 10^{-3.5}$ bar and $m_{\text{H}^+} \approx 10^{-6.16}$ mol kg^{-1} . The resultant solution is a concentrated ≈ 14 molal CaCl_2 deliquescent brine (note that 2 moles of H_2O are added to the solution per mole of $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$ dissolved, thus increasing the total mass of H_2O in the liquid phase to about 2.03 kg at equilibrium). Although $p_{\text{HCl}(g)}$ increases rapidly to $10^{-3.5}$ bar, the brine is not acidic because $m_{\text{H}^+} = 10^{-6.16}$ mol kg^{-1} (for comparison, note that m_{H^+} in a pH-neutral, dilute solution at $146^\circ\text{C} \approx 10^{-5.82}$ mol kg^{-1}).

The shape of the curve for m_{H^+} in Figure 4.6 can be explained with reference to the reaction:



for which the following equation can be derived, noting that $m_{\text{H}^+} = a_{\text{H}^+}$ in accordance with the Mesmer pH scale,

$$m_{\text{H}^+} = \frac{K_{eq} a_w}{a_{\text{OH}^-}}. \quad (4.3.1.3)$$

In this equation, K_{eq} stands for the equilibrium constant and a denotes activity. The molality of H^+ is always equal to m_{OH^-} as $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$ is added to solution due to charge-balance constraints. The initial increase in m_{H^+} as $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$ is added to the solution occurs because a_{OH^-} initially decreases more rapidly than a_w . This condition changes after addition of about 2 moles $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$. The activity of water then decreases more rapidly than a_{OH^-} .

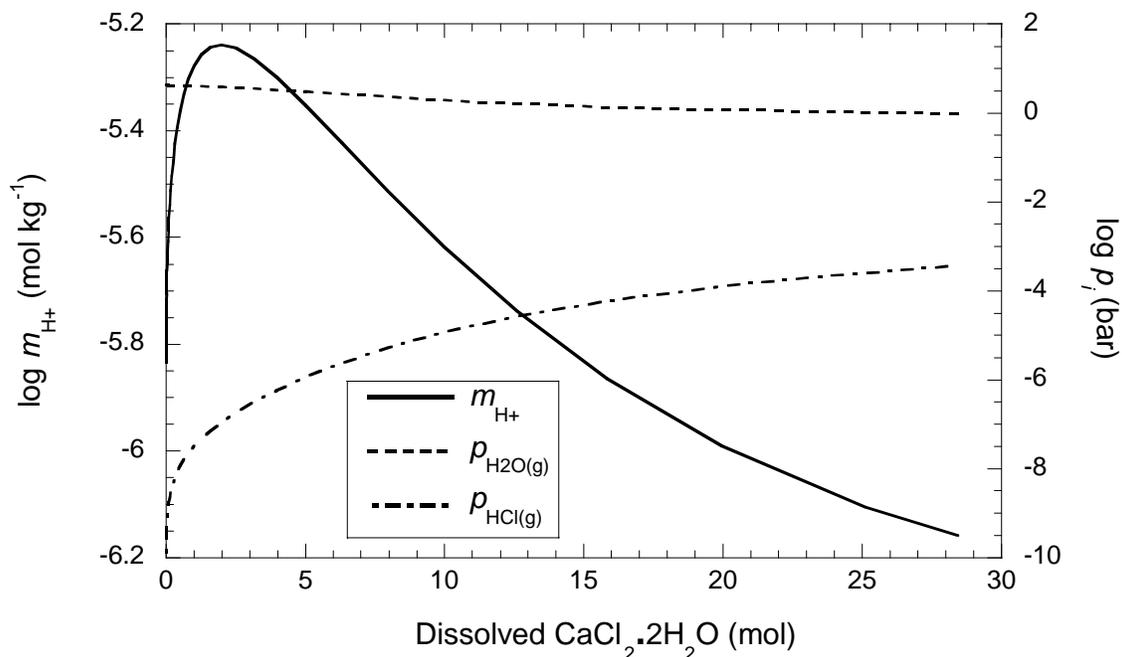


Figure 4 . 6

Calculated variations in m_{H^+} , $p_{H_2O(g)}$ and $p_{HCl(g)}$ attending the incremental addition of $CaCl_2 \cdot 2H_2O$ to an aqueous solution at $146^\circ C$, 1 bar. A saturated solution is attained after addition of 28.5 moles of $CaCl_2 \cdot 2H_2O$. This solution is chemically equivalent to a deliquescent brine equilibrated with the salt and a gas phase.

Although the results shown in Figure 4.6 indicate that a $CaCl_2:2H_2O$ deliquescent brine could exist stably at high temperatures under closed-system conditions, the results also indicate that the solutions would not be acidic. This is important because the corrosion potential (E_{corr}) for Alloy 22 in air-saturated brines is strongly pH-dependent, decreasing rapidly with increasing pH (Cragolino, 2003)⁹.

Modeling of reaction of $CaCl_2$ deliquescent brines with other minerals in dust indicate that brines will be prevented from becoming acidic for any reason (*e.g.*, acid generation by hydrolysis of metals released from Alloy 22 during localized corrosion). To evaluate this possibility, EQ3/6 was used to simulate reaction of dust minerals with the equilibrated $CaCl_2$ brine discussed above. Results for calcite, which comprises about 8% of the wind-blown dust that is likely to enter the repository in the future (Section 4.1), are shown in Figure 4.7. The model used to generate this figure assumes that small amounts of calcite are added incrementally to the brine, and that the calcite dissolves instantaneously and completely until the evolved brine eventually equilibrates with this carbonate mineral. The assumption of instantaneous dissolution is reasonable for calcite because this mineral dissolves rapidly even at low temperatures, and because its reactive surface area is likely to be extremely high given the inherently small grain size of dust particles. It is also assumed, to avoid convergence issues during evaluation of the model, that the amount of calcite

⁹ The probability of localized corrosion of Alloy-22 will depend on the *difference* between E_{corr} and the repassivation potential, E_{rp} . E_{corr} and possibly E_{rp} will be functions of acidity/pH. EPRI is not aware of E_{rp} measurements as a function of acidity/ pH for Alloy-22. Hence, the exact impact of decreasing acidity on localized corrosion of Alloy-22 cannot be unambiguously assessed at this time.

initially present is equal to the amount of residual $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$ remaining after the brine equilibrates with this salt mineral. As noted earlier, non-chloride solids are indeed at least equal to, if not greatly in excess of, the abundance of chloride salts in dusts.

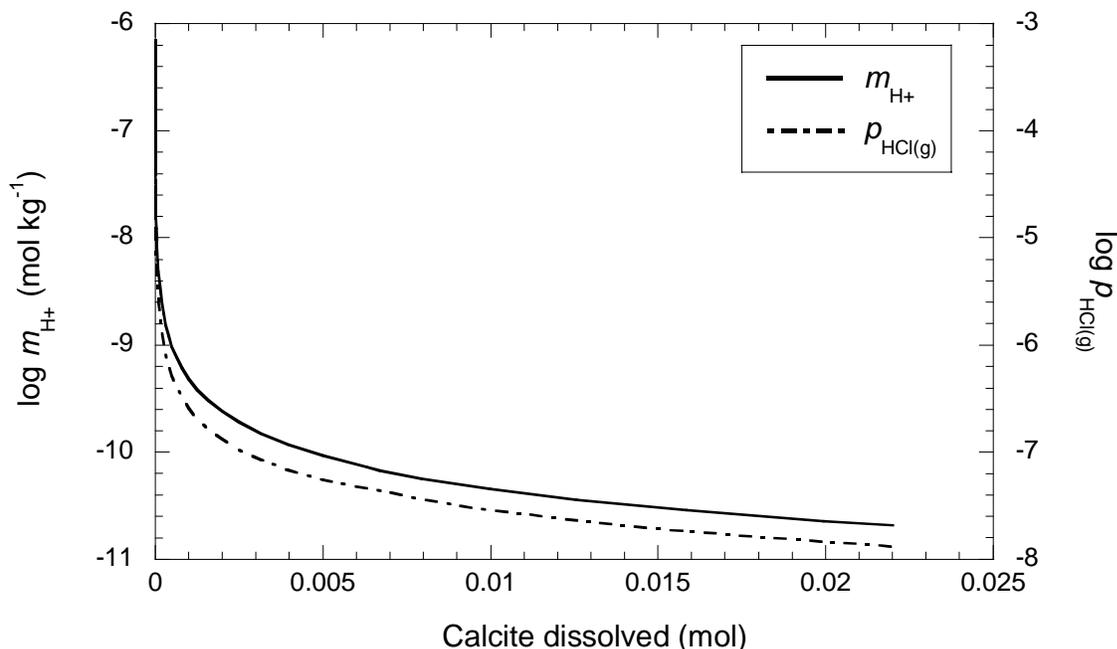


Figure 4.7
Diagram illustrating the effects of calcite dissolution on the equilibrium m_{H^+} and $p_{\text{HCl}(\text{g})}$ of a $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$ deliquescent brine at 146°C, 1 bar.

As can be seen in Figure 4.7, reaction of calcite with the brine causes the molality of H^+ to drop steeply from an initial value of $10^{-6.16} \text{ mol kg}^{-1}$ to about $10^{-9} \text{ mol kg}^{-1}$. Additional reaction then causes m_{H^+} to decrease more gradually until calcite eventually equilibrates when $m_{\text{H}^+} \approx 10^{-10.6} \text{ mol kg}^{-1}$. The trends in m_{H^+} with increasing reaction progress are qualitatively similar to those for $p_{\text{HCl}(\text{g})}$. Both trends indicate that the solution becomes significantly more alkaline with increasing calcite dissolution. Such buffering against acidification is extremely effective for the case of calcite. The residual $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$ salt considered in this model dissolves completely after just 0.007 moles of calcite are added to the brine. At this stage of reaction progress, the solution is no longer a deliquescent brine, but $p_{\text{H}_2\text{O}(\text{g})}$ nevertheless remains approximately equal to 1 bar.

Similar results to those shown in Figure 4.7 have been obtained in the present study for a number of aluminosilicate minerals. This is important because these “basic” minerals comprise about 53% of the dust that is expected to settle in the repository (Section 4.1). Simulation results obtained using a highly simplified model involving albite, representing the feldspar component of wind-blown dust, and Na-beidellite, representing a likely reaction product of albite dissolution, are shown in Figure 4.8. As can be seen, dissolution of trace amounts of albite in the deliquescent CaCl_2 brine discussed earlier leads to a sharp decrease in m_{H^+} until Na-beidellite precipitates. Continued dissolution of albite then causes more of this clay mineral to precipitate, resulting in a small decrease in m_{H^+} until both minerals equilibrate with the evolved brine and residual $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$. As noted above for the case of calcite, reaction of the brine with these

alumino-silicate minerals results in a solution that is considerably more alkaline than the starting solution. Although the dissolution rates of albite and other alumino-silicate minerals are generally much slower than those of carbonate minerals, the combination of high waste-package temperatures and high surface areas associated with dust-sized particles suggests that these reactions will be important and will significantly augment the overall ability of other dust minerals, including carbonates, to strongly buffer against the acidification of deliquescent brines. An important consequence of such buffering behavior is that the potential for localized corrosion of Alloy 22 would be greatly diminished (*e.g.*, Cragolino, 2003).

As noted in Section 4.1, other salt minerals in dust may also reduce the corrosivity of a deliquescent brine. To evaluate this possibility quantitatively, EQ3/6 was used to simulate formation of a stable CaCl_2 brine at 146°C (as discussed above), followed by reaction of the brine with other salt minerals in dust. Soda niter (NaNO_3) and thenardite (Na_2SO_4) were assumed to be present in the model as representative nitrate and sulfate salts that are moderately to strongly deliquescent. As noted in Section 4.1, the NO_3^- and SO_4^{2-} contents of wind-blown and ESF dusts greatly exceed that of Cl^- . As a conservative bounding assumption, thirty moles of each salt, including $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, were assumed to be present. About 28.5 moles of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ must dissolve in 1 kg of water to form the saturated brine, however, so only a small residual amount exists when the brine begins to react with the other salts.

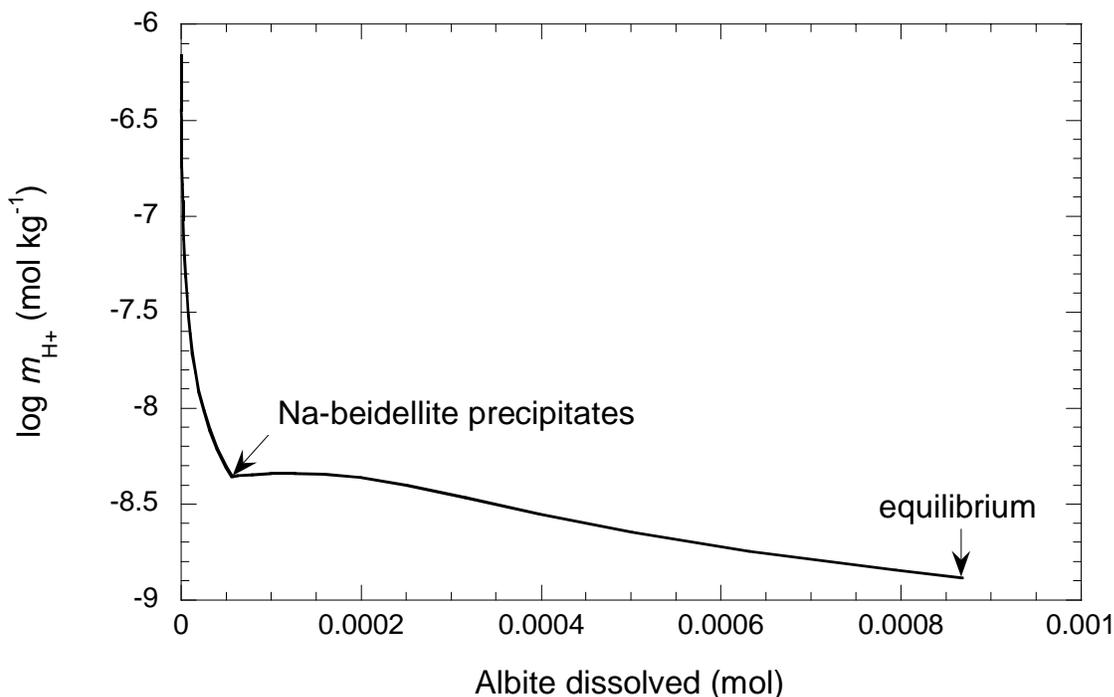


Figure 4 . 8
Diagram illustrating the effects of albite dissolution and precipitation of a Na-beidellite reaction product on the equilibrium pH of a $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ deliquescent brine at 146°C , 1 bar.

Key results that are relevant to the corrosivity of the simulated brine are shown in Figure 4.9, where the molar ratio of $(\text{NO}_3^- + \text{SO}_4^{2-})$ to Cl^- is plotted versus the number of moles of each salt

reacted (*i.e.*, numbers on the x -axis refer to the number of moles of NaNO_3 dissolved in the brine, which is equal to the number of moles of Na_2SO_4 dissolved, normalized to the initial amount of Cl^- in the brine, ≈ 28 moles). Reaction of the initial CaCl_2 brine with 0.07 moles NaNO_3 and 0.07 moles Na_2SO_4 (*i.e.*, $x = 0.25\%$) results in complete dissolution of the residual $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and precipitation of anhydrite (CaSO_4). Anhydrite continues to precipitate with continued dissolution of NaNO_3 and Na_2SO_4 until 0.86 moles of the salts have reacted ($x = 3.1\%$). Halite (NaCl) then precipitates, and halite and anhydrite continue to precipitate until all the remaining soda niter and thenardite are dissolved. The final solution is a concentrated brine equilibrated with halite and anhydrite. As these reactions proceed, the ratio $(m_{\text{NO}_3^-} + m_{\text{SO}_4^{2-}})/m_{\text{Cl}^-}$ rises steadily and eventually exceeds the nominal threshold value of 0.2, above which localized corrosion of Alloy 22 is strongly inhibited, after dissolution of only about 4 moles of the salts ($x = 14.3\%$). These results suggest that an inhibitive effect on the initiation of localized corrosion of waste packages will be provided by the reaction of Cl^- -type brines with the dominant NO_3^- and SO_4^{2-} salts that will exist in dusts coating the canister's surfaces.

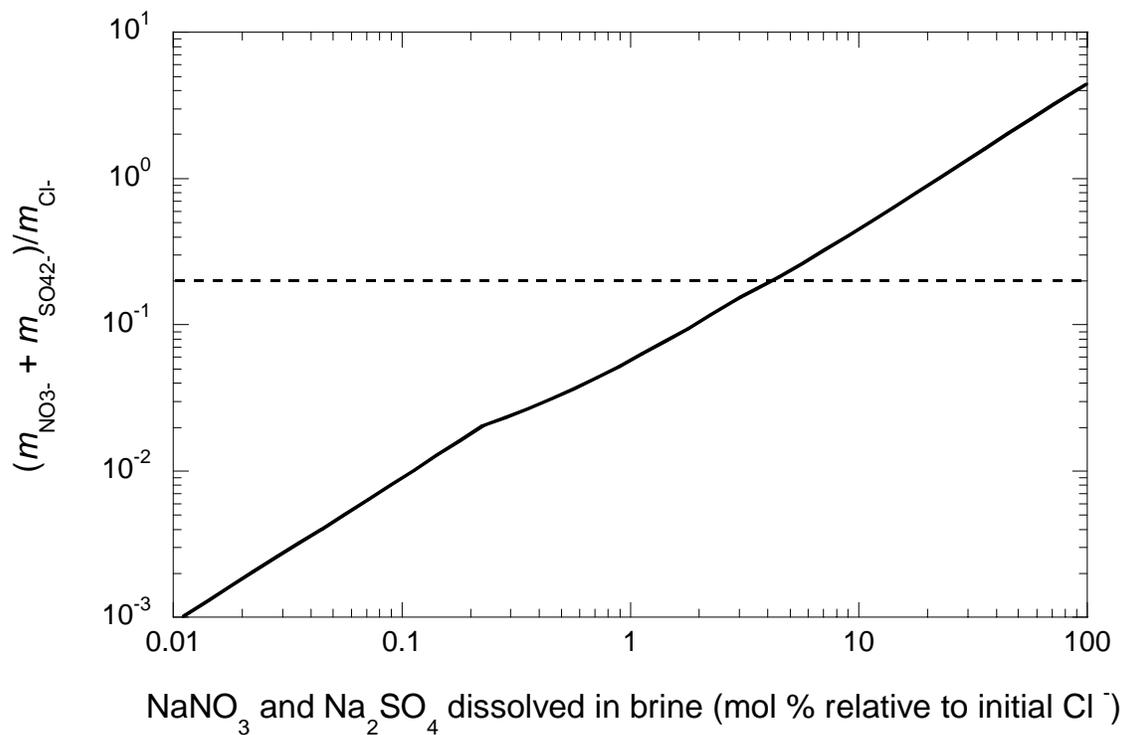


Figure 4.9
Calculated variations in $(\text{NO}_3^- + \text{SO}_4^{2-})/\text{Cl}^-$ molar ratio during reaction of a CaCl_2 brine with soda niter (NaNO_3) and thenardite (Na_2SO_4) at 146°C , 1 bar. The dashed line indicates the lower threshold value for inhibition of Alloy 22 corrosion by the total concentration of $\text{NO}_3^- + \text{SO}_4^{2-}$.

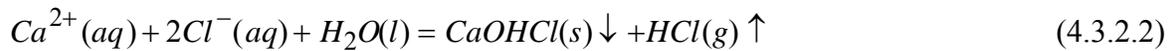
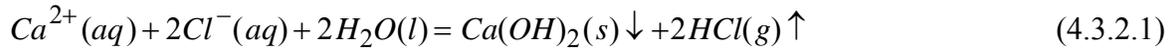
In summary, it is emphasized that deliquescent brines could only possibly persist under closed-system conditions beneath gas-impermeable crusts or in postulated occluded microenvironments. The existence of such microenvironments is speculative because it is highly unlikely that complete isolation of such environments from the in-drift chemical system could be achieved by capping of crevices or other indentations on the surfaces of waste packages by mineral crusts.

