W0070

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ANALYSIS/MODEL COVER SHEET
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Describe use:	

4. Title:
Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier

5. Document Identifier (including Rev. No. and Change No., if applicable):
ANL-EBS-MD-000001 REV 00

6. Total Attachments:

7. Attachment Numbers - No. of Pages in Each:

	Printed Name	Signature	Date
8. Originator	Gregory E. Gdowski	[signature]	3/20/00
9. Checker	Nina D. Rosenberg	[signature]	3/20/00
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12. Remarks:

AP-3.10Q.3 Rev. 02/2000

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12. Remarks:

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OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
ANALYSIS/MODEL REVISION RECORD

Complete Only Applicable Items

2. Analysis or Model Title:

Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier

3. Document Identifier (including Rev. No. and Change No., if applicable):

ANL-EBS-MD-000001 REV 00

4. Revision/Change No.	5. Description of Revision/Change
00	Initial issue

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ABBREVIATIONS AND ACRONYMS

a_0, a_1, a_3, a_4	experimentally determined constants for calculation of Henry's Law constant
AMR	Analysis/Model Report
ASTM	American Society for Testing and Materials
BSW	basic saturated water
C	concentration (mg/L)
CRWMS	Civilian Radioactive Waste Management System
DOE	Department of Energy
DS	drip shield
DTN	Data Tracking Number
DW	drift wall
$D_{O2}(ppm)$	solubility of oxygen in parts per million (ppm) by weight
Eh	electrochemical potential
EBS	Engineered Barrier System
EC	electronic charge
EDA	Enhanced Design Alternative
Eq	equivalents
g	acceleration of gravity (9.81 m/s^2) (Weast and Astle 1981, p. F-144)
γ	surface tension of water-air (J/m^2)
k	Henry's Law constant
K_W	ionization constant for water
KTI	Key Technical Issue
IRSR	Issue Resolution Status Report
LADS	License Application Design Selection
m	molality (moles of solute /1000 g of solvent)
m_{soln}	molality of solutions
M&O	Management and Operating Contractor
MGR	Monitored Geologic Repository
MIC	microbial influenced corrosion
MW	molecular weight
MW_{H2O}	molecular weight of water (18.0153 g/mol) (Weast and Astle 1981, p. B-105)
MW_{O2}	molecular weight of O_2 (31.9988 g/mol) (Weast and Astle 1981, p. B-126)
M_{solute}	molarity (moles of the solute/liter of solution)

ABBREVIATIONS AND ACRONYMS (Continued)

N	normal
NRC	Nuclear Regulatory Commission
P_{total}	total pressure of the air
P^0	vapor pressure of pure substance
P	pressure
$P(0)$	pressure at sea level (101.32 kPa)
pH	negative logarithm of the hydrogen ion molar concentration
PMR	Process Model Report
ppm	parts per million (mass)
R	gas law constant (8.3143 J/mol-K) (Weast and Astle 1981, p. F-96)
R_m	gas law constant (R) divided by the molecular weight of the gas
RH	relative humidity (P_{H2O}/P^0_{H2O})
ρ_{sol}	density of the solution in g/L
ρ_{H2O}	density of water in g/L
QA	Quality Assurance
SAW	simulated acidic water
SCC	stress corrosion cracking
SCW	simulated concentrated water
SDW	simulated dilute water
SNF	spent nuclear fuel
SSW	simulated saturated water
T	temperature
TBD	to be determined
TBV	to be verified
THC	thermal-hydrologic-chemical
TSw	Topopah Springs welded
x_{CO2}	air fraction of carbon dioxide
x_{O2}	air fraction of oxygen
x_{RH}	fractional RH
VP_{H2O}	water vapor pressure
WP	waste package
WPOB	waste package outer barrier
z	elevation above sea level

1. PURPOSE

1.1 PURPOSE AND SCOPE

The purpose of this Analysis/Model Report (AMR) is to specify environments on the surfaces of the Drip Shield (DS) and Waste Package Outer Barrier (WPOB) that are consistent with the relevant environmental conditions of the potential repository at Yucca Mountain, Nevada. Aqueous solution compositions are specified for the purposes of corrosion testing of the Engineered Barrier System (EBS) component candidate materials. Solution compositions include those that would occur under bounding conditions, i.e. low relative humidities (*RH*), and under conditions where less concentrated solutions would occur, i.e. high *RH*. The critical (i.e. minimum) *RH* for corrosion processes to occur is specified based on current understanding of the site geochemistry. The aqueous solution compositions were specified based on the known characteristics of Yucca Mountain waters, laboratory test data, and relevant literature and handbook data.