If such environments were found to exist on the surfaces of waste packages, modeling results indicate that high-temperature deliquescent brines may be stable under closed-system conditions. However, it is unlikely that the brines would be aggressive with respect to localized corrosion of Alloy 22 because the brines are predicted to be near-neutral in terms of acidity. The corrosivity of such brines would be further attenuated by reductions in acidity and increases in the molar ratio of $(\text{NO}_3^- + \text{SO}_4^{2-})/\text{Cl}^-$ resulting from dissolution of minerals that will coexist with the brines.

4.3.2 Brine stability in the in-drift chemical system

In this section, the stability of deliquescent brines in the in-drift chemical environment, which is described in Section 3, is evaluated. Brine stability in this context depends both on the chemistry of the brine on waste packages and on the chemistry of porewater in the surrounding host rock. This is because both liquid phases are in chemical contact with one another via the intervening gas phase residing in the drift and in fractures and pore spaces of the rock.

The stability of deliquescent brines under such conditions has received little attention in NWTRB (2003a). Reactions that could destabilize a CaCl_2 -type brine, for example, include:



where the abbreviation “aq” refers to an aqueous species, “l” denotes the liquid phase, “s” stands for solid, and “g” represents a gaseous, volatile species. The downward-facing arrows indicate precipitation. The upward-facing arrows for $\text{HCl}(\text{g})$, indicate the tendency for this volatile acid-gas species to escape the liquid phase and enter the gas phase inside the drift.

All the above reactions highlight the importance of $p_{\text{HCl}(\text{g})}$ as a determinant of brine stability. This is because the chemical potential of $\text{HCl}(\text{g})$ in the gas phase in contact with the relatively dilute water in the host rock, and the chemical potential of this same species in the gas phase in contact with the concentrated deliquescent brine on a waste package’s surface will tend to equalize as the in-drift system strives to attain equilibrium. Assuming phase and chemical equilibrium on a local scale, *i.e.*, at the location of the host rock and the location of the waste package surface, is reasonable because reactions involving the exchange of gas species between a gas and liquid phase are rapid even at low temperatures. Equilibrium at the local scale will establish a gradient in $p_{\text{HCl}(\text{g})}$ at the drift scale, and thus a gradient in the concentration of HCl in the gas phase (*i.e.*, because $p_{\text{HCl}(\text{g})} = PX_{\text{HCl}(\text{g})}$, where P refers to total atmospheric pressure and X stands for mol fraction). The concentration of $\text{HCl}(\text{g})$ at the waste package will be greater than its concentration in the host rock because the temperature at the wastepackage surface will always be higher than it is in the host rock. Even in the absence of advective transport of drift gases, the concentration gradient will lead to diffusive transport of $\text{HCl}(\text{g})$ away from the waste package surface toward the drift wall, driving the above reactions continuously to the right. This sustained removal of volatile HCl could destabilize any CaCl_2 brine that might form on the waste-package surface, resulting in the precipitation of insoluble, non-deliquescent and alkaline solids such as those shown on the right-hand side of the above reactions.

To evaluate this possibility quantitatively, it is first assumed that porewater in the host rock is condensate generated by the thermal pulse. A representative composition for this solution is taken from the abstracted results of DOE's THC modeling of drift-scale coupled processes for the mean infiltration flux case (see Table 4.7 below; taken from Table 3 of OCRWM, 1999). The partial pressure of $\text{CO}_2(\text{g})$ is considered to be representative of values in the drift during the thermal pulse based on the THC modeling results. Given the condensate's temperature and composition as shown in Table 4.7, the corresponding $p_{\text{HCl}(\text{g})}$ is calculated to be $10^{-14.5}$ bar using EQ3/6 and data0.ypf.

Table 4.7
Condensate chemistry (solute concentrations in mol kg^{-1} , $p_{\text{CO}_2(\text{g})}$ in bars).

Parameter	Value
T (°C)	96
pH	8.1
Ca^{2+}	6.4×10^{-4}
Na^+	1.4×10^{-3}
$\text{SiO}_2(\text{aq})$	1.5×10^{-3}
Cl^-	1.8×10^{-3}
HCO_3^-	1.9×10^{-4}
SO_4^{2-}	6.6×10^{-4}
Mg^{2+}	3.2×10^{-7}
K^+	8.5×10^{-5}
Al^{3+}	2.7×10^{-7}
Fe	7.9×10^{-10}
F^-	2.5×10^{-5}
$\log p_{\text{CO}_2(\text{g})}$	-6.5

The following equation, derived in Section 3, is used to calculate the corresponding value of $p_{\text{HCl}(\text{g})}$ at the waste package's surface (indicated below by subscript c), assuming, as a bounding limit, equilibrium with $p_{\text{HCl}(\text{g})}$ in condensate in the host wall rock (indicated by subscript w):

$$\ln p_{i,c} < \frac{T_w}{T_c} \ln p_{i,w} + \frac{(\mu_i^o(T_w) - \mu_i^o(T_c))}{RT_c} \quad (4.3.2.4)$$

The temperature of the brine at the waste package's surface is assumed to be 146°C because, as discussed in the preceding section, this is the computed maximum temperature at which a CaCl_2 deliquescent brine could exist on the waste package's surface *if it is assumed that the brine is isolated from the in-drift chemical system*. The standard chemical potentials for $\text{HCl}(\text{g})$ at 96°C and 146°C are then calculated using SUPCRT (Johnson *et al.*, 1992) and the reference thermodynamic data shown in Table 4.8. Calculated results are -26002 and -28333 cal mol^{-1} , respectively. Assuming $p_{\text{HCl}(\text{g})}$ in condensate = $10^{-14.5}$ bar, as noted above, then $p_{\text{HCl}(\text{g})}$ at the waste package's surface is calculated to be $10^{-11.5}$ bar.

The question is then considered whether a CaCl_2 brine would be stable on the surface of the waste package, if it is assumed that the partial pressure of $\text{HCl}(\text{g})$ at the surface is controlled by the in-drift chemical system. To do this the modeling approach described in the preceding section, *i.e.*, EQ3/6, is used to simulate a reaction path involving the incremental addition of $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$ to a 1 kg reference mass of $\text{H}_2\text{O}(\text{l})$ until equilibrium between the brine, salt and gas

phase is attained. However, in contrast to the earlier application of this model, in which it was assumed that $p_{\text{HCl}(g)}$ is unaffected by external constraints imposed by the in-drift system, two alternative constraints are now assumed: 1) $p_{\text{HCl}(g)}$ at the waste package surface is fixed at $10^{-14.5}$ bar, and 2) $p_{\text{HCl}(g)}$ at this surface = $10^{-11.5}$ bar. Both these bounding constraints imply that the partial pressure of $\text{HCl}(g)$ at the waste package surface cannot be sustained at values that are greatly in excess of $p_{\text{HCl}(g)}$ in the condensate porewater, or in a liquid phase at the waste package surface that is in equilibrium with the gas phase in the host rock. These constraints are reasonable because any buildup of $\text{HCl}(g)$ at the waste package surface beyond these limits would increasingly stimulate diffusive transport of HCl away from the surface toward the host rock.

Table 4 . 8
Thermodynamic data for $\text{HCl}(g)$ at 25°C and 1 bar. Parameters a , b and c are coefficients that can be used with the Maier-Kelley equation to calculate isobaric heat capacities as a function of temperature, i.e., $C_p^\circ = a + bT + cT^2$.

Parameter	Value	Source
ΔG_f° (cal mol ⁻¹)	-22776.0	Cox <i>et al.</i> (1989)
ΔH_f° (cal mol ⁻¹)	-22063.0	Cox <i>et al.</i> (1989)
S° (cal mol ⁻¹ K ⁻¹)	44.67	Cox <i>et al.</i> (1989)
a (cal mol ⁻¹ K ⁻¹)	6.6280	Barin and Platzki (1995)
b (cal mol ⁻¹ K ⁻²)	0.6608×10^{-3}	Barin and Platzki (1995)
c (cal K mol ⁻¹)	0.1247×10^5	Barin and Platzki (1995)

The results of these comparative models at 146°C are summarized in Table 4.9. As can be seen, and as noted in Section 4.2.1, it is possible to form a stable deliquescent brine in equilibrium with $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$ if it is assumed that $p_{\text{HCl}(g)}$ is unconstrained by the in-drift system (i.e., $p_{\text{HCl}(g)} = 10^{-3.5}$ bar at the end-point of the reaction path when the solution equilibrates with $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$). The resultant brine is a concentrated 14 molal CaCl_2 solution with $p_{\text{H}_2\text{O}(g)} \approx 1$ bar.

In contrast, if it is assumed that $p_{\text{HCl}(g)}$ is constrained by the in-drift system at bounding values of $10^{-11.5}$ or $10^{-14.5}$ bar, then the results shown in Table 4.9 indicate that a CaCl_2 deliquescent brine cannot form, and, if it is assumed to form on a transient basis, would not be stable on waste package surfaces. Addition of $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$ to the aqueous solution under these conditions results in precipitation of calcite and formation of a dilute solution equilibrated with calcite and a gas phase having $p_{\text{CO}_2(g)} = 10^{-6.5}$ bar (Table 4.7). The chemistry of this solution does not change, and calcite continues to precipitate, regardless of how much $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$ is then added to the aqueous phase. This solution is not stable and would eventually dry out because $p_{\text{H}_2\text{O}(g)}$ exceeds the total atmospheric pressure in drifts at Yucca Mountain, thereby obviating the NWTRB scenario (NWTRB, 2003a).

There is additional potential for reaction and transport sequestration of $\text{HCl}(g)$ (and other acid-gas species) in porewaters of the host rock. For example, the pH buffering properties of aluminosilicate minerals that are present in tuff could control the pH to near-neutral values, and this would allow greater and greater incorporation of acid gas species into the water at the drift wall.

Table 4 . 9
Comparison of modeling results on the formation and stability of CaCl₂ deliquescent brines at 146° C.

$p_{\text{HCl}(g)}$ (bar)	Deliquescent brine stable?	$p_{\text{H}_2\text{O}(g)}$ (bar)	Ca ²⁺ (molal)	Cl ⁻ (molal)	Stable minerals
10 ^{-3.5}	yes	1	14.03	28.06	CaCl ₂ ·2H ₂ O
10 ^{-11.5}	no	4.2	0.11	0.21	calcite
10 ^{-14.5}	no	4.3	0.003	0.001	calcite

This possibility is evaluated using EQ3/6 to model a representative assemblage of basic minerals present in dust (see Table 4.2), consisting of albite, a smectite clay (Na-beidellite) and kaolinite (present in wind-blown dust). These minerals are considered in the model because they can coexist at equilibrium with the condensate at 96°C, and because they are also considered in DOE's THC models of drift-scale processes. It is assumed by EPRI that HCl(g) will migrate to the host rock, dissolve into the condensate, and react with the selected minerals. It is also shown in Table 4.5 that albite, Na-beidellite and kaolinite exist in sufficient quantities to react with all the HCl(g) that is added to the condensate.

Results, shown in Figure 4.10, indicate that the concentration of H⁺ in the condensate would be strongly buffered by reactions with the model minerals. As HCl(g) is added to the condensate, albite and kaolinite dissolve and Na-beidellite precipitates. This results in an increase in m_{H^+} from about 10^{-8.3} to 10^{-5.7} mol kg⁻¹ after about 8 moles of HCl(g) dissolves into the condensate. Thereafter, continued addition of HCl(g) results in precipitation of halite (NaCl). The concentration of H⁺ is then fixed at 10^{-5.7} mol kg⁻¹ as HCl(g) continues to be added to the solution. The final mineral assemblage, albite + Na-beidellite + kaolinite + halite, thus provides an infinite buffering intensity with respect to H⁺ molality, which effectively resists further acidification of the model system.

It is also noted that porewater in the host rock is likely to be continuously connected to site waters further away from the drift via water films in partially saturated porous media. As the concentration of dissolved acid-gas species condenses and builds up in the pore water, diffusion into the continuously connected bulk water of the surrounding rock will act to remove this concentration gradient, promoting greater incorporation of HCl(g) into the porewater. Thus, both buffering and diffusive transport in the water-tuff system will act, over long periods of time, to further incorporate HCl(g). This, in turn, will drive the brine decomposition reactions noted above to the right-hand side, preventing the persistence of such brines on waste packages.

Finally, the relative surface areas (proportional to equilibrium volumes) of the respective brine on the waste package and water in drift walls must be considered. A fuller review of this topic is made in Section 7.4 on boiling during the low-temperature interval. On a mass-balance basis, it is clear that if the surface-area ratio between a deliquescent brine and water in the drift wall is low, then the decomposition reactions for brine cited above will proceed strongly to the right-hand side, leading to the formation of benign decomposition products. This is because a large ratio of drift-wall-area: area-of-brine-on container will require more HCl(g) to be transferred to the larger amount of water in the drift wall before chemical equilibrium will be reached. As noted in Section 7.4, the available surface area for water in the drift may be 20 to 100 times larger than for the entire surface of the waste packages, even assuming that all of the waste package surface would be coated with a film of deliquescent brine.

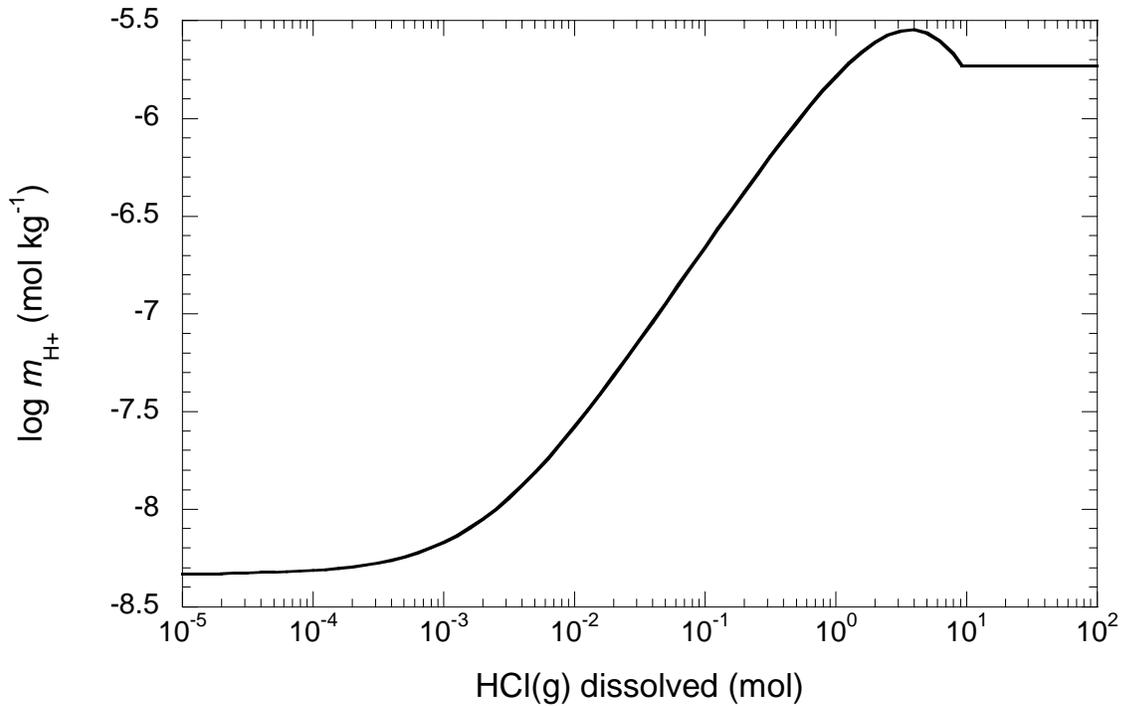


Figure 4 . 10
Diagram illustrating the effects of buffering by albite + Na-beidellite + kaolinite (\pm halite) on m_{H^+} as HCl(g) is added to condensate at 96°C, 1 bar.

In summary, scoping evaluations were conducted using simplified conceptual models that are consistent with the in-drift chemical environment and reasonable constraints on the partial pressure of acid gases, such as HCl(g). The results of these calculations indicate that deliquescent brines could not form on waste package surfaces and would not be stable should they form under transient conditions. These constraints are likely to be fixed over long periods of time by chemical buffering of acidity and acid-gas partial pressures by mineral-water reactions in the host rock, and by the much larger volumes of water in the rock walls of emplacement drifts compared to any deliquescent brines that might form on waste package surfaces.

5

LOCALIZED CORROSION OF ALLOY-22

5.1 Inhibition of Localized Corrosion of Alloy 22 Based on Composition of Deliquescent Solution

The NWTRB (2003a) has asserted that data from both DOE [YMP] (Farmer, 2003) and the Center for Nuclear Waste Regulatory Analysis (CNWRA) (Cragolino, 2003) “suggest to the Board that crevice corrosion of Alloy 22 is likely to initiate during the thermal pulse (approximately the first thousand years after repository closure, when temperatures will exceed 95°C for the current repository design.” The specifically cited information relates to corrosion in the presence of acid-chloride brines.

Analyses by EPRI-sponsored contractors, presented in Chapter 4, indicates that such acid-chloride brines are highly unlikely to form, to be stable, or to persist in the emplacement drift environment during this period.

For example, analyses of dust upon which a deliquescent brine might form indicate the presence of non-chloride salts (especially NO_3^- and SO_4^{2-}) that will cause the formation of a mixed-anion deliquescent brine rather than a pure Ca-Cl brine. Figure 5.1 (see also Figure 4.3) compares the $[\text{NO}_3^-] / [\text{Cl}^-]$ molar ratio for various dusts and precipitation sources with those found to inhibit the localized corrosion of Alloy 22 in CNWRA and DOE experimental studies. A critical $[\text{NO}_3^-] / [\text{Cl}^-]$ molar ratio of less than 0.12 and 0.2 was identified as necessary for localized corrosion to occur on mill annealed and welded Alloy 22 samples, respectively, in Cl^- brines at a temperature of 95°C (Cragolino, 2003). The DOE reports similar findings, with a $[\text{NO}_3^-] / [\text{Cl}^-]$ molar ratio of 0.1 sufficient to inhibit localized corrosion on welded and as-received Alloy 22 at temperatures of 90°C and 100°C, respectively (Farmer 2003). In contrast, the measured nitrate:chloride molar ratio in dust at Yucca Mountain from which deliquescent brine may arise ranges from 1.3 to 6.5 (3.0 to 9.0 if the $[\text{NO}_3^- + \text{SO}_4^{2-}] / \text{Cl}^-$ ratio is considered). Thus, the inherent, natural ratio of nitrate (and other competing anions, such as sulfate) to chloride in dusts will effectively inhibit localized corrosion of Alloy 22.

Furthermore, the predominant solids of dust, carbonate and basic alumino-silicate minerals, will neutralize the acidity of a contacting deliquescent brine that may develop. Two processes will tend to control the pH of any deliquescent liquid. First, any acid gases released by the thermal decomposition of deliquescent salts will be neutralized by the calcite in the dust (~10 wt.%). Second, alumino-silicate minerals in the dust (potassium feldspar, kaolinite, montmorillonite, biotite) will buffer the pH in the range 4-5.

Independent analyses by EPRI-sponsored contractors are consistent with experimental results obtained by the DOE [YMP] and reported to the NWTRB (Farmer, 2003, Slide 14) that “There is no evidence of localized corrosion of Alloy 22 due to deliquescence” (based on experiments with pure CaCl_2 [analog to MgCl_2] deposits at 150°C). Chemical analyses of insoluble, non-deliquescent minerals that formed from the decomposition of test solutions of CaCl_2 brine on Alloy 22 showed no evidence of even trace levels of metallic components of the Alloy 22

(Peters, 2003; Farmer, 2003). The absence of any corrosion whatsoever during these experiments designed to simulate deliquescence and subsequent evaporation of the solution is strong evidence that these processes will not cause corrosion of the waste package.

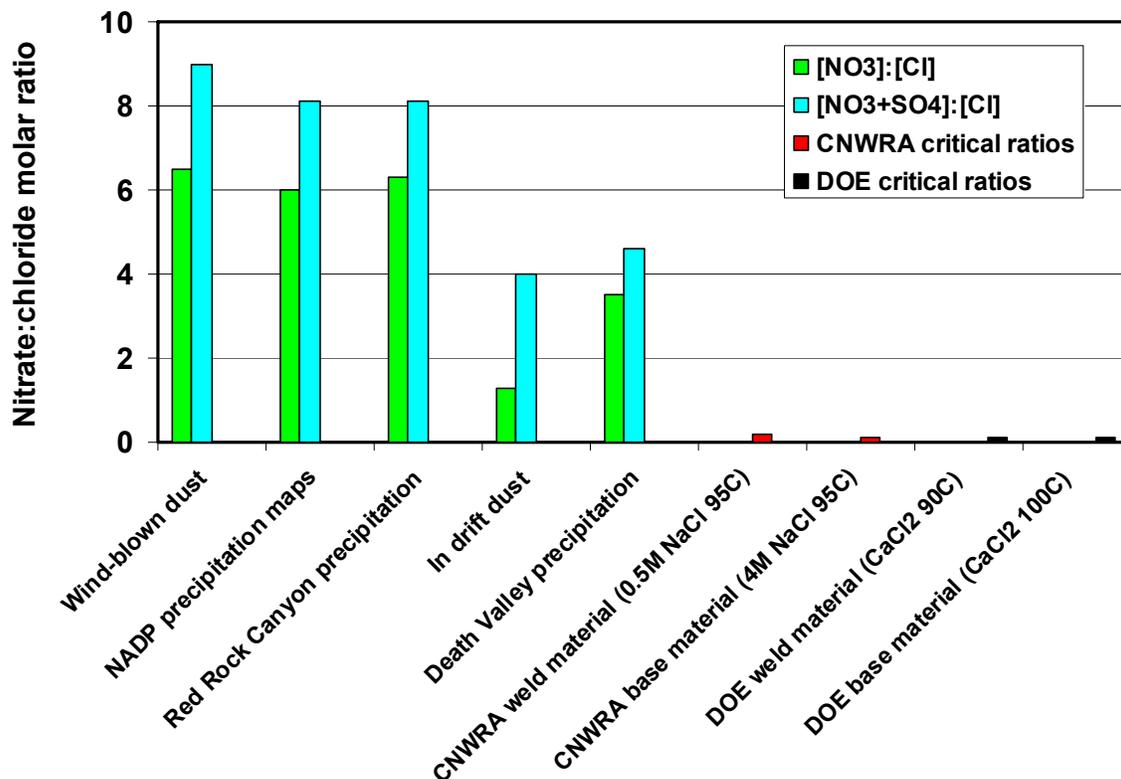


Figure 5 . 1
Comparison of Nitrate / Chloride Molar Concentration Ratios in Dust and Precipitation Samples Relevant to the Yucca Mountain Repository with those Found to Inhibit the Localized Corrosion of Alloy 22.

5.2 Inhibition of Localized Corrosion of Alloy 22 Based on Properties of Dust Deposits as Crevice Formers

Even if aggressive aqueous solutions form on the WP surface by deliquescence, it is unlikely that dust deposits or precipitated salt films will provide the occluded conditions needed for localized corrosion. Unlike the types of crevice formers typically used in laboratory experiments, dust deposits and salt films are permeable and will allow ready access of atmospheric O₂ to the “occluded” region under the deposit. As shown in the analysis below, O₂ can be supplied by diffusion through the deposit at a rate faster than it is consumed, so that the spatial separation of anodic and cathodic reactions (a pre-requisite for localized corrosion) will not occur.

The mechanism of crevice corrosion has been extensively studied (*e.g.*, Brown, 1970, Shrier 1976; Oldfield and Sutton 1978; Szklarska-Smialowska, 1986; Kelly, 2003). Initiation and the early stages of crevice propagation involve the following sequence of events:

1. Local depletion of O₂ (or other oxidant) in the occluded region

2. The spatial separation of anodic and cathodic reactions, with the anodic dissolution of the metal confined to the restricted volume under the crevice former and the cathodic reduction of oxidant occurring on the metal surface outside the crevice
3. Dissolution of metal within the occluded region
4. Hydrolysis of dissolved metal ions resulting in local acidification within the crevice
5. Propagation of localized corrosion inside the crevice supported by the cathodic reduction of oxidant on external surfaces and/or of H^+ inside the crevice

Other processes, such as the migration of charge-balancing anions (typically Cl^- ions) into the occluded region, are also involved (*e.g.*, Brown, 1970; Shrier, 1976; Oldfield and Sutton, 1978; Szklarska-Smialowska, 1986; Kelly, 2003), but are not important for the current discussion. In general, any process that interferes with any of these steps will prevent the initiation or, in the case of Step 5, the propagation of localized corrosion.

In the laboratory, crevice corrosion is typically studied using a sample in which a crevice former (often PTFE) is tightly clamped against the face of the metal coupon (Cragnolino, 2003; Farmer, 2003). This sample design maximizes the opportunity to create a differential O_2 concentration cell between the inside and outside of the creviced areas and, hence, the possibility of localized attack. However, such a crevice design is not a good representation of the types of crevice that might form between the waste package surface and a permeable dust deposit or precipitated salt film. Therefore, data derived from such laboratory studies are highly conservative and over-estimate the probability of initiating localized corrosion.

The importance of the occluded region in initiating crevice corrosion can be seen by comparing the repassivation potentials for pitting on exposed surfaces (E_{rp}) and for crevice corrosion on PTFE-metal specimens (E_{rcrev}). Figure 5.2 shows the results of cyclic polarization tests on planar and creviced samples for Alloy 825 in a dilute groundwater solution at $95^\circ C$

, in which E_{rp} and E_{rcrev} are shown as a function of the depth of attack determined at the end of the test (Dunn *et al.*, 1996). In the earliest stages of localized corrosion, the repassivation potential of the planar surface undergoing pitting attack is up to 300 mV more positive than that for the creviced sample. This difference in potential illustrates the ability of the PTFE crevice former to sustain the localized environment within the occluded region. It is interesting to note that, as the depth of penetration increases, the values of E_{rp} and E_{rcrev} become the same. This is because well developed pits form a crust of corrosion products that creates an occluded environment. A permeable dust deposit would not support local acidification within the “crevice,” and it is reasonable to expect that the repassivation potential in such a case would be closer to that for the planar specimen undergoing the early stages of pitting attack than to that for the creviced sample. Here, the solution was deaerated, so the only effect of the creviced region is to maintain the localized acidity resulting from the hydrolysis of metal ions within the crevice. Under naturally corroding conditions in aerated solutions, the crevice would also serve to separate the cathodic reduction of O_2 on areas outside the occluded region from metal dissolution inside the crevice.

The inability of a dust deposit or precipitated salt film to support localized corrosion can be assessed using the conceptual model illustrated in Figure 5.3. A permeable dust deposit is assumed to be present on the surface of the waste package. Absorption of moisture from the

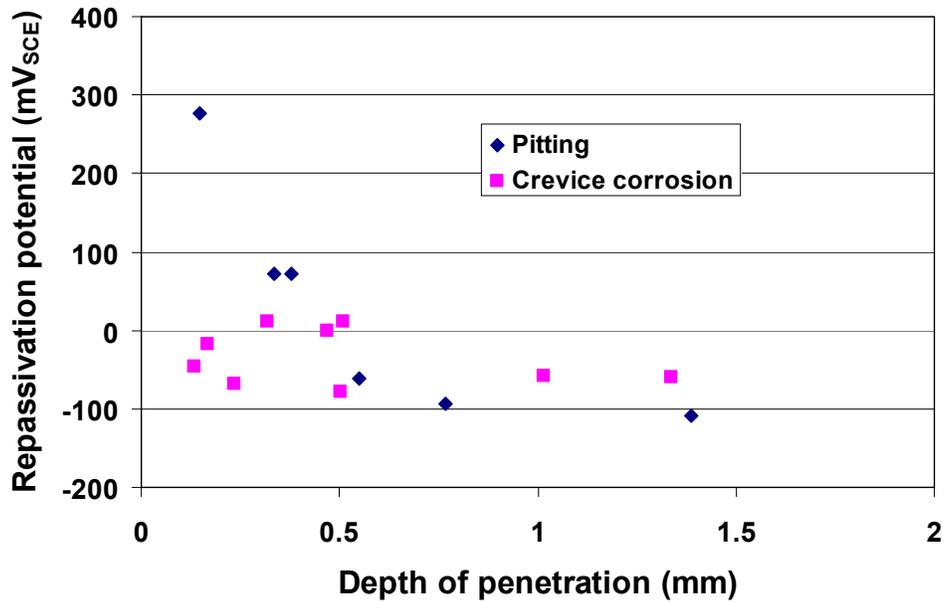


Figure 5 . 2
Comparison of Repassivation Potentials for Pitting of Planar Samples and Crevice Corrosion of Creviced Samples (after Dunn et al., 1996). Data shown for Alloy 825 in deaerated dilute groundwater solution at 95°C.

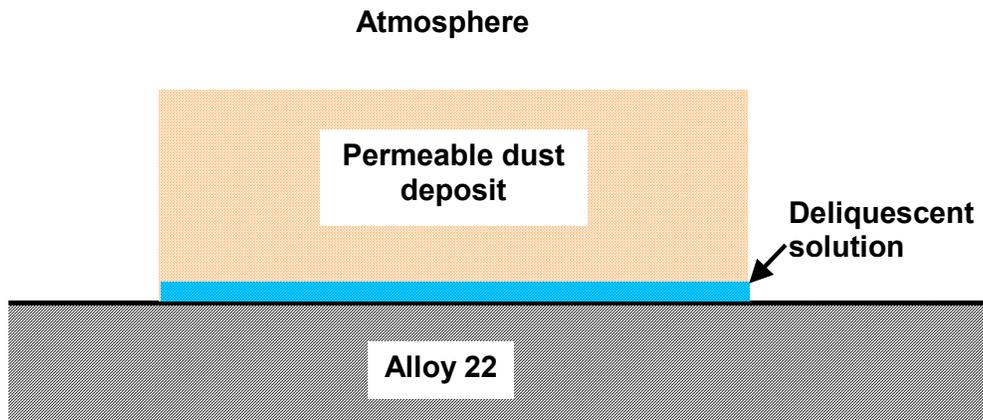


Figure 5 . 3
Schematic Illustration of the Conceptual Model for the Formation of a Thin Deliquescent Liquid Film Under a Permeable Dust Deposit or Precipitated Salt Film. (Note that a continuous surface water film is assumed here for simplicity. In reality, the water film is likely to be discontinuous along the surface. This would not change the conclusions from the simplified conceptual model).

atmosphere and the subsequent deliquescence of soluble salts within the dust leads to the formation of a thin, highly concentrated aqueous solution in direct contact with the Alloy 22 surface. Since the first stage in the development of localized corrosion is the creation of a differential O₂ concentration cell, crevice corrosion is only possible under such a deposit if the

rate at which O₂ is consumed is faster than that at which it is re-supplied by diffusion through the porous layer.

Here, the focus is only on whether a permeable deposit can generate the differential O₂ concentration cell required to initiate crevice corrosion. In addition, a dust deposit would tend to buffer the pH against changes caused by the hydrolysis of dissolved metal cations, as discussed earlier.

Considerable effort has been put into predicting the mass transport of O₂ and other species through porous barriers in those countries considering the deep geologic disposal of nuclear waste in water-saturated repositories (Pusch *et al.*, 1982; Muurinen *et al.*, 1985; Neretnieks, 1985; Cook, 1988). Theoretical models have been extensively validated against experimental data (Neretnieks, 1985; Muurinen *et al.*, 1985; Oscarson *et al.*, 1992). In addition, the diffusion of O₂ through saturated and partially saturated soils is of great importance in agronomy and soil science (Collin and Rasmuson, 1988). The phenomenon of O₂ transport through porous layers is, therefore, well studied and highly predictable.

Diffusive mass transport in porous media is treated via the use of an effective diffusion coefficient D_{EFF} (Collin and Rasmuson, 1988; Cook, 1988). The effective diffusion coefficient is related to the diffusion coefficient in bulk solution D₀ by

$$D_{\text{EFF}} = \tau_f \cdot \varepsilon \cdot D_0 \quad (5.2.1)$$

where τ_f is the tortuosity factor and ε is the porosity and account for the tortuousness nature and total volume of the pore network, respectively. This approach has been used to account for the corrosion behavior of various materials in contact with porous materials and corrosion product layers (King *et al.*, 1995a, 1996; Shoesmith *et al.*, 2003).

The steady-state rate of supply of O₂ to the surface of the waste package (expressed as a current density) is given by

$$i_{\text{O}_2} = \frac{4F\tau_f\varepsilon D_{\text{O}_2} c_{\text{O}_2}}{x} \quad (5.2.2)$$

where F is the Faraday constant, D_{O₂} is the diffusion coefficient of O₂ in bulk solution, c_{O₂} is the concentration of dissolved O₂ at the film/air interface (the O₂ concentration at the waste package/film interface being assumed to be zero), and x is the thickness of the deliquescent water film. Here it is assumed that O₂ reduction on the surface of the waste package is given by



The density, porosity and tortuosity factor for dust deposits that may form on waste package surfaces are not known. Conservative estimates based on relatively high density deposits can be obtained from various studies on compacted alumino-silicate minerals and simulated corrosion deposits. Figure 5.4 shows the dependence of ε and τ_f as a function of density for montmorillonite, an alumino-silicate clay mineral (Oscarson *et al.*, 1992). Both ε and τ_f decrease with increasing compaction density, as expected. Although it is feasible to hand compact these clays at densities of ~1 g/cm³ or lower, it is necessary to use a hydraulic press and pressures of several tons per square inch to achieve higher densities. Based on this consideration, the density

of wind-deposited dust on the surface of the waste package is likely to be $\leq 1 \text{ g/cm}^3$. Therefore, the porosity and tortuosity factor of the pore network in the dust deposits will be of the order of 0.6 and 0.2, respectively (Figure 5.4).

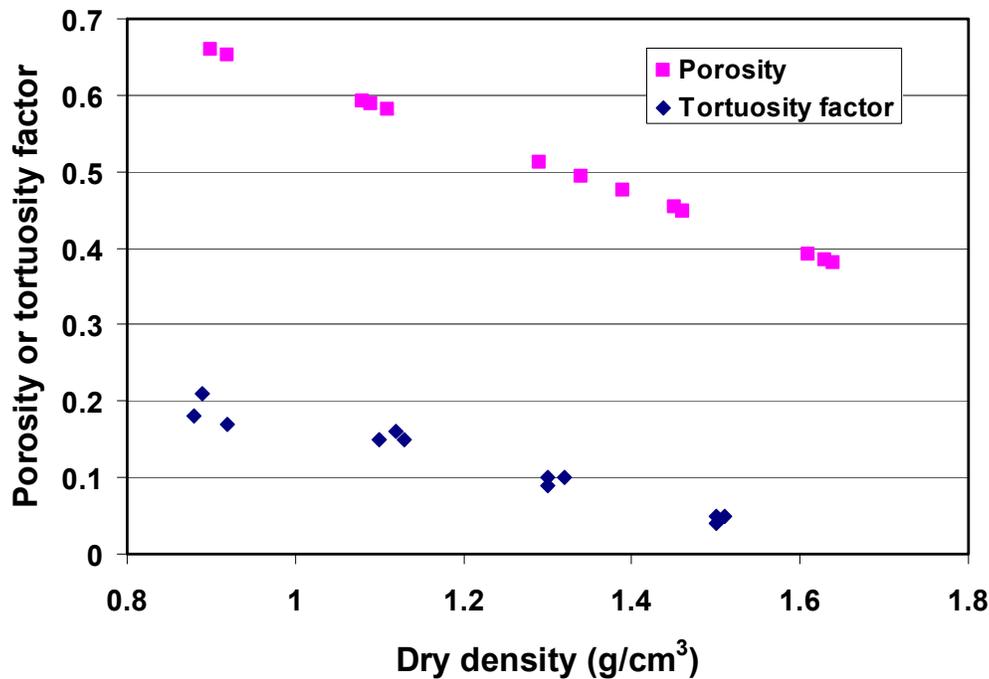


Figure 5 . 4
Dependence of the Porosity and Tortuosity Factor of Compacted Montmorillonite on Dry Density (Oscarson et al., 1992).

Support for these values comes from the study of simulated steam generator deposits, reported by Millet and Fenton (1993). The porosity and tortuosity (related to the tortuosity factor) were measured for hand-compacted magnetite powder at temperatures between 25°C and 280°C. For deposits with porosities of 0.55 and 0.65, the tortuosity factor was found to vary between 0.64 and 1.0. Based on these two studies, the porosity and tortuosity factor for dust deposits or precipitated corrosion products on the surface of the waste package are conservatively estimated to be 0.5 and 0.2, respectively.

The diffusion coefficient of O₂ in concentrated chloride solution is $1.7 \times 10^{-5} \text{ cm}^2/\text{s}$ at 25°C (King et al., 1995b; Kear et al., 2004). As for other solutes, the temperature dependence of D_{O₂} would be expected to be the same as that for the viscosity of water, approximately 19 kJ/mol (Oscarson et al., 1992).

The concentration of dissolved O₂ in solution in contact with air depends on both the temperature and salinity of the solution (Battino et al. 1983). Figure 5.5 shows the temperature dependence of the concentration of O₂ in water in contact with air at a total pressure of 101.325 kPa, and the polynomial used to fit the data (Battino et al. 1983). An increase in the solute concentration in solution results in the “salting-out” of O₂. For example, the concentration of dissolved O₂ in $5 \text{ mol}\cdot\text{dm}^{-3} \text{ CaCl}_2$ (used here to represent the deliquescent solution) is a factor of 0.127 of that in

water at the same temperature (Battino *et al.*, 1983). (The selection of this value for the salting-out coefficient is considered to be conservative, since the corresponding ratio for 4.4 mol·dm⁻³ NaCl (saturated concentration at 25°C) is 0.240 and, based on evidence for nitric acid, the salting-out coefficient decreases with increasing temperature (Battino *et al.*, 1983)).

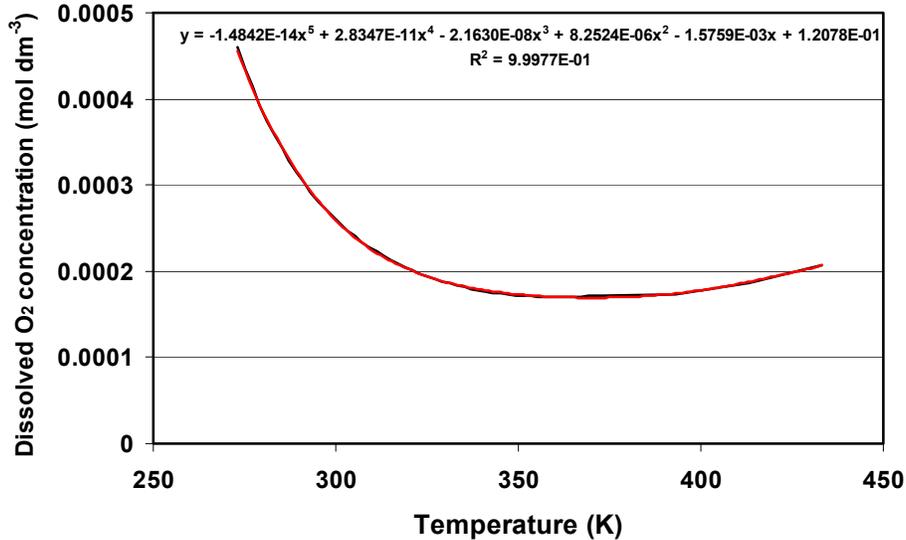


Figure 5 . 5
Temperature Dependence of the Concentration of Dissolved Oxygen in Water in Contact with Air at a Pressure of 101.325 kPa (after Battino et al. 1983).