This AMR was written as per the Work Direction and Planning Document *Environment on the Surface of the Drip Shield and the Waste Package Outer Barrier* (CRWMS M&O 1999a). The information contained in this AMR will feed the AMRs ANL-EBS-MD-000003 *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* (CRWMS M&O 2000a) and ANL-EBS-MD-000004 *General Corrosion and Localized Corrosion of Drip Shield.* It also is a basis for the Waste Package (WP) Process Model Report (PMR).

This AMR takes into consideration the Enhanced Design Alternative II (EDA II), which has been selected as the preferred design for the EBS by the License Application Design Selection (LADS) program team (CRWMS M&O 1999b). The salient features of the EDA II design for this analysis are: a waste package (WP) consisting of an outer barrier of Alloy 22 and an inner barrier of Type 316L stainless steel, ventilation at 3 to 10 m^3/s for 50 years and potentially 300 years, a DS of Ti Gr7, and backfill over the drip shield. The backfill may be sand (silica), tuff, or marble ($CaCO_3$).

This AMR addresses Subissue 2 in the U.S. Nuclear Regulatory Commission (NRC) document *Issue Resolution Status Report; Key Technical Issue: Evolution of the Near-Field Environment* (NRC 1999a). Subissue 2 in this document is entitled "Effects of Coupled Thermal-Hydrologic-Chemical Processes on the Waste Package Chemical Environment." It also addresses Subissue 1 in the US-NRC document *Issue Resolution Status Report; Key Technical Issue: Container Life and Source Term* (NRC 1999b). Subissue 1 in this document is entitled "The Effects of Corrosion Processes on the Lifetime of the Containers."

This AMR is part of an effort to define the environment as required by the "Problem Definition" section of the American Society for Testing and Materials (ASTM) Standard (ASTM 1999a) that is concerned with the prediction of the long-term behavior of materials used in EBS for geological disposal of high-level radioactive waste.

1.2 ANALYSIS/MODEL DESCRIPTION AND LIMITATIONS

The characteristics of the environment on the DS and WPOB are discussed in terms of: the compositions of Yucca Mountain waters; the temperature (*T*) of the EBS components; the effective *RH* at the EBS components; the gas phase composition (in terms of CO_2 partial pressure); and dust and aerosol deposition of hygroscopic salts. Water vapor is not included in the gas phase composition but is considered separately as *RH*. Future revisions of this AMR will provide experimental and documented information on the types of mineral/salt scale that could form on the EBS components.

At the present time, representative and bounding "aggressive" aqueous solution chemistries that result from evaporative/boiling concentration of Yucca Mountain waters have been postulated based on experimental and theoretical considerations, and the known characteristics of Yucca Mountain waters. "Aggressive" aqueous solutions are defined as those with elevated boiling points and high ionic strengths. These aqueous solutions are employed in corrosion testing of candidate EBS component materials.

For the purposes of this analysis, it is assumed that water, which contacts the EBS components, is in equilibrium with the *T* of the component and the effective *RH* at the component. This is a conservative assumption in that if the evaporation rate is less than the water flux to the surface, more dilute water would exist. With regards to the water chemistries that develop, the primary controlling factor is the precipitation of minerals with limited solubility and hence is assumed to occur quite readily during the evaporative concentration of these waters.

The water chemistry is discussed in terms of ionic content, the deliquescence point of the salts formed because of complete water evaporation, the aqueous solution *pH* including a qualitative discussion of the dependence on CO_2 partial pressure, and the boiling points of saturated aqueous salt solutions. The deliquescence point of a salt is the minimum *RH* at which the salt will absorb water from the atmosphere and form an aqueous solution.

Water film formation on the DS and WPOB is necessary for electrochemical corrosion of EBS components to occur. In the absence of deposits of hygroscopic salts, aqueous films will form on the surfaces of the EBS components with film thickness increasing with increasing *RH*. The presence of gaseous species, such as CO_2 and SO_2, which can be sorbed by these films, may alter the corrosiveness of these films.

Aqueous solutions on the EBS components will also result from water absorption by hygroscopic salts deposited on the EBS components or by evaporative concentration of water that contact the EBS components. Hygroscopic salts may be deposited on the EBS components by the dust and aerosols entrained in the ventilation air and/or by waters which completely evaporate upon contact with the EBS components. The hygroscopic salts will form aqueous solutions when the *RH* reaches the deliquescence point of salts.