The last parameter required to calculate the diffusive flux of dissolved O₂ to the waste package surface through the porous deposit is the thickness of the deliquescent water film. Atmospheric corrosion is possible in water layers as thin as 15-20 monolayers (<0.001 mm) (Shreir, 1976). Farmer (2003) summarized the results of thermalgravimetric analysis tests in which mass changes due to deliquescence and the subsequent decomposition of the brines on Alloy 22 were studied. An initial mass increase of ~1.7 mg was reported due to the adsorption of water and the formation of a thin surface liquid film. For the size of sample used in these tests (nominally 2''x0.5''x0.125'', surface area ~17 cm²), the estimated thickness of the surface film is 10⁻⁴ cm (1 μm). Water films on the surface of waste packages can also be expected to be thin, especially since there will be continuous evaporation of the water. Here a range of water film thicknesses of 0.001-0.1 mm is assumed. Although the thickness of the dust deposit may be much greater (Figure 5.3), the rate-determining step will be the diffusion of O₂ through the thin film of solution, since the diffusion coefficient in partially saturated porous media is several orders of magnitude greater than that in the aqueous phase (Collin and Rasmuson, 1988).

Prior to the initiation of localized corrosion, the rate of consumption of O₂ on the waste package surface (both the exposed surface and that under dust deposits) is equal to the passive current density i_{pass} . Cragnolino (2003) has given the following expression for the temperature dependence of i_{pass} , which is used here to represent the rate of consumption of O₂

$$i_{pass} = i_0 \cdot \exp[-\Delta E/RT] \tag{5.2.4}$$

where R is the gas constant, the pre-exponential factor i_0 has a value of 0.023 A/cm^2 , and the activation energy ΔE has a value of 44.7 kJ/mol .

Figure 5.6 compares the rate of consumption of O_2 based on Equation (5.2.4) and the rate of replenishment of O_2 to the waste package surface due to the diffusion of O_2 through the surface liquid film based on Equation (5.2.2) (thickness 0.001, 0.1, and 0.1 mm). The predicted rate of O_2 consumption is between ~ 3 and 6 orders of magnitude *slower* than its rate of re-supply, depending upon the temperature and the thickness of the water film. The O_2 consumption and replenishment curves converge at higher temperatures because the activation energy for the passive current density is higher than that of the diffusion of O_2 .

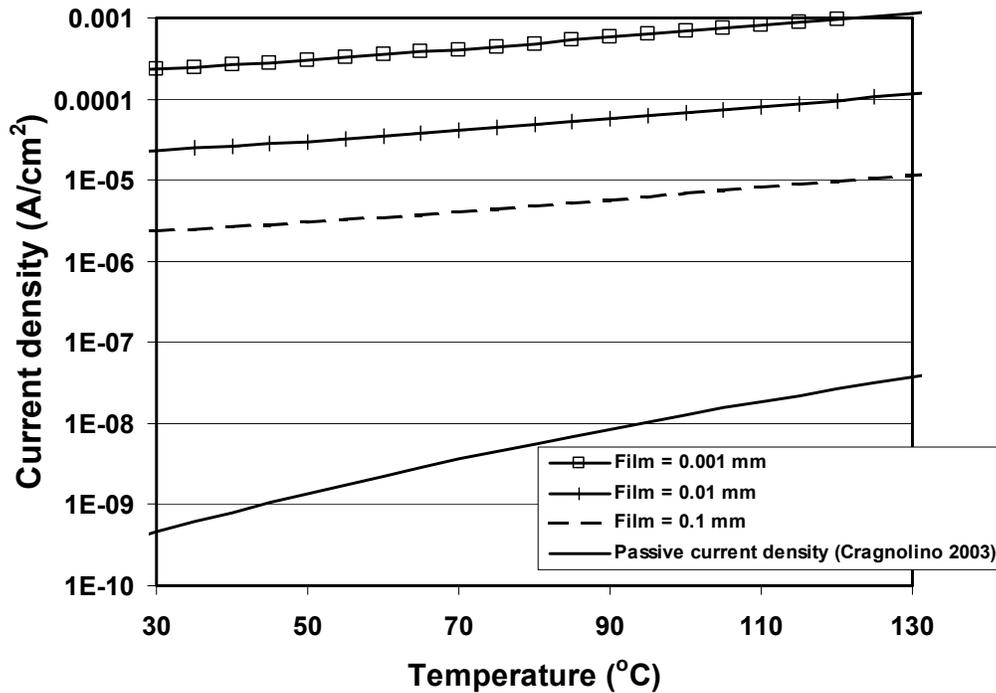


Figure 5 . 6
Predicted Rate of Oxygen Consumption due to Passive Corrosion and of Oxygen Replenishment by Diffusion Through Surface Water Films of Different Thicknesses as a Function of Temperature (porosity 0.5, tortuosity factor 0.2).

The data in Figure 5.6 can be used to predict the interfacial concentration of O_2 under the deposit relative to that at the exposed surface. Under steady-state mass-transport conditions, the ratio of the interfacial O_2 concentration (c_0) to that at the film/atmosphere interface (c_{bulk}) is given by

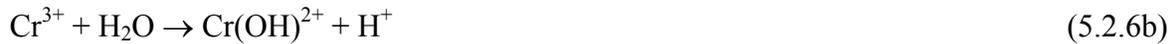
$$\frac{c_0}{c_{\text{bulk}}} = 1 - \frac{i_{\text{pass}}}{i_{\text{O}_2\text{flux}}} \quad (5.2.5)$$

where $i_{\text{O}_2\text{flux}}$ is the rate of replenishment of O_2 through the water film (expressed as a current density). The O_2 concentration c_{bulk} is also that at the waste package surface in areas not covered by a porous deposit, if it is assumed that the rate of supply of O_2 in such areas is fast compared

with its rate of consumption. Thus, the ratio c_0/c_{bulk} represents the degree to which the dust deposit serves to create a differential O_2 concentration cell.

As can be seen from Figure 5.7, the extent to which a differential O_2 concentration cell is created by the dust deposit is minimal. The rate of supply of O_2 through the porous layer is so much faster than its rate of consumption that the interfacial O_2 concentration beneath the deposit is, conservatively, depleted by only $\sim 0.3\%$ (0.1 mm thick water layer, temperature 130°C). For the more realistic water layer thickness of 0.001 mm, the maximum depletion of O_2 at the waste package surface is only $\sim 0.003\%$ compared with that in the bulk solution.

The consequence of this rapid O_2 supply to the waste package surface under the porous deposit is that both anodic and cathodic reactions take place at the same location. Thus, the cathodic reduction of O_2 (Reaction (5.2.3)) is coupled to the anodic dissolution of Alloy 22 (taken here as being represented by the dissolution of Cr under passive conditions)



or, overall



The overall corrosion reaction under the porous deposit (as it is on the exposed waste package surface) is, therefore,

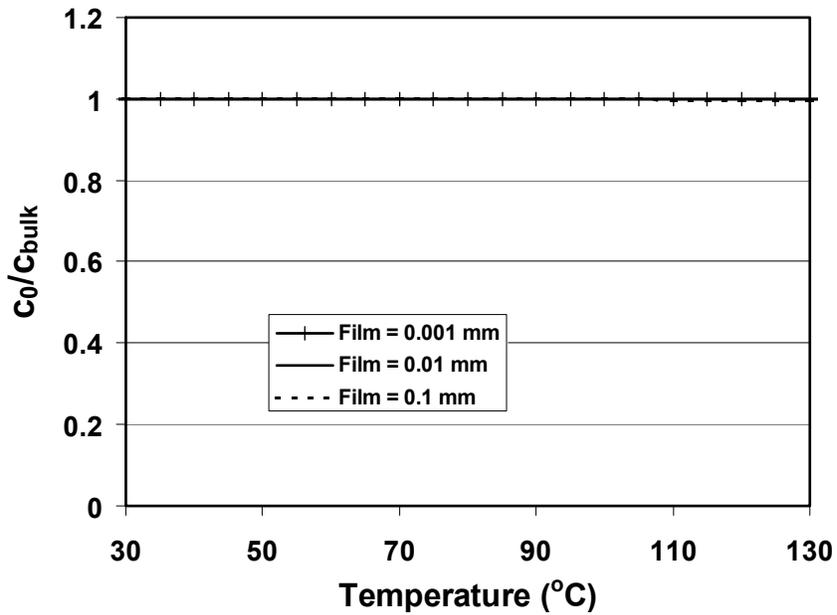


where the stoichiometry given in the reaction shown in Equation (5.2.8) emphasizes that H_2O is both a reactant and a product of the corrosion reaction. Thus, the permeability of the dust deposit neither causes the creation of a differential $[\text{O}_2]$ cell nor local acidification.

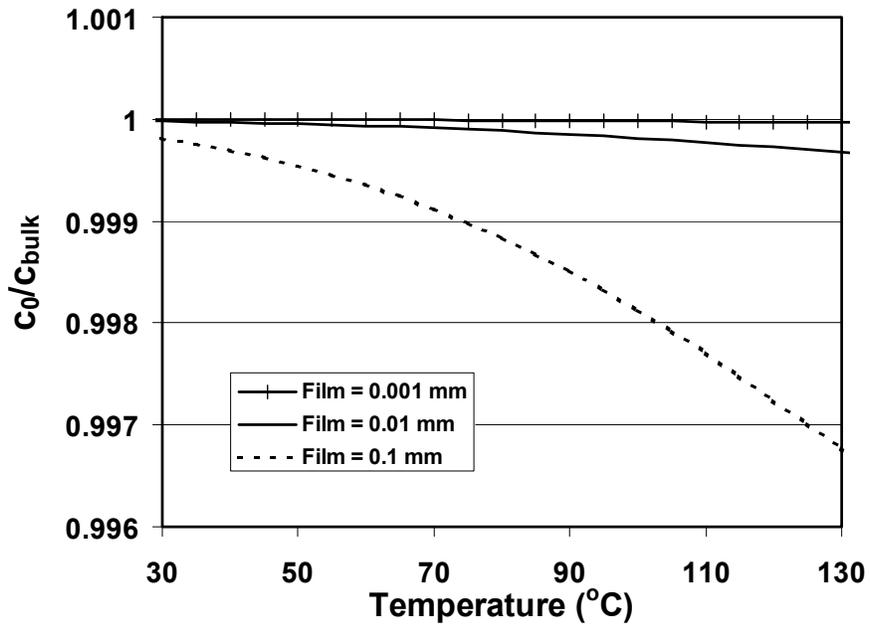
In summary, therefore, there is strong evidence to indicate that porous crevice formers, such as dust deposits or precipitated salt films, will not initiate localized corrosion on the surface of the waste package. The rate of supply of O_2 to the “occluded” surface under the deposit far exceeds its rate of consumption, so that neither the differential O_2 concentration conditions nor the local acidification required for the initiation of crevice corrosion will be established.

5.3 Stifling of Localized Penetration

Even in the unlikely event that localized corrosion will initiate on the surface of the waste package, there is ample evidence from a number of alloy systems that the corrosion rate decreases with time. This effect has been addressed in previous analyses of the lifetime of waste packages undergoing localized corrosion (EPRI, 2000; 2002a; Shoesmith and Kolar, 1998; Shoesmith and Massari, 2001).



(a) Extended Vertical Scale



(b) Expanded Vertical Scale

Figure 5 . 7
Predicted Ratio of the Interfacial Oxygen Concentration Under a Dust Deposit to that on the Exposed Surface of the Waste Package Based on the Data in Figure 5.6.

There are a number of mechanisms by which crevice corrosion, if ever initiated on the surface of a waste package, could be stifled, including:

1. Neutralization or buffering of the low-pH established within the occluded region by:
 - a. neutralization of H^+ by reaction with calcite minerals in dust
 - b. neutralization of H^+ by alumino-silicate minerals in dust
2. Loss of critical crevice chemistry
 - a. ion-exchange onto clay and mica minerals replacing aggressive Ca^{2+} and Mg^{2+} cations by less-aggressive Na^+ and K^+
3. Loss of spatial separation of anodic and cathodic reactions by changes to the permeability of the crevice former
 - a. Dissolution of calcite minerals by H^+ leading to an increase in porosity of the dust pile and, hence, more rapid transport of O_2 to the waste package surface
4. Mass transport limitations produced by blockage of crevice region by precipitated corrosion products leading to diffusion control of the propagation process

The net result of any or all of these stifling mechanisms is that the localized corrosion penetration rate decreases with time. Expressed as the time-dependence of the depth of localized penetration (d),

$$d = B \cdot t^n \quad (5.3.1)$$

where B is a temperature-dependent growth constant and the exponent n determines the time dependence of the penetration. There are numerous examples of this form of the equation for the time dependence of localized corrosion of various alloy systems, including iron and steels, Ti, and Cu (EPRI 2000, 2002a; Shoesmith and Kolar 1998). The value of the exponent n is generally <0.5 . Diffusion control of the propagation rate would give a value for n of 0.5.

As noted above, EPRI has included a power-law expression for penetration by localized corrosion in its TSPA calculations using the IMARC model (EPRI 2000; 2002a; Shoesmith and Kolar 1998, Shoesmith and Massari 2001). Localized corrosion is only possible over a certain range of temperatures and, hence, for a certain period of time. Even taking conservative estimates for the range of susceptible temperatures, the waste package will only be susceptible to localized corrosion for a few thousand years. Figure 5.8 shows the time dependence for the maximum penetration of the Alloy 22 waste package by localized corrosion for values of n of 0.1 and 0.5, considered to be the lower and upper limits for the time exponent (EPRI, 2002a; Shoesmith and Massari, 2001). The value of B was taken as the 95th percentile from the (Weibull) distribution for this parameter, derived from corrosion rates in 10 wt.% ferric chloride solution for a range of less-corrosion resistant Ni-Cr-Mo alloys. Even for this conservative approach, the maximum wall penetration for localized corrosion is $<25\%$ of the Alloy 22 wall thickness for an n value of 0.5 and only $\sim 1\%$ for $n = 0.1$. Even if localized corrosion does initiate on the Alloy 22 waste packages (based on analogy to related alloy systems), therefore, loss of containment capability or failure is unlikely to result.

5.4 Overall Assessment of the Localized Corrosion of Waste Packages Due to Deliquescence

There is strong evidence to indicate that localized corrosion will not initiate on the Alloy 22 waste packages due to deliquescence of aggressive solutions in dust piles on the container surface of waste packages. Even if the improbability of initiation is not accepted, through-wall

penetration is unlikely based on sound corrosion science arguments about the penetration behavior of localized corrosion. These arguments can be summarized as follows:

Initiation of localized corrosion will not occur because deliquescent solutions formed from dust samples will exhibit high nitrate: chloride mole ratios. Nitrate, and sulfate, inhibit the aggressive effects of chloride ions. Furthermore, the ion-exchanging and pH-buffering and neutralizing capacity of the alumino-silicate and carbonate minerals in typical Yucca Mountain wind-blown dusts will prevent the formation of low-pH environments, especially those dominated by Ca^{2+} and Mg^{2+} .

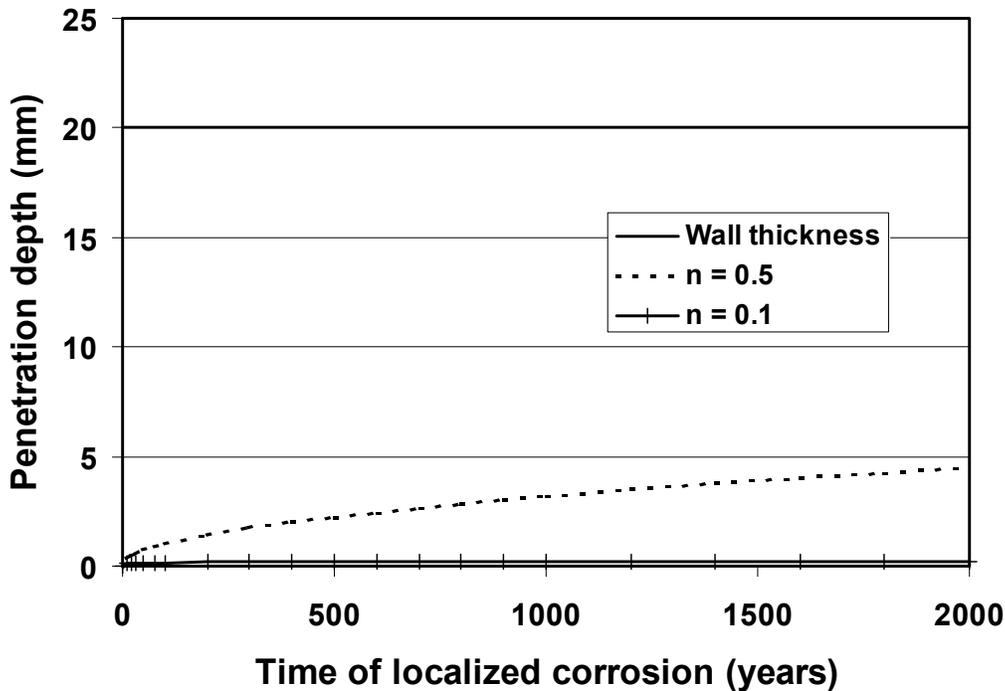


Figure 5 . 8
Comparison of the Time Dependence of the Penetration due to Localized Corrosion for Two Values of the Exponent n for Power-law Growth and the Wall Thickness of the Alloy 22 Waste Package.

Initiation of localized corrosion will not occur because the dust deposits are highly permeable to atmospheric O_2 and will not support the spatial separation of anodic and cathodic sites pre-requisite for localized corrosion. Based on well-established and validated models for mass transport through porous layers, atmospheric O_2 will diffuse to the waste package surface through the dust pile at a rate 3-6 orders of magnitude faster than it is consumed by corrosion. Therefore, the differential O_2 concentration cell that forms as a pre-requisite to the initiation of localized corrosion cannot be established under a dust deposit.

Even in the unlikely event that localized corrosion does initiate, propagation will be stifled before the wall of the container is completely penetrated. There is ample evidence indicating that the rate of localized corrosion slows with time and that for thick-walled waste packages penetration will effectively cease well before the waste package is penetrated.

6

IMPACT OF EARLY WASTE PACKAGE FAILURE ON SAFETY COMPLIANCE

The regulations promulgated to address the licensing of a nuclear waste repository clearly establish that a probabilistic approach is appropriate for the licensing process. The NRC (NRC, 2003) recognizes that using total system performance assessment (TSPA) is a viable and necessary approach to provide risk-based insights and guidance to any license application for a nuclear waste repository. NRC (2003) utilizes a risk-informed TSPA approach to categorize possible technical issues into high-risk, medium-risk, and low-risk significance, the latter being information that is expected to have little impact on risk estimates (*i.e.*, compliance with the safety standard). Furthermore, NRC (2003) firmly endorses the view that consideration of the concept of multiple barriers (*i.e.*, TSPA) complements risk insights. This is because “multiple barriers, as an element of a defense-in-depth approach, results in a robust repository system that is more tolerant of failures and external challenges.” (NRC, 2003).

Accordingly, EPRI-sponsored contractors have conducted a series of risk-based sensitivity calculations of the impact of early failure of waste packages with respect to compliance with the regulatory safety standard. The results of these calculations are reported elsewhere (EPRI, 2003). Figure 6.1 below presents the results from this sensitivity analysis.

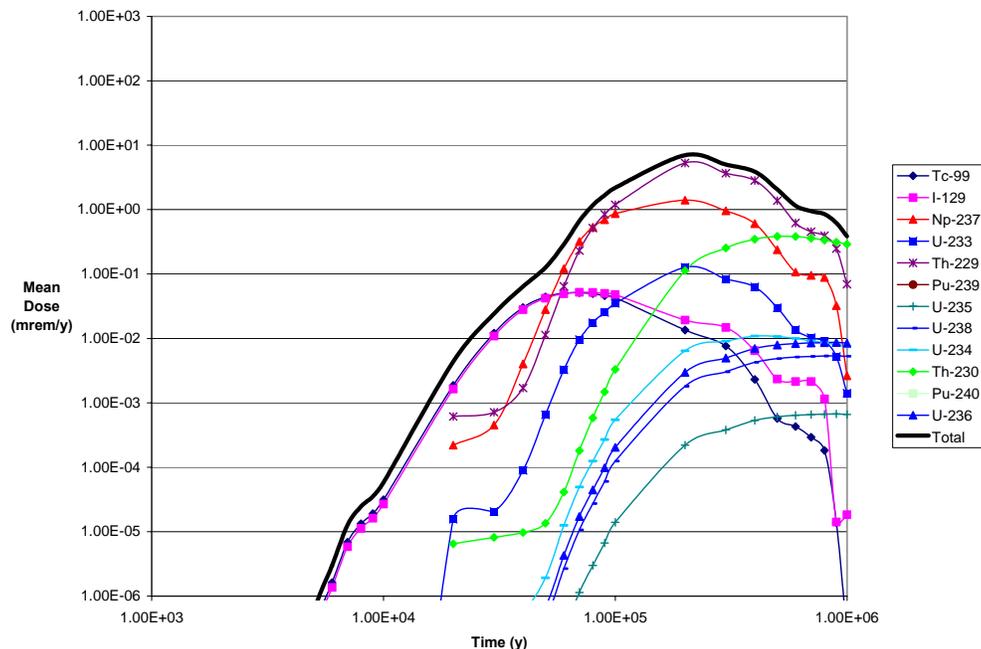


Figure 6 . 1
IMARC 8.0 analysis with 108 branches, with the initial failure fraction of waste packages set equal to unity.

This analysis has important implications. Compliance with regulatory criteria is not completely dependent on long-term containment by the container that is part of the waste package, nor is compliance sensitively dependent on the number of possible juvenile failures assumed for the analysis. Even if all of the waste packages failed early by postulated localized corrosion arising from deliquescent brine formation, analyses indicate that the regulatory criteria will be met at all times, even after the 10,000-year regulatory time period.

Figure 6.2 presents the calculated repository performance if both the waste package containers and drip shields of a repository at Yucca Mountain are postulated to fail at the time of repository closure. Analyses indicate that the regulatory criteria will be met throughout the 10,000-year time period for regulatory compliance. Thus, it is clear that safe containment of nuclear waste within a repository at Yucca Mountain is assured by a system of multiple barriers and isolation processes.

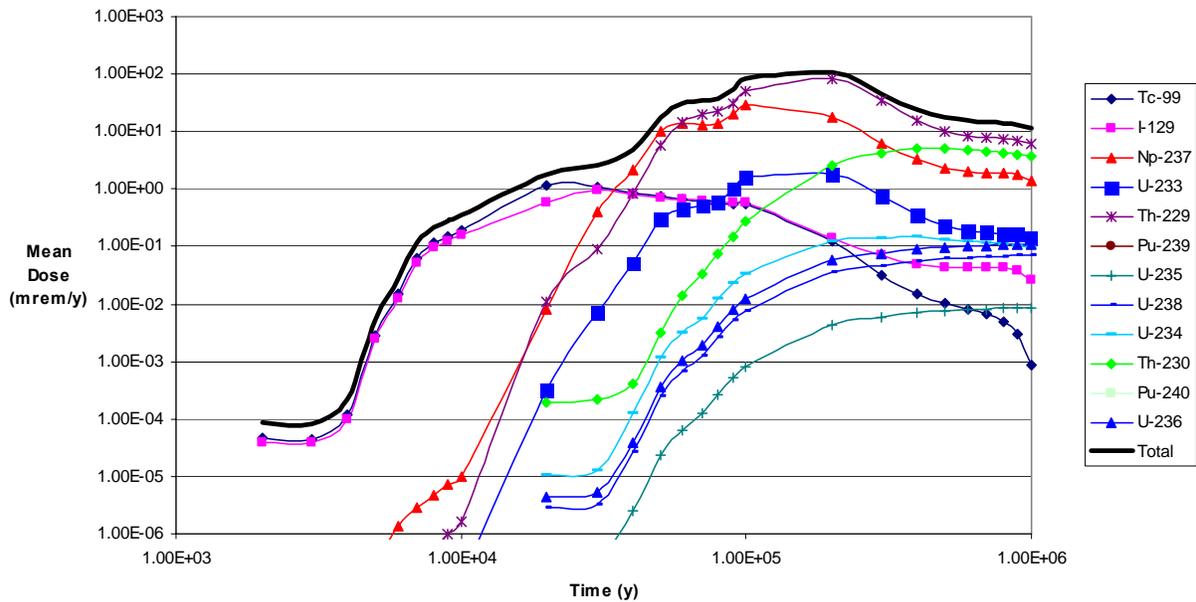


Figure 6 . 2
MARC 8.0 analysis with 108 branches, with the initial failure fraction of waste packages and drip shields set equal to unity.

7

REFLUX DURING LOW-TEMPERATURE INTERVAL

Following the transition period, retrograde cooling of the drift environment eventually leads to the temperature of the drift walls falling below the boiling point of water. This is the beginning of the “low-temperature interval,” in which water may seep from the crown of the drift onto the drip shield. If the drip shield is significantly failed (*i.e.*, localized cracks in drip shield will not suffice to allow passage of seepage water), or if there is condensation of water on the lower surface of the drip shield, water may also fall onto a hot waste package. There has been speculation by consultants for the State of Nevada (Pulvirenti *et al.*, 2003; Staehle, 2003; and Shettel, 2003) that refluxing of water by a cycle of dripping-evaporation/boiling-condensation on the waste package surface, may lead to acid-brine compositions developing on the waste package surface that would promote corrosion of the Alloy 22.

7.1 Source Waters, Chemical Divides and Brine Types

Drever (1997) (Figure 7.1) summarizes the origin of the brines that are formed by evaporating dilute natural waters in which the major species are Na^+ , Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} and Cl^- (see also Hardie and Eugster, 1970). The critical first ‘divide’ reached in early evaporation reflects whether $2m_{\text{Ca}^{2+}}$ is greater than or less than the initial alkalinity ($m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}}$). In either case, calcium carbonate is precipitated. If $2m_{\text{Ca}^{2+}} < \text{alkalinity}$ ($m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}}$), all of the calcium is removed in calcite during this step.

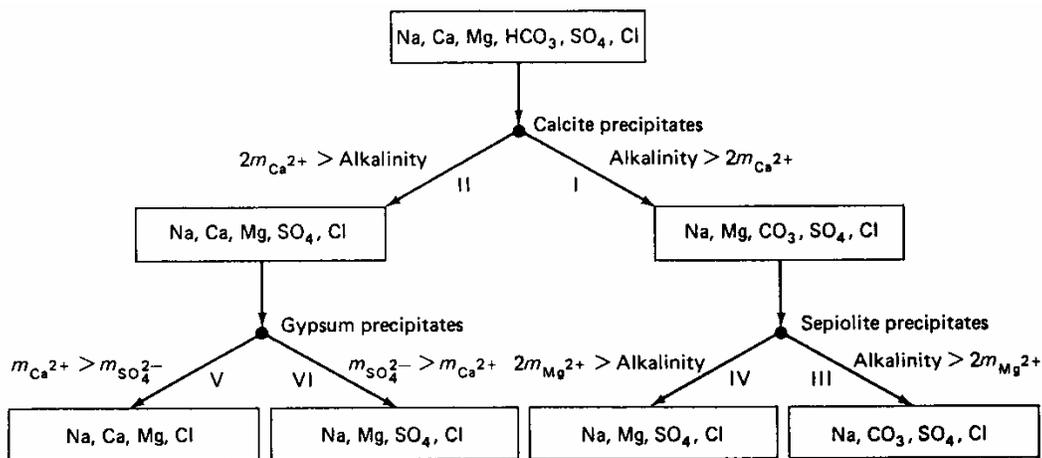


Figure 7 . 1
Some possible paths for the evaporation of natural waters, modified from Hardie and Eugster (1970) as given by Drever (1997).

The ultimate brine chemistry then depends on whether $2m_{\text{Mg}^{2+}}$ is less or greater than the alkalinity that remains after calcite precipitation. If less, which would indicate an initial water in which

$$(2\text{mCa}^{2+} + 2\text{mMg}^{2+}) < \text{Alkalinity (mHCO}_3^- + 2\text{mCO}_3^{2-})$$

the result will be a **Na-HCO₃-CO₃** brine. This pathway is evidently the one that would be taken by evaporating the reference J-13 ground water and 90% of perched waters at Yucca Mountain, which themselves are predominantly Na-HCO₃-CO₃ type waters (Rosenberg *et al.*, 2001). In part because of CO₂ loss during heating and evaporation, the pH of these waters rises to near 10.

The evaporation of waters in which initially

$$(2\text{mCa}^{2+} + 2\text{mMg}^{2+}) > \text{Alkalinity (mHCO}_3^- + 2\text{mCO}_3^{2-}) \quad (7.1.2)$$

also results in early calcite precipitation with removal of all of the alkalinity, followed by gypsum precipitation. If the remaining Ca then exceeds the SO₄, the final solution is a **Na-Ca-Mg-Cl** brine. If the opposite is true, the final solution is a **Na-Mg-SO₄-Cl** brine. The pH of such brines are expected to be near 5, reflecting equilibrium with atmospheric CO₂ pressures in the repository (Rosenberg *et al.*, 2001).

The unsaturated zone (UZ) water analyses available to Rosenberg *et al.* (2001) were from Sonnenthal *et al.* (1998). These were of water samples obtained by axial compression of nonwelded tuffs. These were chiefly Ca-Cl-SO₄-rich pore waters with an average pH of 5.6 with $2\text{mCa}^{2+} > \text{mHCO}_3^-$. Based on sample frequency, Rosenberg *et al.* (2001) concluded that evaporation of these UZ pore waters would result in 8% evolving into **Na-HCO₃-CO₃** alkaline brines, 19% becoming **Na-Ca-Mg-Cl** brines, and 73% **Na-Mg-SO₄-Cl** brines. Of these brines, the most corrosive is the **Na-Ca-Mg-Cl** brine.

More recent work by Peterman *et al.* (2003) and Yang *et al.* (2002; 2003) has involved not only extraction of UZ water samples by uniaxial compression, which is limited to sampling of the nonwelded tuffs, but also extraction by ultracentrifugation. The latter approach permits pore water sampling from the welded tuffs, which constitute perhaps 80% of the tuff units in the repository horizon (Peterman, 2003, personal communication). The focus of work to date has been on the evolution of major species and pH with evaporation and brine formation, with less attention on trace species such as F, As, Pb or Hg.

Recent analyses (Peters, 2003) indicate that seepage brines, that might develop from the known distribution of site pore waters, are typically benign. The frequency for developing corrosive Ca-Cl brines is estimated to be less than 1%. In many cases, the potential seepage waters are found to contain appreciable amounts of NO₃⁻, which acts as an inhibitor to crevice corrosion (Farmer, 2003, Cragolino, 2003).

7.2 Modeling the Behavior of Corrosion-Relevant Species During Brine Formation

In addition to possible inflow of seepage waters, brines may develop directly on the waste package surface during the low-temperature interval due to a cycle of evaporation and condensation. Concentrations of corrosion-relevant species in an evolving in-drift environment have been estimated by geochemical modeling. Pabalan *et al.* (2003) used the Environmental Simulation Program (ESP) to compute the evaporative concentration of J13 and UZ waters to form brines and deliquescent salts. The DOE has performed similar calculations using the EQ3/6 (version 8) geochemical code (OCRWM, 1999; Bechtel SAIC, 2003a; 2003b). These

studies, as well as analyses by EPRI experts, have considered the evolution of pH, carbonate species, Cl^- , NO_3^- , SO_4^{2-} and F^- in their modeling efforts. The importance of such calculations is that they:

- provide validation to fundamental understanding of isolation processes (NRC, 2003),
- serve to bound the range of possible brine compositions that may develop,
- enable a series of extrapolation and sensitivity calculations to be made regarding final composition as a function of a range of possible initial waters, environmental conditions (e.g., partial pressure of CO_2), and dust mineralogies, and
- provide guidance and an independent verification to experiments on evaporative and condensation processes in the drift environment.

7.3 Experimental Data on Refluxing

“Acid reflux” is a term used here to refer to the generation of acidity resulting from the boiling and condensation of aqueous solutions¹⁰. It is the main focus of the present review because recent experimental results reported by researchers supported by the State of Nevada (Pulvirenti *et al.*, 2003; Staehle, 2003; and Shettel, 2003)) indicate that this phenomenon could produce extremely acidic brines and condensates on surfaces of the drip shield and waste package. These experiments are reviewed in this report, and questions regarding the analysis, interpretations, and limitations of these experiments are presented.

A series of “distillation/reflux experiments” was carried out on behalf of the State of Nevada to evaluate the effects of evaporation and condensation on the compositions of residual solutions and condensates that could come into contact with the drip shield and waste package. The results have been interpreted by these workers to mean that extremely acidic solutions could exist on these EBS components and could significantly accelerate their corrosion rates.

The experiments by Pulvirenti *et al.* (2003) were intended to investigate changes in solution chemistry when initial “feed” solutions of various salts were evaporated nearly to dryness in a conventional distillation apparatus (Figure 7.2). The feed solutions included representative unsaturated zone (UZ) porewaters and saturated zone (J13) waters that were evaporated to various extents in the experiments of Rosenberg *et al.* (2001) (*i.e.*, 1xUZ, 62xUZ, 1243xUZ, 1xJ13, 157xJ13 and 250x rewetted J13 water). Solutions of individual components, or component mixtures, of these porewaters were also considered (e.g., $\text{CaCl}_2 + \text{KNO}_3$, $\text{MgSO}_4 + \text{KNO}_3$, MgSO_4 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$). However, Pulvirenti *et al.* (2003) did not include the volumetrically dominant and reactive carbonate and alumino-silicate minerals in dusts that are known to be present (Peters, 2003, Farmer, 2003; Chapter 4 of this report) and to coat waste package surfaces. The absence of these minerals immediately calls into question the relevance and applicability of such tests to realistic conditions in the emplacement drift and on waste package surfaces. The acidic brines and gas condensates found in this set of tests by Pulvirenti *et al.* (2003) simply would never form, had the tests been run with a more realistic representation

¹⁰ Rosenberg *et al.* (2001) performed experiments involving the evaporation of J13-like waters and UZ waters at 75-80°C in the presence and absence of crushed tuff. They followed the evolution of pH, carbonate species, Cl^- , NO_3^- , SO_4^{2-} and F^- during their experiments. These experiments have been previously reviewed by EPRI (2002a, 2002b), and are not considered here.

(i.e., including carbonate and aluminosilicate phases) of the dusts anticipated to exist at Yucca Mountain.

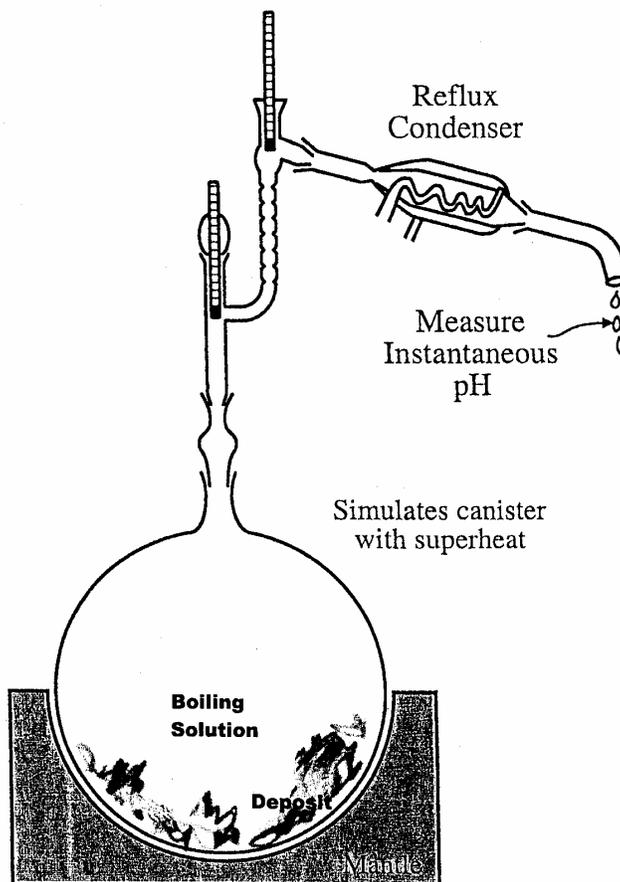
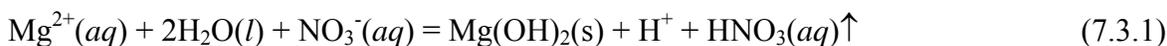


Figure 7 . 2
Schematic diagram of experimental apparatus used in the distillation experiments (Staeble, 2003).

Some of the experiments were reported by State of Nevada researchers to produce extremely acidic residual solutions and condensates ($\text{pH} < 1$) during the final stages of boiling¹¹. They reported that feed solutions containing magnesium and nitrate produced the most acidic condensates and residual solutions. The J13-based waters produced only alkaline condensates and alkaline residual solutions.

Pulvirenti *et al.* (2003), Staeble (2003) and Shettel, (2003) postulated that the acidic residual fluids were produced by hydrolysis of Mg^{2+} (mainly, but also of Ca^{2+} to a lesser extent) and precipitation of alkaline solids such as $\text{MgO}(s)$, $\text{Mg}(\text{OH})_2(s)$ and $\text{MgOHCl}(s)$. The extent of acidification is apparently related to mass transfer of acid gases by a postulated reaction such as:

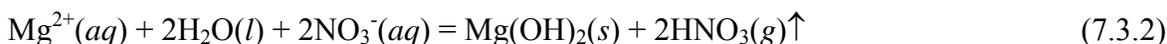
¹¹ The reported measured pH values range between -0.9 and 1.6 , although the meaning of a negative pH is unclear. Furthermore, the well-established difficulties (*e.g.*, Ives and Janz, 1961) of using a glass-electrode for measuring pH in solutions containing Na^+ and alkaline solids, such as $\text{Mg}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$, are not addressed by Pulvirenti *et al.* (2003).



where the upward facing arrow emphasizes that the volatile aqueous species $\text{HNO}_3(\text{aq})$ exsolves to equilibrate with the coexisting gas phase (“air”) of the open drift.

The probability of the above reaction occurring is zero. The precipitation of a magnesium hydroxide occurs only from solutions at strongly alkaline pH values. By way of illustrating this fact, consider that the solubility product for $\text{Mg}(\text{OH})_2$ is $K_{\text{sp}} = 10^{-11.16}$. For $\text{Mg}(\text{OH})_2$ to precipitate in an acid solution of $\text{pH} \sim 1$ would require a dissolved Mg^{2+} concentration of $10^{14.8}$ moles/liter, a chemically impossible value.

Developing an alternative, defensible interpretation of any actual reaction mechanisms in these refluxing brine tests is uncertain because the solids precipitating in the experiments have yet to be analyzed and reported for independent analysis. Furthermore, it is not clear that the reported low pH measurements are reliable, given the previously noted concern for erroneous pH measurements using glass electrodes in Na^+ -containing solutions. One obvious variant is to consider the explicit need for charge balance in any solution. A simpler and possibly more credible version of the above reaction is:



This would then lead to the formation of additional acid gas species and the alkaline residue phase $\text{Mg}(\text{OH})_2(\text{s})$. The $\text{HNO}_3(\text{g})$ would also tend to be exsolved into, and equilibrate with, the coexisting gas phase of the open drift.

Acid gases are also implicated by Pulvirenti *et al.* (2003), Staehle (2003) and Shettel *et al.* (2003) in the formation of acidic condensates. The acidity is apparently generated by a complex sequence of reactions involving:

- association of $\text{HNO}_3(\text{aq})$, $\text{HCl}(\text{aq})$ and possibly $\text{HF}(\text{aq})$ in the evaporating solutions,
- volatilization of these species to a gas phase containing evaporated water vapor,
- transport of the gases to a cooler (below the boiling point) region of the experimental apparatus where the evaporated water vapor condenses,
- dissolution of $\text{HNO}_3(\text{g})$, $\text{HCl}(\text{g})$ and $\text{HF}(\text{g})$ into the dilute condensate, and
- essentially complete dissociation of $\text{HNO}_3(\text{aq})$, $\text{HCl}(\text{aq})$ and $\text{HF}(\text{aq})$ in the condensate.