Waters that contact the DS and WPOB will undergo evaporative concentration because of the elevated temperatures of these EBS components relative to the surrounding environment. (The elevated temperatures are due to the heat that is generated within the WPs by the radioactive decay of its contents.) At elevated temperatures where the EBS materials are more susceptible to

degradation by corrosion, it is expected that concentrated salt solutions (brines) will form on the EBS components because of the low effective *RH*.

The formation of brines in natural systems is limited to certain types that are dependent on the chemistry of the dilute source water. Depending on the relative ratios of the cations and anions in the source water, various mineral phases will precipitate out of the solutions and hence change the ionic composition of the waters. The brines have different characteristics, such as deliquescence points of their salts, boiling points of saturated solutions, and solution pHs. These characteristics determine their aggressiveness to the EBS components.

Types of brines that might form from Yucca Mountain waters are discussed. This analysis assumes that the composition of seepage water will have similar characteristics of waters that have been sampled at Yucca Mountain. These include pore and perched waters in the unsaturated zone, and ground water from the saturated zone. The brines that form from the salts that are deposited on the EBS components when the *RH* reaches the deliquescence point should evolve similarly to those that evolve from dilute waters.

Laboratory experimental work is presented on the evaporative/boiling concentration of simulated J-13 well water under various conditions. J-13 well water is from the saturated zone and is considered to be the same type of water as the perched waters from the unsaturated zone. The evaporative/boiling concentration testing include water contact with crushed Yucca Mountain rock. The experimental studies show that there is some interaction between the concentrated aqueous solution and this silica base rock, which may be considered a surrogate for one of the potential backfill materials.

A discussion is presented about the aqueous test solutions for corrosion testing of the EBS component candidate materials, including the relevance of these solutions to those expected to contact the EBS components under repository relevant conditions.

The primary limitation of the results presented in this AMR relates to the issue of the composition of the "dilute" water that contacts the EBS components. In order to account for the variation in solution chemistry of waters that will contact the EBS components, examples of the solution chemistries of the two types of water considered characteristic of Yucca Mountain were considered. A more thorough analysis of the range of waters sampled at Yucca Mountain would give the variation in the brine type and solution composition of the waters that may contact the EBS components. The dependence of the analysis that determines the type of brine on the relative ratios of the cations and anions requires precise solution analysis. Future revisions of this AMR will include a larger sampling of Yucca Mountain waters provided that their solution analysis is complete.

Another limitation of the analysis is that the compositional range and quantity of the hygroscopic salts contained in the aerosols and dust that could be entrained in the ventilation air is unknown at the present time. If ventilation air results in significant deposition of hygroscopic salts, then this process needs to be further investigate for its effect on aqueous solutions in contact with the EBS components.

1.3 RELATION TO ASSESSING SYSTEM PERFORMANCE

The information contained in this AMR defines environmental conditions in which the degradation of the DS and WPOB will be assessed. The various degradation modes of the EBS component candidate materials include: general corrosion, localized corrosion, and stress corrosion cracking. This AMR also defines the critical *RH* for corrosion processes to occur. The critical *RH* is the minimum *RH* at which aqueous solutions will form on the EBS components. At *RH* values below the critical *RH* aqueous solutions are not expected to form, and hence, aqueous electrochemical corrosion processes are not expected to occur.

1.4 RELATIONSHIP TO PRINCIPAL FACTORS

The "principal factors" of the "Post-Closure Safety Case" and "other factors" of the "Post-Closure Safety Case" have been identified in *Repository Safety Strategy: Plan to Prepare the Postclosure Safety Case to Support Yucca Mountain Site Recommendation and Licensing Considerations* (CRWMS M&O 2000b). The "performance of the drip shield" and the "performance of the waste package barriers" have been identified as "principal factors" of the repository system concept for Site Recommendation and License Application considerations. The "environments on the drip shield" and the "environments on the waste package" have been identified as "other factors." The importance of understanding the environments on the drip shield and waste package is that they will strongly influence the performance of these EBS components, since their performance is based, in part, on their corrosive degradation in the environments on their surfaces. This AMR addresses the environment on the DS and WPOB.

1.5 RESOLUTION OF COMMENTS IN THE NRC'S ISSUE RESOLUTION STATUS REPORTS

This AMR addresses Subissue 2 in the U.S Nuclear Regulatory Commission (NRC) document *Issue Resolution Status Report; Key Technical Issue: Evolution of the Near-Field Environment* (NRC 1999a) and Subissue 1 in the US-NRC document *Issue Resolution Status Report; Key Technical Issue: Container Life and Source Term* (NRC 1999b).

1.5.1 Subissue 2 in Issue Resolution Status Report Key Technical Issue: Evolution of the Near-Field Environment

Subissue 2 is entitled "Effects of Coupled Thermal-Hydrologic-Chemical Processes on the Waste Package Chemical Environment." This AMR addresses only those issues with the environments on the DS and WPOB surfaces.

The following are the "Data and Model Justification Acceptance Criteria" and the responses based on this AMR:

1) Available data relevant to both temporal and spatial variations in conditions affecting coupled THC effects on WP chemical environment were considered.

   Response: The AMR considered the range of water chemistries sampled at Yucca Mountain in order to specify aqueous solution chemistries of "bounding" and "typical" water. This can be construed as considering the spatial variation across the repository. Temporal variations

are manifested as variations in *T* and *RH*. The characteristics of the water chemistry is considered in terms of *T* and *RH*.

2) DOE's evaluation of coupled THC processes properly considered site characteristics in establishing initial and boundary conditions for conceptual models and simulations of coupled processes that may affect the WP chemical environment.

   Response: This AMR considered the accessible *T* and *RH* range that is based site characteristic of a fixed nominal total pressure at the potential repository. The *T* and *RH* will determine the characteristics of the aqueous solutions in contact with the EBS components. The partial pressures of CO_2 will affect aqueous solution pH. Aqueous test solutions were formulated for which the effect of low partial pressures of CO_2 on pH is simulated. This AMR also considers the range of chemistries of waters sampled at Yucca Mountain.

3) Sufficient data were collected on the characteristics of the natural system and engineered materials, such as the type quantity, and reactivity of material, to establish initial and boundary conditions for conceptual models and simulations of THC coupled processes that affect the WP chemical environment.

   Response: The available data on the characteristics of the natural system were used in the AMR. The need for additional data on the water chemistry of pore waters is noted. For the purposes of this revision of this AMR, the DS and WPOB materials were assumed not to significantly affect the composition of the chemical environment. Companion AMRs discuss the low general corrosion rates of Alloy 22 and Ti Gr7.

4) A nutrient and energy inventory calculation should be used to determine the potential for microbial activity that could impact the WP chemical environment.

   Response: Microbial effects on the chemical environment were not considered in this revision of the AMR. Later AMR revisions will address this issue.

5) Should microbial activity be sufficient to allow microbial influenced corrosion (MIC) of the WP, then the time-history of temperature, humidity, and dripping should be used to constrain the probability for MIC.

   Response: Microbial effects on the chemical environment were not considered in this revision of the AMR. Later AMR revisions will address this issue.

6) Sensitivity and uncertainty analyses (including consideration of alternative conceptual models) were used to determine whether additional new data are needed to better define ranges of input parameters.

   Response: This AMR characterizes the brines that would evolve from dilute waters contacting the surfaces of the EBS components under $RH < 100\%$ conditions. Three types of natural brines were identified. A limited number of dilute waters at Yucca Mountain were characterized in terms of the brines that would evolve by evaporative concentration. Future revisions of this AMR will analyze other dilute water sampled at Yucca Mountain, including

waters from the field studies. This analysis will be done provided that relevant chemical analysis is performed.

7) If the testing program for coupled THC processes on WP chemical environment is not complete at the time of license application, or if sensitivity and uncertainty analyses indicate additional data are needed, DOE has identified specific plans to acquire the necessary information as part of the performance confirmation program.

   Response: The response to this criterion is beyond the scope of this AMR.

The following are the "Data Uncertainty and Verification Acceptance Criteria" and the responses based on this AMR.

1) Reasonable or conservative ranges of parameters or functional relations were used to determine effects of coupled THC processes on the WP chemical environment. Parameter values, assumed ranges, probability distributions, and bounding assumptions are technically defensible and reasonably account for uncertainties.

   Response: In this AMR the "chemical environment" on the DS and WPOB surfaces are considered in terms of 1) the chemical composition of the dilute waters that contact these EBS components, and 2) the accessible temperature of and relative humidity at these EBS components. The aqueous solution chemical composition is assumed to be limited to the compositional range of Yucca Mountain waters. The range of Yucca Mountain waters is assumed to be characterized by two types of water: 1) the perched water in the unsaturated zone and the saturated zone water, and 2) pore water in the unsaturated zone. The maximum *RH* is limited by the atmospheric pressure in the potential repository. The maximum temperature is assumed limited by the 350°C limit requirement for the fuel cladding.