With respect to generation of acid-gas condensates, the similarity of the above refluxing equation to those decomposition equations for the previous case of possible deliquescent brines should be noted. Both produce acid-gas species at the waste package surface. Equilibrium of these acid gas species between brines on the hot waste package and water in the cooler drift walls will act to continuously remove brine forming on the waste package surface by refluxing.

Both the acidic residual solutions and acidic condensates were found by the State of Nevada researchers to be corrosive to Alloy 22 and Ti-7. Corrosion rates of Alloy 22 in the range of 0.1 to 1 mm yr^{-1} were observed, with rates as high as 10 mm yr^{-1} (Staehle, 2003). Pitting of Alloy 22 was observed on the surface of one of the test coupons (Pulvirenti *et al.*, 2003).

The State of Nevada researchers concluded on the basis of these results that a much broader range of possible water types could exist on the surfaces of the waste package and drip shield

than has heretofore been considered by the YMP. They also contend that the corrosion behavior of Alloy 22 and Ti-7 has not been adequately investigated over this broader range of solution compositions and temperatures. Staehle, (2003) concludes that these environmental conditions “cannot be readily quantified nor their effect on corrosion predicted.”

Their conclusions, however, do not appear to be supported or scientifically justified by their test results reported to date. There are several major concerns, objections and limitations to their results and interpretations, attributable to skewed selection of reactants, unrealistic test methodology, incomplete analytical procedures, unrealistic modeling assumptions, and failure to address important inconsistencies of their results. These concerns are summarized below:

- Omission of carbonate and alumino-silicate phases, known to predominate in dust that will occur on the waste package surface and in the walls of the drift, and selection of only relatively trace nitrate, chloride and sulfate salts, invalidates any claim for realistic simulation of repository-relevant conditions.
- Use of a problematic method for measuring the key pH parameter makes the claimed evolution of acidic residual solution uncertain.
- The absence of detailed solids analyses leaves an open constraint on the range of possible precipitated solid phases, hence possible reactions, in the residual solution. The breakdown of deliquescent salts may produce acid gases, but the residual solids likely to result are alkaline. The formation of acid residual solids and solutions from deliquescent salt breakdown, as proposed by the State of Nevada consultants, has no logical explanation.
- The interpretation of precipitation of strongly alkaline solids, such as possibly $Mg(OH)_2$ in an acidic residual solution is contradictory and unrealizable.
- The simple distillation apparatus of boiling flask and reflux-condensation tube do not realistically simulate the full chemical system of the actual emplacement drift (see earlier section) In particular, in a real repository acid gases evolved from the brine during refluxing will be continuously dissolved and removed into pore waters at the cooler walls of the drift. The efficiency of this process is even greater when quantitative consideration is given to the relative surface areas between reflux brine and water in the drift walls, as discussed in the following section.

Thus, the interpretations and conclusions derived by Pulvirenti *et al.* (2003), Staehle (2003) and Shettel (2003) must be viewed skeptically. Furthermore, it is unclear if or how their past test data can be meaningfully applied to the issue of refluxing during the low-temperature interval. Availability of their entire experimental approach and interpretative models for independent review is required in order to improve the usefulness of any future tests and credibility of associated interpretations.

7.4 Mass Balance, Distribution and Chemistry of Acid Gases in Drifts

Condensation of corrosive acid gases on the surface of the waste package needs to be put in the context of the surface area of the waste package relative to that of the drip shield and drift walls, which can also be expected to be subject to such condensation. If the temperature of all three surfaces were the same (which will not be the case in an actual repository), the amount of condensation would be expected to be proportional to their relative surface areas. Even slight differences in temperature (always highest for the waste package and lowest at the drift walls)

lead to preferential condensation on the cooler surface (drift wall) and preferential evaporation on warmer surfaces (waste packages and drip shield).

As a first approximation of surface area, the simplified circumferences of the tunnel, drip shield, and waste package in a vertical plane drawn perpendicular to the long axis of the tunnel is computed and compared. These circumferences will be directly proportional to the areas of interest.

Based upon information available at the Web site http://www.ocrwm.doe.gov/documents/ser_b/tables/tbl12_09.htm, the diameter of the emplacement drift is 5.5 m. The circumference of the drift is then 17290 mm. The sum of inside and outside linear dimensions of the drip shield, both sides of which would be exposed to corrosion, totals 12720 mm. To be conservative in the calculation, the largest waste package, which is 5 DHLW/DOE SNF long or short, is considered. This has a diameter of 2110 mm, and a circumference of 6630 mm. These values and their relative percentages of the total areas are shown in Table 7.1.

Table 7 . 1
Relative Ratios of Surface Areas for Components within Emplacement Drift.

	Circumference (mm)	Percent of total if tunnel wall has zero roughness	Percent of total if tunnel wall has roughness of 2x	Percent of total if tunnel wall has roughness of 7x
Tunnel Walls	17290	47.2	64.1	86.2
Drip Shield	12720	34.7	23.7	9.1
Waste Package	6630	18.1	12.2	4.7
Total of Circumferences	36640 mm	36640 mm (100%)	53925 mm (100%)	140380 mm (100%)

A roughness factor, R, is defined as the ratio of the actual surface of a rock or mineral, to its geometric surface area. The actual surface is often measured by gas (BET) adsorption. White and Peterson (1990) compared the BET-measured surface areas and geometric surface areas of a wide variety of minerals and rocks, and estimated that the mean value of R was 7 (see also Langmuir *et al.*, 1991, for further discussion of surface roughness). For the drift tunnel walls, the circumference of 17290 mm is proportional to the geometric surface of the tunnel walls. If $R = 7$, the surface of the waste package constitutes less than 5% of the surface areas exposed in the emplacement drift.

A more rigorous approach to estimating the reactive surface area of the tunnel walls, involves using the average particle size and surface area of mineral grains in the tuff. Dobson *et al.* (2003) studied the dissolution of welded Topopah Spring Tuff, and found that the experimental solution chemistry was most consistent with an average tuff spherical grain-size diameter (d) of 60 μm (394 cm^2/g of tuff). With a circumference of πd , a contiguous layer of these grains on the tunnel wall will present an area that is π or 3.14 times greater than the geometric area of the tunnel walls. Assuming conservatively that a 1 mm skin of the tunnel walls constitutes the reactive surface area of the tunnel, this skin is comprised of 16.7 sandwiched layers of tuff grains, and presents a surface area that is $3.14 \times 16.7 = 52.4$ times greater than the geometric surface area of the tunnel. Based upon this calculation, the tunnel walls, drip shield and waste

package comprise 97.9%, 1.37% and only 0.72% of the total areas exposed in the emplacement drift, respectively.

There are important implications from this basic analysis on whether refluxing brines, which generate acid-gas species, will persist on the waste package and drip-shield surface. If the surface area of these metals is about 1-5% of the total area exposed to condensation of moisture and acid gases in the repository drift, it can be expected that any acid-gas will be partitioned preferentially into the much larger available surface area of water at the drift walls. In fact, since the waste package is always hotter than either the drip shield or the tunnel walls, equilibrium considerations (see previous section on chemical system of emplacement drift) alone will act to drive acid-gases from the hot brine and into the much larger reservoir of water at the drift walls. In turn,

- the relatively high available surface area (hence volume) of water in this region,
- the pH-buffer capacity of minerals in the tuff contacting this water, and
- the diffusive transport of dissolved acid-gas species away from the drift walls into the continuous reservoir of site water,

will effectively remove and neutralize acid gas condensates in the tunnel atmosphere. This removal and neutralization of acid condensates within the tuff will lead to enhanced decomposition of refluxing brines into dry, inert solids.

7.5 Conclusions on State of Nevada Corrosion Studies

Recent concerns have been raised regarding the possible development of corrosion-aggressive brines on the surface of waste packages during both the transition interval (NWTRB, 2003a; Peters, 2003) and low-temperature interval (Pulvirenti *et al.*, 2003; Staehle, 2003; Shettel, 2003; Farmer, 2003). Independent analyses reported here show the extremely low probability of developing such adverse corrosive solutions. These analyses also indicate the instability and lack of persistence of such postulated brines based on basic thermodynamic arguments and the lack of significant impacts on isolation performance and regulatory compliance even if such solutions did develop and persist. Furthermore, a detailed critique has been made of test procedures, analyses and interpretations made by Pulvirenti *et al.* (2003), Staehle (2003) and Shettel (2003) regarding the development of such brines. Unresolved omissions, deficiencies and lack of relevance of these studies invalidate any possibility of using these results to develop scientifically credible insights for chemical processes occurring within the emplacement drifts of a repository at Yucca Mountain.

8

REVIEW OF NWTRB ANALYSIS

At meetings of the U. S. Nuclear Waste Technical Review Board (Board) held in May and September 2003, the U. S. Department of Energy (DOE) presented its views on how the proposed high-temperature design for a nuclear waste repository at Yucca Mountain would behave. The Board's position regarding the validity of DOE's technical arguments on this matter was stated in a November 25, 2003 report titled "An Evaluation of Key Elements in the U. S. Department of Energy's Proposed System for Isolating and Containing Radioactive Waste" (NWTRB, 2003a). The report concentrates on the first 1000 years following repository closure when temperatures in the drifts would be above the boiling point of water. This period is referred to by the NWTRB as the "thermal pulse", broadly corresponding to the "dry-out interval" and "transition interval" previously defined by the DOE (Peters, 2003) and presented in Chapter 2 of this report.

Among other conclusions in its report, the Board states¹²:

"Based on the DOE's calculations of temperature and relative humidity in its currently proposed high-temperature design, all the conditions necessary to initiate localized corrosion of the waste packages will likely be present during the thermal pulse because of the deliquescence of salts on waste package surfaces, and thus it is likely that deliquescence-induced localized corrosion will be initiated during the thermal pulse".

and

"Localized corrosion is likely to propagate during the remainder of the thermal pulse and is likely to continue even after the thermal pulse at temperatures below 95°C. As a result of the high temperatures of the current repository design and operation, this process will result in the perforation of the waste packages.

Thus, in essence, the Board concludes that localized corrosion of the waste packages is likely to initiate during the thermal pulse, and, once initiated, is likely to propagate unabated throughout the period of the thermal pulse and thereafter, and, by implication, if propagated, the safe, long-term isolation of nuclear waste will likely be unacceptably compromised.

EPRI believes such conclusions as stated above are incorrect and not technically defensible. It is highly unlikely that localized corrosion would be initiated, or propagated during the thermal pulse, or lead to unacceptable repository performance. This is because:

- aggressive deliquescent brines of the sort postulated by the Board are unlikely to form, be stable, or persist in the in-drift chemical and physical environment, and
- even if such brines were to form, any localized corrosion that might be initiated is more likely to stifle than to propagate indefinitely.

¹² p. *iii*, Executive Summary, NWTRB, 2003a.

The Board also indicates their belief that total system performance assessment (TSPA) should not be used to dismiss these corrosion concerns. This position conflicts with guidance from the U.S. National Academy of Sciences (1995) and the fundamental legal requirements for demonstration of compliance with regulatory standards, as set forth by the Nuclear Waste Policy Act.

The technical basis for EPRI's disagreement with the NWTRB (2003a) conclusions have been presented in earlier sections of this report. Summary points regarding these key areas of disagreement are presented below.

8.1 Stability of Deliquescent Brines

The Board believes that brines formed by the deliquescence of salts on waste package surfaces could initiate localized corrosion during the thermal pulse. This view is not consistent with the results of recent thermogravimetric experiments carried out on behalf of the DOE (Farmer, 2003), which indicate that such brines would not be thermodynamically stable in the in-drift chemical and physical environment. This instability would result from the partitioning of acid-gas species between the brine and a coexisting gas phase (representing air circulating through drifts). Mass transfer is accompanied by precipitation of one or more non-deliquescent minerals, which in turn allows water in the residual liquid to evaporate, eventually to dryness. Such destabilization of the original brine would thus prevent the onset of localized corrosion.

The Board acknowledges these experiments, but believes they provide an inadequate basis for the DOE to conclude, in the Board's words, "...that the period when conditions necessary for crevice corrosion would be too brief for measurable corrosion to occur¹³...". The Board then raises five specific criticisms of the experiments to support this view¹⁴. EPRI's responses to these criticisms are summarized below.

1. *The Board believes that the types of brines tested so far may not be representative or bounding of actual brines that could exist in the repository. The Board also feels that the DOE has not shown that simple CaCl₂ (or MgCl₂) brines are "worst case" brines. They note, for example, that mixtures of salts could deliquesce at lower relative humidities and thus at higher temperatures than the pure salts making up the mixtures.*

There are two responses to this criticism. First, it is unlikely that other types of brines could be much worse from a corrosion standpoint than the pure CaCl₂ brine already considered by the DOE. This is because the pure CaCl₂ salt is deliquescent near the maximum temperature and minimum relative humidity (RH) expected in drifts at Yucca Mountain.

Second, EPRI agrees with the Board that salts other than, or in addition to, CaCl₂ may exist on surfaces of the waste packages. Indeed, EPRI's independent data and analyses show :

- The inherent, natural nitrate / chloride ratio in dust (the source for potential formation of deliquescent brine) is orders of magnitude greater than the ratio that the CNWRA and the DOE have experimentally shown to be necessary for inhibition of localized corrosion of ALLOY 22 alloy.

¹³ p. 9, first paragraph, (NWTRB, 2003a).

¹⁴ p. 9, numbered paragraphs, and p. 10, Table 2 (NWTRB, 2003a).

- The presence of reactive aluminosilicate and carbonate minerals, significantly more abundant than chloride in wind-blown dust, will react with incipient deliquescent brine to buffer the concentration of H^+ to near neutral values, preventing the development of corrosion potential sufficient for localized corrosion. This buffering occurs whether the incipient brine is under open-system or closed-system (occluded) conditions.
- The same aluminosilicate/carbonate buffering of acidity also leads to an exchange of aggressive divalent cations (Mg^{2+}/Ca^{2+}) in brines for non-aggressive monovalent cations (Na^+/K^+).

Furthermore, it is unlikely that the deliquescent brines of salts speculated by the NWTRB would be any more stable than the $CaCl_2$ brines used in DOE's experiments. This is because these other salts will contain anionic constituents (e.g., NO_3^- , F^-), which, like Cl^- , will react with H^+ as the salts deliquesce to form acid-gas producing species [e.g., $HNO_3(aq)$, $HF(aq)$]. Volatilization of these species to the gas phase in drifts will destabilize the brine in the same manner as has been observed in DOE's experiments.

2. *The Board asserts that "The experiments have been performed only over a very narrow part of the temperature and relative humidity range at which deliquescence could occur".*

Although EPRI agrees with the Board's statement as it stands, it is unlikely that the basic processes leading to brine destabilization would differ significantly over the range of temperatures and relative humidities that will exist in drifts during the thermal pulse. That being said, it is important to acknowledge that the DOE's experiments do point to a strong temperature dependence of the brine destabilization reactions. At $150^\circ C$ and 22.5 % relative humidity, a $CaCl_2$ deliquescent brine was observed to become unstable, by precipitation of insoluble, alkaline solids followed by complete evaporation of the residual liquid film, within about 20 hours. At $125^\circ C$ and the same relative humidity, insoluble solids similar to those observed at $150^\circ C$ precipitated from the brine, but a liquid film was still present after more than 110 hours. At $100^\circ C$, the initial deliquescent brine appeared to be unchanged throughout the duration of the test (about 65 hours), and no solids were observed to precipitate. Thus, although the rate at which the initial $CaCl_2$ brine becomes unstable is strongly temperature dependent, this temperature dependence appears to be favorable with respect to corrosion susceptibility, i.e., with increasing temperature, any brine that forms will become benign more quickly.

3. *The Board notes that the thermogravimetric apparatus (TGA) used in DOE's experiments is an open system because gaseous reaction products are physically removed (i.e., "swept away") in the gas stream flowing over the brine. The Board believes, however, that the drift environment might not behave as an open system "over short periods of time." The Board also questions whether the TGA "...appropriately simulates the microenvironments associated with crevices..." that may exist on surfaces of the waste packages.*

With the possible exception of short-term transients and the existence of microenvironments, the Board acknowledges that the open-system conditions simulated in the TGA are generally appropriate for the in-drift system. EPRI agrees with this view that the open system conditions are appropriate for the in-drift system. The in-drift system is likely to behave as an open system because air will circulate through the drifts during the thermal pulse as a result of natural variations in barometric pressure and by buoyancy driven flow arising from differences in temperature between the waste packages and surrounding rock.

However, EPRI disagrees with the Board's implied view that if open-system conditions do not exist for any reason (including the speculative transients and microenvironments cited by the Board), then brine destabilization as observed in the DOE's TGA experiments would not occur. Even in the complete absence of advective air flow in the drifts, there will always be a thermodynamic driving force during the thermal pulse that is likely to destabilize any deliquescent brines that form on surfaces of the waste packages. Even under stagnant air-flow, an assumption not supported by independent analysis of natural ventilation at Yucca Mountain (*e.g.*, Danko and Bahrami, 2003; 2004), this chemical driving force will prevent formation of a stable deliquescent brine because:

- gases in the drift will tend to equilibrate with both the brine on the container surfaces of waste packages and with the porewater in the host rock immediately surrounding the drift, and
- the temperature at the surface of the waste package will always be higher than the temperature of the porewater.

Thus, at steady state, the chemical potential of any acid-gas species in the brine will tend to closely approach the value of the chemical potential for that species in the porewater, but the temperature of the porewater will be less than that of the brine. The partial pressure of the gas will consequently be lower in the host rock than it is at the waste package surface. The resultant concentration gradient will cause the acid-gas species to diffuse away from the waste package surface toward the drift wall. Diffusion rates will be rapid at these elevated temperatures, both in any deliquescent brine on the waste packages, and in the drift atmosphere. Because diffusional transport in the gas phase is a rapid process, it is likely that significant amounts of acid-gas species could be stripped out of the brine in an analogous fashion to the loss of acid gases that are swept away in the gas phase in an open system. The chemistry of the porewater and gas phase in the host rock will thus establish important constraints on the chemical stability of any deliquescent brines on wastepackage surfaces.

Lastly, independent analyses by EPRI contractors for speculative closed-system/occluded conditions, rather than realistic open-system conditions, are reported in earlier sections of this report. These analyses indicate that even under the highly speculative occluded condition, benign solutions are formed (non-acidic / low hydrogen ion concentration, low divalent-cation concentration, high nitrate / chloride ratio), rather than corrosion-aggressive solutions.

4. *The Board notes that samples of Alloy 22 used in DOE's TGA experiments did not contain crevices, which are necessary precursors to crevice corrosion.*

As noted in the preceding discussion, it is unlikely that a deliquescent brine could exist in isolation of the drift system within a "microenvironment" inside a crevice. The crevice would necessarily be large enough to allow dust and water vapor to enter, which implies a sufficiently open communication to the rest of the drift environment. The brines are thus unlikely to be stable in the open system of the TGA, and the presence or absence of crevices may thus be irrelevant.

5. *The Board asserts that DOE has not explained seemingly contradictory results between the TGA experiments and other types of experiments.*

EPRI agrees with the Board that any contradictory results should be explained. The examples cited by the Board¹⁵ do not appear to be truly contradictory, however. As noted by the Board (NWTRB, 2003a), the corrosion of Alloy 22 observed in cyclic polarization experiments carried out at LLNL, and the lack of any such corrosion in the TGA experiments, may be related to the fact that the TGA system is an open system whereas the cyclic polarization system may be a “less open” or even closed system. However, it is more likely to reflect the fact that a cyclic polarization test is a deliberately accelerated, and very conservative, test for susceptibility to localized corrosion. The TGA tests represent non-polarized, and hence more representative, conditions. The Board’s reference to the CNWRA study¹⁶ (Cragolino, 2003) seems completely irrelevant to any of DOE’s TGA results. EPRI has commented previously on the experiments carried out on behalf of the State of Nevada by the Catholic University of America and believes these experiments are unreliable and based on conditions not representative of a repository at Yucca Mountain, hence the results should not be used in comparisons with other more realistic experiments by the DOE (see Chapter 5 of this report).