2) Uncertainty in data due to both temporal and spatial variations in conditions affecting coupled THC effects on WP chemical environment were considered.

   Response: This AMR considers the "chemical environment" on the DS and WPOB in terms of temperature, relative humidity, and dilute water chemistry contacting these EBS components. It also specifies the critical relative humidity for humid air and aqueous phase corrosion processes. Bounding and typical solution chemistries are given. The applicability of these solutions to EBS component degradation should be considered in terms of the temporal and spatial conditions (*T*, *RH*, water composition, partial pressure CO_2).

3) DOE's evaluation of coupled THC processes properly considered the uncertainties in the characteristics of the natural system and engineered materials, such as the type, quantity, and reactivity of material, in establishing initial and boundary conditions for conceptual models and simulations of THC coupled processes that affect the WP chemical environment.

   Response: In this AMR the primary uncertainty in the characteristics of the natural system is the composition of the "dilute" waters that will contact the DS and WPOB surfaces. This AMR considers the range of water chemistries to be bound by the dilute waters sampled at Yucca Mountain.

This AMR revision assumes that the DS and WPOB do not effect the chemical environment because of the small rate of general corrosion of the present candidate materials. Future revision will consider changes in the chemical environment due to the reactivity of the candidate materials.

4) The initial conditions, boundary conditions, and computational domain used in sensitivity analyses involving coupled THC effects on WP chemical environment were consistent with available data.

   Response: No sensitivity analyses were performed in this AMR.

5) DOE's performance confirmation program should assess whether the natural system and engineered materials are functioning as intended and anticipated with regard to coupled THC effects on WP chemical environment.

   Response: The response to this criterion is beyond the scope of this AMR.

The following are the "Model Uncertainty Acceptance Criteria" and the responses based on this AMR.

1) Appropriate models, tests, and analyses were used that are sensitive to the THC couplings under consideration for both natural and engineering systems as described in the following examples. The effects of THC coupled processes that may occur in the natural setting or due to interactions with engineered materials or their alteration products include (i) TH effects on gas and water chemistry; (ii) hydrothermally driven geochemical reactions such as zeolitization of volcanic glass, which could affect water chemistry and WP environmental conditions; (iii) dehydration of hydrous phases liberating moisture that may affect the WP environment; (iv) effect of microbial process on the WP environment; and (v) changes in water chemistry that may result from the release of corrosion products from the WP and interactions between cementitious materials and groundwater, which, in turn, may affect the WP chemical environment.

   Response: This AMR addresses items (i) thermal-hydrologic (TH) effects on gas and water chemistry. Concerning item (v), the present revision of this AMR assumes that the corrosion products from the DS and WPOB will not affect the water chemistry. This assumption is based on the general corrosion rates of the candidate materials being very small. Future revision of this AMR will consider this issue in more detail. Concerning item (iv), microbial processes were not considered in this revision of this AMR, but will be in a future revision. Concerning items (ii) and (iii), consideration of these effects is beyond the scope of this AMR.

2) Alternative modeling approaches consistent with available data and current scientific understanding were investigated, and their results and limitations were appropriately considered.

   Response: This AMR has considered the evolution of brines that will develop on the DS and WPOB surfaces both theoretically and experimentally. The theoretical approach applied the principal of "chemical divide" and also considers other characteristics of natural system

brines. The experimental approach follows the evaporative concentration evolution of the brines under laboratory conditions.

3) DOE provided a reasonable description of the mathematical models included in its analyses of couple THC effects on WP chemical environment. The description should include a discussion of alternative modeling approaches not considered in its final analysis and the limitations and uncertainties of the chosen model.

   Response: The principal of the "chemical divide" was applied for analyses of coupled THC effects on the chemical environment on the DS and WPOB surfaces were used in this AMR.

The following are the "Model Verification Acceptance Criteria" and the responses based on this AMR.

1) The mathematical models for WP chemical environment are consistent with conceptual models based on inferences about the near-field environment, field data and natural alteration observed at the site, and expected engineered materials.

   Response: The only mathematical model (chemical divide) employed in this AMR is bsed on natural systems. The chemical environments specified in this AMR are based on field data, natural systems, and experimental studies.