Several other, more general observations further support these specific responses to the Board’s position regarding the stability of deliquescent brines during the thermal pulse.

First, the Board emphasizes the likelihood that CaCl₂ brines will cause the corrosion of waste packages. It is true that the dust that may settle on waste packages in the repository will likely contain calcium, magnesium and chloride. However chloride is a minor constituent in the salts from dust that might form corrosive deliquescent brines. The Board’s report¹⁷ acknowledges that crevice corrosion is inhibited, “...if the molar ratio of nitrate to chloride ions in the brine is higher than approximately 0.1-0.2.” In fact, this ratio averages 1.3 in the dust now present in the repository (Peterman *et al.*, 2003) and averages 6.5 in the windblown atmospheric dust that is likely to enter the repository after closure¹⁸. This supports the DOE’s argument that there will always be sufficient nitrate present to exceed the molar ratio of nitrate to chloride ions in the brine needed to inhibit localized corrosion.

Second, the Board asks the DOE for an explanation of why any gaseous hydrochloric acid released from deliquescent brines would dissipate rapidly without causing corrosion of waste packages¹⁹. The Board has not considered the neutralization capacity of the dust itself, and the fact that repository wall rock and engineered materials in the tunnels, including steel supports and concrete, are cooler and have a vastly greater mass and surface area than the waste packages, comprising perhaps 90% or more of exposed reactive materials in the repository. These materials are all highly reactive to acid gases, and can be expected to rapidly neutralize and consume any acidity produced from the breakdown of deliquescent salts.

Third, the Board argues²⁰ that “The DOE has not demonstrated the ubiquitous presence of nitrate in the unsaturated zone pore water above the repository footprint.” The Board apparently failed to take into account the OCRWM/USGS report summarizing the geochemistry of the unsaturated

¹⁵ p. 22, endnote 29, (NWTRB, 2003a).

¹⁶ Results indicate no localized corrosion of Alloy 22 at or below 95°C in 0.5 molar Cl despite the fact that the susceptibility to corrosion increases with increasing temperature and increasing Cl concentration.

¹⁷ p. 8, paragraph 2, lines 2 & 3 (NWTRB, 2003a).

¹⁸ Table 4-1 this report.

¹⁹ p. 9, numbered paragraph 3, last sentence (NWTRB, 2003a)

²⁰ p. 10, Table 2, #2 under “*Inhibition of localized corrosion*” (NWTRB, 2003a).

zone (UZ) at Yucca Mountain (OCRWM, 2000) or the journal article on the same subject by Yang *et al.* (2003). These documents, which tabulate all available chemical analyses of porewaters at or near Yucca Mountain, show that nitrate is a major constituent of essentially all UZ porewaters, and that its concentration often exceeds that of chloride and sulfate in pore water from the tuffs that lie stratigraphically above the repository horizon. This conclusion should not be significantly different whether the porewater data have been collected adjacent to or above the repository footprint.

8.2 Corrosion Behavior of the Waste Package and Drip Shield

The adoption of a container wall thickness $> 2\text{cm}$ means that the waste package is deliberately designed to allow some corrosion damage without failing.

Localized corrosion propagates at a rate that inevitably decreases with time (see Chapter 5 of this report). This is due to the influence of diffusion and IR drops within propagating sites. Thus, the very large majority of initiated local corrosion sites would be expected to die (by stifling or repassivation) well before wall penetration occurred. Despite the general availability of much evidence to support such a time-dependency, the Board concludes²¹ that:

“Localized corrosion occurs in specific areas on the surface of the metal, often widely spaced, but it may proceed very rapidly and often increases with elapsed time” (emphasis added).

This is not so. Such increases are very rare and would require the extremely poor corrosion properties associated with much lower grade alloys than Alloy 22.

Assuming the environment can drive initiation and subsequently sustain propagation (by no means certainties in Yucca Mountain), the distribution of penetration depths for a “population” of propagating sites will depend primarily on the properties of the material. For an alloy like Alloy 22, designed specifically with a metallurgy intended to resist localized corrosion, very large maximum penetration depths would not be anticipated. A small amount of evidence exists to support this view. EPRI’s IMARC calculations (EPRI, 2002a), which assume such metallurgical features would operate, indicate limited damage should be sustained by the Alloy 22 container over the thermal pulse, even if localized corrosion initiates at $\sim 160^\circ\text{C}$ the approximate upper temperature limit for deliquescence, is not subsequently arrested by a temperature threshold, and the drip shield is assumed to be non-existent. It is acknowledged that the growth constants used in the EPRI model could be disputed, but sensitivity calculations indicate that values appropriate for a very much poorer material than Alloy 22 would have to be used for failure to occur.

The Board contends that crevice corrosion is virtually certain to begin for high surface temperatures²². The DOE results, obtained with well-defined crevices, are stated as the basis for this conclusion (Farmer, 2003). The use of the words “virtually certain” can be disputed, as discussed in Section 5 of this report.

²¹ p. 5, fifth paragraph (NWTRB, 2003a).

²² p. 8, first paragraph (NWTRB, 2003a).

To sustain crevice propagation requires the maintenance of a differential oxygen cell, such that oxygen reduction outside the crevice can sustain metal dissolution in the de-aerated acidic environment within the crevice. This is achieved in the DOE experiments (Farmer, 2003). It is very unlikely that a deliquescent deposit can sustain the necessary oxygen-concentration cell (see Chapter 5). Investigators who have tried to initiate crevice corrosion on Alloy 22 know that a tight, well-formed crevice is necessary if corrosion is to occur. An unconstrained deposit will not form a tight crevice, and the crevice former (the deposit itself) will be permeable to oxygen, thereby destroying the necessary oxygen concentration cell. Thus any “crevice” formed on the Alloy 22 container surface should rapidly stifle or repassivate.

Although not rationalized in these terms, the DOE claim²³ that “...*the period of existence of conditions necessary for crevice corrosion would be too brief for measurable corrosion to occur*” is a much more likely scenario than the long-term maintenance of an environment conducive to a crevice propagating to extreme local wall-penetration depths.

Based on the above discussion, EPRI is uncertain what the NWTRB means by the comment²⁴ “*Samples used in the TGA experiments did not contain crevices, a necessary precursor to crevice corrosion*”.

The Board also dismisses the ability of nitrate to offset the aggressive influence of chloride. The Board’s assertion²⁵ that “*it is not clear whether the nitrate will be depleted by microbial activity within the host rock*” is not a valid one. If the nitrate is already present in the rock, despite the already present microbial activity, then there is no reason why excavation activities would cause nitrates to disappear. In the critical period when the nitrate is required to suppress the influence of chloride, the temperature will be high (>100°C) at the drift wall. Providing the temperature is > 70°C, there is evidence to show that microbial activity will be suppressed under Yucca Mountain conditions (Else *et al.*, 2003). Furthermore, the proximal potential source of nitrate, the dust upon which deliquescent brines might form, is strongly enriched in nitrate (see Section 4.1 and 4.2).

Many of the above arguments apply also to the Board’s discussion on seepage-induced localized corrosion²⁶.

The Board states²⁷: “Furthermore, the DOE assumes that drip shields will not corrode to the point of leaking during the thermal pulse despite the fact that there are very little, if any, corrosion data supporting this assumption and despite the fact that titanium, the drip shield material of construction, is known to be susceptible to fluoride-based corrosion and hydrogen embrittlement, as well as to crevice corrosion in elevated-temperature, high-chloride environments.”

EPRI strongly disagrees with this view for several reasons.

²³ p. 8, third paragraph (NWTRB, 2003a).

²⁴ p. 9, fourth numbered paragraph (NWTRB, 2003a).

²⁵ p. 9, second un-numbered paragraph (NWTRB, 2003a).

²⁶ Beginning on p. 11 (NWTRB, 2003a).

²⁷ p. 15, second paragraph under the heading “*Will the drip shield prevent corrosion by diverting seepage water?*” (NWTRB,2003a).

First, there is ample evidence from a number of sources that Grade-7 titanium will not experience crevice corrosion below 200°C even in extremely saline aggressively oxidizing environments. If it is reasonably assumed that the LLNL rates for general corrosion of the slightly inferior Grade-16 titanium are conservative for Grade-7 (Hua *et al.*, 2004), and that results from the German program in high temperature saline environments (on Grade-7) are valid (Smailos, *et al.*, 1986; Smailos and Koster, 1987), then there is also ample evidence that the general corrosion rates of Grade-7 titanium will be very low.

This leaves the possibility of hydrogen embrittlement, and the influence of fluoride. Based on very conservative assumptions for hydrogen absorption rates and susceptibilities to hydrogen cracking EPRI's IMARC calculations indicate that failure of the drip shield due to embrittlement will not occur before the waste package temperature is below the 95°C accepted in this report as a reasonable threshold for localized corrosion of the waste package (EPRI, 2002a).

This leaves the issue of the influence of fluoride. This issue is unresolved based on published DOE studies. The evidence available is contradictory, and data from measurements of natural fluoride (*e.g.*, Bechtel SAIC, 2003) indicate active geochemical processes keep dissolved fluoride at low levels at Yucca Mountain.

8.3 Total System Performance Assessment

As indicated in Chapter 1, the NWTRB has indicated that:

“The Board believes that total system performance assessment should not be used to dismiss these corrosion concerns.”

EPRI disagrees with this position and concurs with the National Academy of Sciences Panel for Technical Bases for Yucca Mountain Standards (NAS, 1995, page 8):

“Any standard to protect individuals and the public after the proposed repository is closed will require assessments of performance at times so far in the future that a direct demonstration of compliance is out of the question. The only way to evaluate the risks of adverse health effects and to compare them with the standard is to assess the estimated potential failure behavior of the entire repository system and its potential effects on humans. This procedure, involving modeling of processes and events that might lead to releases and exposures, is called performance assessment.”

Focusing on a narrow sub-system performance, in this case speculative localized corrosion, represents a bottom-up approach to safety assessment, in which any and all scientific issues or processes are automatically given equal weight and importance. It fails to recognize the multiple redundancy of barriers and processes in a geological repository, a point appropriately acknowledged by the NWTRB (NWTRB, 2003a). It is only by integrating all barriers and processes into a top-down, total-system model that a valid and balanced evaluation of safety can be made. Such an integrated, total system performance assessment (TSPA) provides the means to explore a wide range of alternative conceptual models, speculative “what if?” scenarios, and the sensitivity of different designs and isolation strategies for achieving long-term isolation and safety.

The use of TSPA allows a comparison of different features, events or processes to be made on a common basis, to identify those features, events and processes that contribute most to safety. Without placing individual processes within a system context, it is indefensible, and potentially misleading, to assert that any particular aspect of a repository system is of paramount importance to the primary goal of long-term protection of public health and safety. Furthermore, TSPA provides a justifiable and systematic basis by which to prioritize R&D needs, and to address the key questions regarding necessity and sufficiency of understanding to demonstrate compliance with regulatory criteria.

EPRI would welcome the opportunity to place the Board's perspectives on potential brine development and localized corrosion into a TSPA context. In order to establish confidence in long-term safety, EPRI believes it is vital that all credible opinions be examined within a systematic performance assessment context. The Board is urged to place their technical judgments and alternative models into a TSPA context, in order to permit a timely and defensible resolution of such issues, consistent with the legal requirements of the Nuclear Waste Policy Act and the regulatory requirements of the USNRC's 10 CFR Part 63.

9

SUMMARY

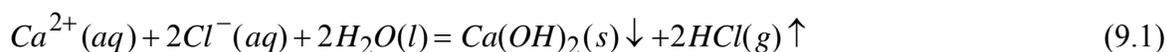
The NWTRB has postulated a scenario for the formation of a deliquescent divalent cation-chloride (*e.g.*, CaCl_2) brine that they believe could lead to earlier than expected penetration of nuclear waste packages at a repository at Yucca Mountain, and thereby compromise compliance with established regulatory criteria. EPRI conducted an independent technical analysis of this scenario, as described in the previous sections of this report. The analyses conducted by EPRI contractors have specifically examined and responded to a series of decision points in the NWTRB's speculative scenario, as cited below. If, and only if, *all* of the following decision-points (questions) below can be answered affirmatively would NWTRB's scenario result in potential non-compliance with established regulatory safety criteria:

- *Can a pure CaCl_2 (or MgCl_2) brine form via deliquescence involving deposited dust on the waste package surface?*

No. Extensive collection and review of the compositions of dust that may contact waste packages shows that inorganic salts of chloride, nitrate, sulfate etc. are volumetrically minor (<10%) compared to alumino-silicate and carbonate minerals in these dusts. Furthermore, the volumetric proportion of chlorides to the remaining inorganic salts is minor. Thus, any deliquescent brine that might form from dust on waste package surfaces would be (1) a mixture of chlorides and other anions, such as nitrate and sulfate, that inhibit localized corrosion, and (2) would be in contact with abundant mineral phases that will act to buffer and neutralize any acidity, as well as lead to substitution of alkali ions in place of divalent ions, associated with any formed brine.

- *If such a brine could form, would it be stable ?*

No. Such brines would not be stable in the in-drift chemical system because acid gases produced by reactions, such as



would be continuously removed from contact with the brine by advection, or by diffusion driven by concentration gradients set up at steady state by differences in temperature and by the tendency for the chemical potential of the acid-gas species to have the same value at the canister surface as in fractures and pore spaces of the host rock. The loss of acid gases at the canister will drive reactions such as Equation 9.1 continuously to the right, thus destabilizing any deliquescent brine that might form and resulting in the precipitation of non-deliquescent minerals. It is important to emphasize that such brine-destabilization scenarios are not speculative: they have been demonstrated experimentally under repository-relevant conditions (Farmer, 2003).

- *If the brine is stable and persists, will chemical conditions (*e.g.*, pH, nitrate / chloride ratio, rate of O_2 supply) necessary for initiation of localized corrosion be maintained?*

No. Bounding chemical calculations have been made to simulate the evolution of brine chemistry under closed system conditions in which the brine is assumed to be occluded or covered by a gas-impermeable "crust". Such closed-system conditions have been postulated by the NWTRB,

apparently without any referenced evidence. Analyses by EPRI contractors indicate that a CaCl_2 deliquescent brine, for example, would be stable under such conditions, but that the brine would be neutral and prevented from becoming acidic (*e.g.*, by hydrolysis of metal ions dissolving into the brine during localized corrosion of Alloy 22), by reactions with the volumetrically dominant carbonate and aluminosilicate phases present in the dust. The corrosion potential for Alloy 22 is strongly dependent on pH, and localized corrosion is unlikely at neutral pH values and above, even if a concentrated CaCl_2 brine persists (*e.g.*, Cragnolino, 2003).

Furthermore, the molar ratio of nitrate (an inhibitor of localized corrosion) to chloride must be *below* a threshold of 0.12 to 0.2 to initiate localized corrosion (*e.g.*, Cragnolino, 2003). Yet analyses in this report confirm the molar ratio of nitrate to chloride in dusts, the source of any deliquescent brine is 1.3 and 6.5 in ESF dusts and wind-blown dusts respectively, effectively suppressing any possibility for initiating localized corrosion.

Lastly, the analyses in this report indicate that porous crevice formers, such as dust deposits or precipitated salt films, will not initiate localized corrosion. The rate of supply of O_2 to the “occluded” surface under the deposit far exceeds its rate of consumption. Hence, neither the differential O_2 concentration conditions nor the local acidification required for the initiation of crevice corrosion can be established.

- *If localized corrosion is initiated, will penetrations propagate through the entire wall-thickness of the container?*

No. Even in the unexpected event that localized corrosion will initiate on the surface of the waste package, analyses reported here reveal that there is ample evidence from a number of alloy systems that the rate of such crevice corrosion will decrease with time. For thick-walled material, such as the Alloy 22 waste packages, the decreasing rate of penetration leads to stifling of localized corrosion before they fully penetrate through the waste package wall. There are a number of contributing mechanisms by which crevice corrosion, if ever initiated on the surface of a waste package, could be stifled, including neutralization of the low-pH established within the occluded region, loss of critical crevice chemistry, loss of spatial separation of anodic and cathodic reactions by changes to the permeability of the crevice former, or mass transport limitations produced by blockage of the crevice region by precipitated corrosion products leading to diffusion control of the propagation process. The net result of any or all of these stifling mechanisms is that the localized corrosion penetration rate decreases with time and ceases before penetrating the waste package.

- *If there is localized failure of the waste package, will this cause the regulatory safety standard to be exceeded?*

No. As endorsed by the US National Academy of Sciences (NAS, 1995, page 8 and Chapter 3), EPRI-sponsored contractors have applied EPRI’s total system performance assessment (TSPA) code, IMARC (EPRI, 2003), to evaluate the consequences of NWTRB’s speculative scenario on compliance with the established regulatory safety criteria. In these analyses, all waste packages are assumed to fail early. Indeed they are assumed to fail immediately after repository closure, resulting in absolutely the most conservative, bounding case of the NWTRB’s scenario. The IMARC analysis confirms that the regulatory safety criteria, EPA’s 40 CFR Part 197 and the NRC’s 10 CFR Part 63, will be met at all times during the 10,000 year regulatory compliance period. Indeed, compliance continues to occur even beyond this period, even if it is assumed that

all of the waste packages failed early in the thermal pulse by postulated localized corrosion arising from deliquescent brine formation.

In summary, multiple lines of evidence using credible, and even highly conservative and bounding, assumptions have been applied to the speculative deliquescent-brine scenario postulated by the NWTRB. These multiple analyses indicate that

- such pure brines (*e.g.*, CaCl₂-type brines) will not form,
- such brines will not be stable if formed,
- such brines, if they are stable, will not lead to initiation of localized corrosion,
- localized corrosion, if it initiates, cannot be sustained,
- penetration through the container of the waste package will likely not occur, even if localized corrosion is sustained, and lastly,
- early, localized penetration of waste packages would not compromise the ability of a repository at Yucca Mountain to comply with established regulatory safety criteria.

Thus, not one of the required assumptions and conjectures regarding the NWTRB's deliquescent scenario is supported. It is EPRI's judgment that further concern about this issue is without foundation or merit.

10

REFERENCES

- Barin, I. and G. Platzki, 1995, *Thermochemical data for pure substances*. 3rd Ed. VCH Publishers, New York, New York.
- Battino, R., T.R. Rettich and T. Tominaga, 1983, "The solubility of oxygen and ozone in liquids." *J. Phys. Chem. Ref. Data* V. 12, 163-178.
- Bechtel SAIC, 2003a, *Technical Basis Document No. 5: In-Drift Chemical Environment. Revision 1*. Prepared by Bechtel SAIC Co., Las Vegas NV, for U.S. Dept. of Energy, OCRWM, Las Vegas NV. Contract No. DE-AC28-01RW12101.
- Bechtel SAIC, 2003b, *Technical Basis Document No. 6: Waste Package and Drip Shield Corrosion. Revision 1*. Prepared by Bechtel SAIC Co., Las Vegas NV, for U.S. Dept. of Energy, OCRWM, Las Vegas NV. Contract No. DE-AC28-01RW12101.
- Bodvarsson, G., 2003, *The Character of the Unsaturated Zone*, Presented to the Nuclear Waste Technical Review Board. May 13, 2003, Washington, DC.
- Boyle, W., 2003, *Logic for Evaluating Engineered Barrier System Performance*, Presented to the Nuclear Waste Technical Review Board. May 13, 2003, Washington, DC.
- Brown, B.F., 1970, "Concept of the Occluded Corrosion Cell." *Corrosion*, V. 26, p. 249.
- Cragolino, G.A, 2003, *Corrosion Research at the Center for Nuclear Waste Regulatory Analyses*, Presented to the Nuclear Waste Technical Review Board. May 13, 2003, Washington, DC.
- Collin, M. and A. Rasmuson, 1988, "A comparison of gas diffusivity models for unsaturated porous media." *Soil Sci. Soc. Am. J.* V. 52, 1559-1565.
- Cook, A.J., 1988, *A Desk Study of Surface Diffusion and Mass Transport in Clay*. British Geological Survey Report, WE/88/34.
- Cox, J.D., D.D Wagman, and V.A Medvedev, 1989, *CODATA key values for thermodynamics. Final report of the CODATA Task Group on key values for thermodynamics*. Hemisphere Publ. Corp., New York, New York, 271 p.
- Danko, G. and D. Bahrami, 2003, "Powered, Natural Passive Ventilation at Yucca Mountain", in *Proceedings of the 10th High-level Radioactive waste Management Conference*, pp. 683-689, American Nuclear Society.
- Danko, G. and D. Bahrami, 2004, "Coupled, Multi-scale Thermohydrological- Ventilation Modeling with MULTIFLUX", *Proceedings of the SME Annual Meeting*, February 23-25, 2004, Denver, Colorado.