2) DOE appropriately adopted accepted and well-documented procedures to construct and test the numerical models used to simulate the WP chemical environment.

   Response: No numerical models were used to simulate the chemical environment on the DS and WPOB surfaces in this AMR revision.

3) Abstracted models for coupled THC effects on WP chemical environment were based on the same assumptions and approximations shown to be appropriate for closely analogous natural or experimental systems. Abstracted model results were verified through comparison to outputs of detailed process models and empirical observations. Abstracted model results are compared with different mathematical models to judge robustness of results.

   Response: Abstracted models for coupled THC effects on the chemical environment are beyond the scope of this AMR.

The following are the "Integration Acceptance Criteria" and the responses based on this AMR:

1) DOE has considered all the relevant features, events, and processes. The abstracted models adequately incorporated important design features, physical phenomena, and couplings, and used consistent and appropriate assumptions throughout.

   Response: This AMR considers *T*, *RH*, dilute water chemistry, and CO_2 partial pressure on the chemical environment. The interaction with the EBS components was not considered in this revision. Abstracted models are not considered in this AMR.

2) Models reasonably accounted for known temporal and spatial variations in conditions affecting coupled THC effects on WP chemical environment.

   Response: Spatial variations were accounted for by including the range of Yucca Mountain waters. Temporal variations were accounted for by considering aqueous solution chemistry as a function of *T* and *RH*.

3) Not all THC couplings may be determined to be important to performance, and DOE may adopt assumptions to simplify performance assessment analyses. If potentially important couplings are neglected, DOE should provide a technical basis for doing so. The technical basis can include activities such as independent modeling, laboratory or field data, or sensitivity studies.

   Response: This AMR considers the effect of *T*, *RH*, dilute water chemistry and CO_2 partial pressure on the chemical environment. The dilute water chemistry includes the range of solution chemistry characteristic of waters that have been sampled at Yucca Mountain. These are believed to be the important factors determining the "chemical environment."

4) Where simplifications for modeling coupled THC effects on WP chemical environment were used for performance assessment analyses instead of detailed process models, the bases used for modeling assumptions and approximations were documented and justified.

   Response: Performance assessment analyses are beyond the scope of this AMR.

The following are the "Programmatic Acceptance Criteria" and the responses based on this AMR.

1) Data and models were collected, developed, and documented under acceptable QA procedures.

   Response: Data and models in this AMR were collected, developed, and documented under the YMP quality procedures.

2) Deficiency reports concerning data quality on issues related to coupled THC effects on WP chemical environment were closed.

   Response: All deficiency reports concerning data in this AMR are in the process of being closed.

3) If used, expert elicitations were conducted and documented in accordance with the guidance in NUREG-1563 or other acceptable approaches.

   Response: No expert elicitations were conducted in support of this AMR.

1.5.2 Subissue 1 in Issue Resolution Status Report Key Technical Issue: Container Life and Source Term

Subissue 1 is entitled "The Effects of Corrosion Processes on the Lifetime of the Containers." This issue relates to the adequacy of DOE's consideration of the effects of corrosion processes on the lifetime of the DS and WPOB. This AMR addresses concerns with "environmental conditions within the WP emplacement drifts."

The following are the "Acceptance Criteria for Subissue 1" and responses based on this AMR:

1) DOE has identified and considered likely modes of corrosion for container materials, including dry-air oxidation, humid-air corrosion, and aqueous corrosion processes, such as general corrosion, localized corrosion, MIC, SCC, and hydrogen embrittlement, as well as the effect of galvanic coupling.

   Response: This AMR specifies the critical *RH* for humid air corrosion and aqueous corrosion processes. The critical *RH* is the minimum *RH* at which aqueous solutions will form from the hygroscopic salts deposited on the EBS component. The presence of aqueous solutions is necessary for electrochemical corrosion of the EBS components. Based on current understanding of the hygroscopic properties of "representative Yucca Mountain water," the critical relative humidity is modeled by the deliquescence points of a saturated sodium nitrate solution as a function of temperature. The other aspects of this criterion are addressed in other AMRs.

2) DOE has identified the broad range of environmental conditions within the WP emplacement drifts that may promote the corrosion processes listed previously, taking into account the possibility of irregular wet and dry cycles that may enhance the rate of container degradation.