- Dobson, P.F., T.J. Kneafsey, E.L. Sonnenthal, N. Spycher, and J.A. Apps, 2003, "Experimental and numerical simulation of dissolution and precipitation: implications for fracture sealing at Yucca Mountain, Nevada." *Jour. Contaminant Hydrology*, V. 62-63, 459-476.
- Drever, J.I., 1997, "The Geochemistry of Natural Waters." *Surface and Groundwater Environments*. 3rd Ed. Prentice Hall, Upper Saddle River, NJ.
- Dunn, D.S. and C.S. Brossia, 2002, "Assessment of passive and localized corrosion processes for Alloy 22 as a high-level nuclear waste container material." CORROSION Conference, Denver, CO, April 2002.
- Dunn, D.S., N. Sridhar, and G.A. Cragnolino, 1996, "Long-Term Prediction of Localized Corrosion of Alloy 825 in High-Level Nuclear Waste Repository Environments." *Corrosion* 52, 115-124.
- Else, T.A., C.R. Pantle and P.S. Amy, 2003, "Boundaries for Biofilm Formation: Humidity and Temperature"; *Appl. Environ. Microbiol.*, V. 69, 5006-5010)
- EPRI, 2000, *Evaluation of the candidate high-level radioactive waste repository at Yucca Mountain using total system performance assessment. Phase 5*, EPRI Report Number 1000802, Electric Power Research Institute, Palo Alto, CA.
- EPRI, 2002a, *Evaluation of the Proposed High-Level Radioactive Waste Repository at Yucca Mountain Using Total System Performance Assessment: Phase 6*, EPRI Report Number 1003031, Electric Power Research Institute, Palo Alto, CA.
- EPRI, 2002b, *Integrated Yucca Mountain Safety Case and Supporting Analysis: EPRI's Phase 7 Performance Assessment*, EPRI Report Number 1003334, Electric Power Research Institute, Palo Alto, CA.
- EPRI, 2003, *Scientific and Technical Priorities at Yucca Mountain*, EPRI Report Number 1003335, Electric Power Research Institute, Palo Alto, CA.
- Farmer, J., 2003, *Materials Performance*, Presented to the Nuclear Waste Technical Review Board. May 13, 2003, Washington, DC.
- Ge, Z., A.S. Wexler, and M.V. Johnston, 1998, "Deliquescence behavior of multicomponent aerosols." *J. Phys. Chem., A*, V. 102, 173-180
- Hall, D., and J. Walton, 2003, "Physical separation processes and EBS water chemistry-a modeling study." *10th Intl. High Level Waste Management Conference*, American Nuclear Soc., Las Vegas, NV, April 2003.
- Hardie, L. A., and H. P. Eugster, 1970, "The evolution of closed-basin brines." *Mineralogical Soc. Am. Spec. Publ.*, V. 3, 273-290.
- Helgeson, H.C., J.M. Delany, H.W. Nesbitt and D.K. Bird, 1978, "Summary and critique of thermodynamic properties of rock-forming minerals," *Am. J. Sci*, V. 278A.

- Hua, F., K. Mon, P. Pasupathi, G. Gordon and D. W. Shoesmith, 2004, "Corrosion of Ti Grade 7 and Other Ti Alloys in Nuclear Waste Repository Environments – A Review," *Corrosion 2004*, New Orleans, Paper No. 04689, NACE International, Houston, TX.
- Ives, D.J.G. and G.J. Janz, 1961, *Reference Electrodes*, Academic Press, New York.
- Izbicki, J, 2003, Personal communication. U.S. Geological Survey, San Diego, CA
- Johnson, J. W., E.H. Oelkers, and H.C. Helgeson, 1992,. "SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species and reactions from 1 to 5000 bars and 0° to 1000°C." *Computers and Geosciences*, V.18, 899-947.
- Kear, G., B.D. Barker, and F.C. Walsh, 2004, "Electrochemical corrosion of unalloyed copper in chloride media – a critical review." *Corros. Sci.* V. 46, 109-135.
- Kelly, R.G., 2003, "Crevice Corrosion," in *Corrosion: Fundamentals, Testing, and Protection*. ASTM Handbook, Volume 13A, ASM International (Materials Park, Ohio).
- King, F., C.D. Litke, M.J. Quinn and D.M. LeNeveu, 1995a, "The measurement and prediction of the corrosion potential of copper in chloride solutions as a function of oxygen concentration and mass-transfer coefficient." *Corros. Sci.* V.37, 833-851.
- King, F., M.J. Quinn and C.D. Litke, 1995b, "Oxygen reduction on copper in neutral NaCl solution." *J. Electroanal. Chem.* V.385, 45-55.
- King, F., M. Kolar and D.W. Shoesmith, 1996, "Modelling the effects of porous and semi-permeable layers on corrosion processes." *CORROSION/96, NACE International*, Houston, TX, Paper No. 380.
- Knauss, K.G., T.J. Wolery, and K.J. Jackson, 1990, "A new approach to measuring pH in brines and other concentrated electrolytes." *Geochim. Cosmochim. Acta*, V.54, 1519-1523.
- Knauss, K.G., T.J. Wolery, and K.J. Jackson,. 1991, "Reply to comment by R. E. Mesmer on A new approach to measuring pH in brines and other concentrated electrolytes." *Geochim. Cosmochim. Acta*, V.55, 1177-1179.
- Langmuir, D., 1997, *Aqueous Environmental Geochemistry*, Prentice Hall, Upper Saddle River, NJ.
- Langmuir, D., R. Schmiermund and G. Kishiyama, 1991, "Hydrodynamic concepts," in *Acidic Deposition: State of Science and Technology. Vol. III. Terrestrial, Materials, Health and Visibility Effects*. P.M. Irving, editor. Section 3. Effects of Acidic Deposition on Carbonate Stone. U.S. National Acid Precipitation Assessment Program. Superintendent of Documents, Govt. Printing Office, Washington, DC. NAPAP Report 19, 105-106.
- Mesmer, R. E., 1991, "Comments on "A new approach to measuring pH in brines and other concentrated electrolytes, by K. G. Knauss, T. J. Wolery and K. J. Jackson." *Geochim. Cosmochim. Acta*, V.43, 1533-1542.

- Millet, P.J. and J.M. Fenton, 1993, "High-Temperature, Aqueous-Phase Diffusion of NaCl through Simulated Deposits of Corrosion Products." *Corrosion* V.49, 536-543.
- Muurinen, A., J. Rantannen, P.P. Hiltunen, 1985, "Diffusion mechanisms of strontium, cesium and cobalt in compacted bentonite." *Mat. Res. Soc. Symp. Proc.* V.50, 1985, 617-624.
- NADP (Natural Atmospheric Deposition Program), WEB SITE:
<http://nadp.sws.uiuc.edu/sites/ntnmap.asp>,
- NAS (National Academy of Science) 1995, *Technical Basis for Yucca Mountain Standards*, National Academy Press, Washington, D.C.
- Neretnieks, I., 1985, "Diffusivities of some dissolved constituents in compacted bentonite." *Nuclear Technology* V.41, 1985, 458-470.
- NRC (Nuclear Regulatory Commission), 2003, June 5, 2003, Memorandum from W. Travers to NRC Commissioners, Baseline of Risk Insights, Attachment 2, in Final Staff Response to March 19, 2003, Staff Requirements Memorandum on the Waste Arena Briefing , US Nuclear Regulatory Commission, Washington, D.C.
- NWTRB (Nuclear Waste Technical Review Board), 2003a, Letter to Dr. Margaret Chu, Director of Office of Civilian Radioactive Waste Management, US Department of Energy, dated November 25, 2003, "An Evaluation of Key Elements in the USDOE's Proposed System for Isolating and Containing Radioactive Waste," US Nuclear Waste Technical Review Board, 2300 Clarendon Blvd., Suite 1300, Arlington, VA.
- NWTRB (Nuclear Waste Technical Review Board), 2003b, Letter to Dr. Margaret Chu, Director of Office of Civilian Radioactive Waste Management, US Department of Energy, dated October 21, 2003, US Nuclear Waste Technical Review Board, 2300 Clarendon Blvd., Suite 1300, Arlington, VA.
- OCRWM, 1999, *Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier*. U.S. Dept. of Energy, Office of Civilian Radioactive Waste Management. Report ANL-EBS-MD-000001 REV 00.
- OWCRM, 2000, *Analysis of Geochemical Data for the Unsaturated Zone*. ANL-NBS-HS-000017, Rev. 00.
- OCRWM, 2003, *In-Drift Precipitates/Salts Model*. U.S. Dept. of Energy, Office of Civilian Radioactive Waste Management Report ANL-EBS-MD-000045 REV 01.
- Oldfield, J.W and W.H. Sutton, 1978, "Crevice corrosion of stainless steels: I-A mathematical mode." *Br. Corros. J.* V.13, 13-22.
- Oscarson, D.W., H.B. Hume, N.G. Sawatsky, S.C.H. Cheung, 1992, "Diffusion of iodide in compacted bentonite." *Soil Sci. Soc. Amer. J.* V.56, 1400-1406.
- Pabalan, R. T., L. Yang, and L. Browning, 2003, *Chemical Evolution of In-drift Waters at the Proposed Yucca Mountain, Nevada, Nuclear Waste Repository*. Center for Nuclear Waste Regulatory Analyses, San Antonio, Texas, U.S.A. 77-78.

- Peterman, Z.E., J.B. Paces, L.A. Neymark, and D. Hudson, 2003, "Geochemistry of Dust in the Exploratory Studies Facility, Yucca Mountain, Nevada." *Intl. High-Level Radioactive Waste Management Conf.*, Las Vegas, NV. April 2, 2003. 637-645.
- Peterman, Z. E., P. L. and Cloke, 2002, "Geochemistry of rock units at the potential repository level, Yucca Mountain, Nevada." *Applied Geochem.*, V.17, 683-698.
- Peterman, Z. E., and B.D. Marshall, 2002, "Geochemistry of pore water from densely welded Topopah Springs Tuff at Yucca Mountain, Nevada." Abstract 137-2 BTH 171, *Geol. Soc. Am. Abstracts with Programs.*, p. 508.
- Peters, M.T., 2003, *The Character of the In-drift Environment*. Presented to the Nuclear Waste Technical Review Board. May 13, 2003, Washington, DC.
- Pulvirenti, A.L. , K.M. Needham, A. Adel-Hadadi, E.J. Bishop, A. Barkat, C.R. Marks and J.A. Gorman, 2003, "Corrosion Behavior of Alloy 22 Under Conditions of Dynamic Groundwater Composition," in *Corrosion 2003*, Paper No. 03693, NACE International, Houston, TX.
- Pusch, R., T. Eriksen, A. Jacobsson, 1982, "Ion/water migration phenomena in dense bentonite." *Scientific Basis for Nuclear Waste Management*, W. Lutze (Ed.), 1982, 649-658.
- Reheis, M.C., 2003, *Dust Deposition in Nevada, California, and Utah, 1984-2002*. U.S. Geol. Survey Open-File Report 03-138. <http://pubs.usgs.gov/of/2003/ofr-03-138/>
- Reheis, M., J. Brune, J. Yount, and J. Budahn, 1999, "Eolian dust from natural traps on Yucca Mountain," in Taylor, E.M., Ed., *Quaternary Geology of the Yucca Mountain Area, Southern Nevada, Field Trip Guide: Pacific Cell, Friends of the Pleistocene*, p. 190-193.
- Reheis, M.C., J.R. Budahn, and P.J. Lamonthe, 2002, "Geochemical evidence for diversity of dust sources in the southwestern United States." *Geochim. et Cosmochim. Acta* V.66(9), 1569-1587.
- Reheis, M.C., and R. Kihl, 1995, "Dust deposition in southern Nevada and California, 1984-1989: Relations to climate, source area, and source lithology." *J. Geophys. Research* V.100(D5), 8893-8918.
- Rosenberg, N.D., G.E. Gdowski, and K.G. Knauss, 2001, "Evaporative chemical evolution of natural waters at Yucca Mountain, Nevada." *Applied Geochem.*, V.16, 1231-1240.
- Shettle, D.L., 2003, *Near-Field Environments and Corrosion*, Presented at the March 26, 2003 meeting of the Advisory Committee on Nuclear Waste, US Nuclear Regulatory Commission, Washington, D.C.
- Shoesmith, D.W. and M. Kolar, 1998, "Waste package performance." In *Alternative Approaches to Assessing the Performance and Suitability of Yucca Mountain for Spent Fuel Disposal.*, EPRI Report No. 108732, Electric Power Research Institute, Palo Alto, CA.
- Shoesmith, D.W. and J.R. Massari, 2001, "Predicted performance of the engineered barrier system in the Yucca Mountain repository." *Proc. 9th International High-level Radioactive Waste Management Conference*, American Nuclear Society, LaGrange Park, IL, May 2001.

- Shoesmith, D.W., M. Kolar, F. King, 2003, "A mixed-potential model to predict fuel (uranium dioxide) corrosion within a failed nuclear waste container." *Corrosion* V.59, 802-816.
- Shreir, L.L., 1976, *Corrosion*. 2nd edition, Newnes-Butterworths, London.
- Smailos, E., W. Schwarzkopf and R. Koster, 1986, *Corrosion Behavior of Container Materials for Disposal of High-Level Wastes in Rock Salt Formations*, Nuclear Science and Engineering, Report EUR 10400EN, Commission of European Communities (OECD), Luxembourg.
- Smailos, E., and R. Koster, 1987, "Corrosion Studies on Selected Packaging Materials for Disposal of High Level Wastes," in *Materials Reliability in the Back End of the Nuclear Fuel Cycle*, IAEA TECDOC 421. International Atomic Energy Agency (IAEA), Vienna, Austria, 7-24.
- Sonnenthal, E., N. Spycher, A. and Simmons, 1998, *Thermo-Hydro-Chemical Predictive Analysis for the Drift-Scale Heat Test*. Report. SPY289M4. V. 1. Lawrence Berkeley National Laboratory, Berkeley, CA.
- Sonnenthal, E., Spycher, N., and Xu, Tianfu, 2003, Linking reaction, transport, and hydrological parameters in unsaturated fractured rock: TOUGHREACT implementation and application." *Proceedings TOUGH Symposium 2003*, Lawrence Berkeley National Laboratory, Berkeley CA, May 12-14, 2003, 1-5.
- Staeble, R., 2003, *Continuing Investigations of Local Environments on Waste Container Surfaces*, Presented at the January 28, 2003 Nuclear Waste Technical Review Board Meeting.
- Szklarska-Smialowska, Z., 1986, *Pitting Corrosion of Metals*, NACE International, Houston, Texas.
- Wexler, A.S. and J.H. Seinfeld, 1991, "Second-generation inorganic aerosol model." *Atmos. Environ.*, V. 25A, 2731-2748.
- White, A. F., and Peterson, M. L., 1990, "Role of Reactive-Surface-Area Characterization in Geochemical Kinetic Models,". Chapt. 35 in *Chemical Modeling of Aqueous Systems II.*, Eds. D.C. Melchior and R.L. Bassett. ACS Ser. 416, Am. Chem. Soc., Washington, DC., 461-475.
- Wolery, T.J., 1992, *EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, User's Guide, and Related Documentation (version 7.0)*. UCRL-MA-110662 PT III, Lawrence Livermore National Laboratory, Livermore, CA.
- Wood, B.J. and D.G. Fraser, 1976, *Elementary Thermodynamics for Geologists*. Oxford Univ. Press, Oxford, U.K., 303p.
- Yang, I.C., Z. E. Peterman, and K.M. Scofield, 2002, "Chemical composition of pore water from boreholes USW SD-6 and USW WT-24 Yucca Mountain Nevada," Abstract 137-2 BTH 171, *Geol. Soc. Am. Abstracts with Programs*, p. 508.

Yang, I.C., Z.E. Peterman, and K.M. Scofield, 2003, "Chemical analyses of pore water from boreholes USW SD-6 and USW WT-24, Yucca Mountain, Nevada." *J. Contaminant Hydrol.* v.62-63, 361-380.

A

Appendix

Table A . 1
Weight percent minerals in wind-blown dust excluding organic matter
(see text—Chapter 4.2).

Sample Trap	T2-89	T3-87	T4-86	T6-89	T15-89	Average	Std Dev
Quartz	22.49	24.39	25.85	25.62	33.32	26.33	3.69
Rutile	0.25	0.41	0.28	0.61	0.34	0.38	0.13
Montmorillonite	7.78	11.45	9.76	3.12	1.04	6.63	3.95
Goethite	1.41	1.34	0.63	1.57	1.96	1.38	0.43
Biotite	4.85	6.42	3.75	5.81	5.94	5.35	0.95
Illite-muscovite	0.00	6.40	0.00	8.66	19.53	6.92	7.18
Illite	8.88	0.00	0.00	1.30	0.00	2.04	3.46
Albite	16.10	11.05	1.21	0.00	0.13	5.70	6.64
Sanidine	10.04	9.62	18.31	9.15	5.14	10.45	4.30
Oligoclase	0.00	4.03	19.49	21.20	16.02	12.15	8.54
Gypsum	0.12	1.97	3.16	0.07	0.00	1.06	1.28
Kaolinite	5.40	4.53	2.51	5.52	2.81	4.15	1.27
Calcite	11.20	12.68	1.34	8.02	0.00	6.65	5.13
Dolomite	0.00	0.00	0.00	2.78	2.99	1.15	1.41
Soluble Salts	11.47	5.71	13.69	6.58	10.70	9.63	3.02
	99.99	100.00	99.98	100.01	99.92	99.98	

About EPRI

EPRI creates science and technology solutions for the global energy and energy services industry. U.S. electric utilities established the Electric Power Research Institute in 1973 as a nonprofit research consortium for the benefit of utility members, their customers, and society. Now known simply as EPRI, the company provides a wide range of innovative products and services to more than 1000 energy-related organizations in 40 countries. EPRI's multidisciplinary team of scientists and engineers draws on a worldwide network of technical and business expertise to help solve today's toughest energy and environmental problems.

EPRI. Electrify the World

Export Control Restrictions

Access to and use of EPRI Intellectual Property is granted with the specific understanding and requirement that responsibility for ensuring full compliance with all applicable U.S. and foreign export laws and regulations is being undertaken by you and your company. This includes an obligation to ensure that any individual receiving access hereunder who is not a U.S. citizen or permanent U.S. resident is permitted access under applicable U.S. and foreign export laws and regulations. In the event you are uncertain whether you or your company may lawfully obtain access to this EPRI Intellectual Property, you acknowledge that it is your obligation to consult with your company's legal counsel to determine whether this access is lawful. Although EPRI may make available on a case by case basis an informal assessment of the applicable U.S. export classification for specific EPRI Intellectual Property, you and your company acknowledge that this assessment is solely for informational purposes and not for reliance purposes. You and your company acknowledge that it is still the obligation of you and your company to make your own assessment of the applicable U.S. export classification and ensure compliance accordingly. You and your company understand and acknowledge your obligations to make a prompt report to EPRI and the appropriate authorities regarding any access to or use of EPRI Intellectual Property hereunder that may be in violation of applicable U.S. or foreign export laws or regulations.

© 2004 Electric Power Research Institute (EPRI), Inc. All rights reserved. Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. ELECTRIFY THE WORLD is a service mark of the Electric Power Research Institute, Inc.

1010941