   Response: The intent of this AMR is to specify the environment on the DS and WPOB over the accessible temperature and relative humidity conditions of the potential repository considering the range of waters that may contact these EBS components. Field studies, laboratory studies, and modeling are being used to accomplish this. The range of aqueous solution chemistry of dilute waters at Yucca Mountain is considered as the source of the eventual "brines" that will evolve on the EBS components. The brines can be categorized into general types, which will have specific consequences for corrosive degradation of the EBS components. This type of analysis of the dilute has begun in this AMR and will be expanded in later revisions of the report.

   The hygroscopic properties of the salts that would result from evaporation to dryness of the brines is necessary for specifying the critical *RH* for humid air and aqueous phase corrosion. The composition of the hygroscopic salt will be dependent on dilute from which they evolve.

   Irregular wet and dry cycles possibly due to dripping water will result in variations in the ionic content as well as the composition of the aqueous solutions on the EBS components. This has not been specifically accounted for in the evolution of the concentrated water solutions from the dilute waters. Testing of this effect is planned.

3) DOE has demonstrated that the numerical corrosion models used are adequate representations, taking into consideration associated uncertainties, of the expected long-term behaviors and are not likely to underestimate the actual degradation of the containers as a result of corrosion in the repository environment.

   Response: This AMR specifies the critical *RH* for humid air corrosion and aqueous corrosion processes. Based on current understanding of the hygroscopic properties of "representative Yucca Mountain water," the critical relative humidity is modeled by the deliquescence points of a saturated sodium nitrate solution as a function of temperature. The other aspects of this criterion are addressed in other AMRs.

4) DOE has considered the compatibility of container materials, the range of material conditions, and the variability in container fabrication processes, including welding, in assessing the performance expected in the container's intended waste isolation function.

   Response: This criterion is addressed in other AMRs.

5) DOE has justified the use of data collected in corrosion tests not specifically designed or performed for the YM repository program for the environmental conditions expected to prevail at the YM site.

   Response: This criterion is addressed in other AMRs.

6) DOE has conducted a consistent, sufficient and suitable corrosion testing program at the time of the LA submittal. In addition, DOE has identified specific plans for further testing to reduce any significant area(s) of uncertainty as part of the performance confirmation program.

   Response: This AMR addresses the characterization of the environmental conditions to which the EBS components can potentially be exposed. Ongoing field studies, laboratory testing, and modeling should better define the potential environments on the EBS components and reduce the uncertainty about the environmental uncertainty. Other aspects of this criterion are addressed in other AMRs.

7) DOE has established a defensible program of corrosion monitoring and testing of the engineered subsystems components during the performance confirmation period to assure they are functioning as intended and anticipated.

   Response: This AMR addresses the characterization of the environmental conditions to which the EBS components can potentially be exposed. Ongoing field studies, laboratory testing, and modeling should better define the potential environments on the EBS components and reduce the uncertainty about the environmental uncertainty. Other aspects of this criterion are addressed in other AMRs.

2. QUALITY ASSURANCE

The Quality Assurance (QA) program applies to this analysis. All types of waste packages were classified (per QAP-2-3) as Quality Level-1 in *Classification of the MGR Uncanistered Spent*

Nuclear Fuel Disposal Container System (CRWMS M&O 1999c). This analysis applies to all of the waste package designs included in *the Monitored Geologic Repository (MGR) Classification Analyses*. The reference (CRWMS M&O 1999c) is cited as an example. The development of this analysis is conducted under activity evaluation *Waste Package Testing and Data Generation* (CRWMS M&O 1999d), which was prepared per QAP-2-0. The results of that evaluation were that the activity is subject to the *Quality Assurance Requirements and Description* (DOE 1998) requirements. This report was prepared in accordance with AP-3.10Q, *Analyses and Models*.

This document may be affected by technical product input information that requires confirmation. Any changes to the document that may occur as a result of completing the confirmation activities will be reflected in subsequent revisions. The status of the input information quality may be confirmed by review of the Document Input Reference System database.

3. COMPUTER SOFTWARE AND MODEL USAGE

3.1 SOFTWARE APPROVED FOR QA WORK

Software used to perform calculations for this AMR was Microsoft Excel Version 8.0 (Microsoft Office 98) loaded on a PowerMac G-3 with Mac OS 8.5.1. Calculations were performed only using spreadsheet software package built-in functions. No macros were used with this software. The equations for which the calculations were performed are included in the text of the report. The results of the spreadsheet calculations were checked by hand calculation with a calculator.

3.2 SOFTWARE ROUTINES

None used.

4. INPUTS

4.1 DATA AND PARAMETERS

4.1.1 Elevation of Proposed Repository Above Sea Level

The elevation of the proposed repository is nominally 1100 m above sea level (CRWMS M&O 1998).

4.1.2 Components of Atmospheric Air Exclusive of Water and the Effective Molecular Weight

The components of atmospheric air exclusive of water vapor are given in Table 1. The molecular weight of each component is also given. The effective molecular weight of atmospheric air exclusive of water is calculated by summing the molecular weights that are normalized by their volume fraction, that is, the normalized molecular weight is its volume fraction times its molecular weight. The effective molecular weight is the sum of the normalized molecular weights.

Table 1. Components of Atmospheric Air Exclusive of Water Vapor (Weast and Astle 1981, pp. B-73 – B-166, C-371, F-172)

Constituent	Content (%) by Volume	Content (ppm) by Volume	Molecular Weight (g/mol)	Normalized Molecular Weight by Volume (g/mol)
N_2	78.084±0.004		28.0134	21.8740
O_2	20.946±0.002		31.9988	6.7025
CO_2	0.033±0.001		44.01	0.0145
Ar	0.934±0.001		39.948	0.3731
Ne		18.18±0.04	20.183	0.00037
He		5.24±0.004	4.0026	0.00002
Kr		1.14±0.01	83.8	0.00010
Xe		0.087±0.001	131.3	0.00001
H_2		0.5	2.0158	0.00000
CH_4		2	16.04	0.00003
N_2O		0.5±0.1	44.01	0.00055

The effective molecular weight of atmospheric air exclusive of water is calculated to be 28.964 g/mol.

4.1.3 Water Vapor Pressure as a Function of Temperature

The water vapor pressure as a function of temperature is listed in Table 2 (Weast and Astle 1981, pp. D-168, D-169). The vapor pressure was given in Torr. The vapor pressure is also given in kPa by applying the conversion factor 760 Torr = 101.32 kPa.

Table 2. Water Vapor Pressure as a Function of Temperature (Weast and Astle 1981, pp. D-168, D-169)

Temp (°C)	kPa	Torr	Temp (°C)	kPa	Torr
0	0.61	4.58	155	543.38	4075.88
5	0.87	6.54	160	618.05	4636.00
10	1.23	9.21	165	700.73	5256.16
15	1.70	12.79	170	792.02	5940.92
20	2.34	17.54	175	892.43	6694.08
25	3.17	23.76	180	1002.56	7520.20
30	4.24	31.82	185	1123.03	8423.84
35	5.62	42.18	190	1254.95	9413.36
40	7.38	55.32	195	1398.32	10488.76
45	9.58	71.88	200	1554.35	11659.16
50	12.33	92.51	205	1723.66	12929.12
55	15.74	118.04	210	1907.15	14305.48
60	19.91	149.38	215	2105.43	15792.80
65	25.00	187.54	220	2319.11	17395.64
70	31.16	233.7	225	2549.41	19123.12
75	38.54	289.1	230	2796.74	20978.28
80	47.34	355.1	235	3061.99	22967.96
85	57.81	433.6	240	3346.30	25100.52
90	70.09	525.76	245	3650.36	27381.28
95	84.51	633.90	250	3975.19	29817.84
100	101.32	760.00	255	4321.80	32417.80
105	120.79	906.07	260	4691.12	35188.00
110	143.26	1074.56	265	5083.73	38133.00
115	169.04	1267.98	270	5500.76	41261.16
120	198.53	1489.14	275	5943.33	44580.84
125	232.09	1740.93	280	6413.05	48104.20
130	270.12	2026.16	285	6910.83	51838.08
135	312.93	2347.26	290	7438.91	55799.20
140	361.41	2710.92	295	7998.20	59994.40
145	415.51	3116.76	300	8589.91	64432.80
150	476.00	3570.48			

4.1.4 Density of Water as a Function of Temperature

Table 3 lists the density (g/L) of water as a function of temperature.

Table 3. Density of Pure Water as a Function of Temperature (Perry and Chilton 1973, p. 3-71, Table 3-29)

Temp (°C)	Density (kg/L)	Temp (°C)	Density (kg/L)	Temp (°C)	Density (kg/L)	Temp (°C)	Density (kg/L)
0	0.99987	20	0.99823	40	0.99225	80	0.97183
1	0.99993	21	0.99802	41	0.99187	85	0.96865
2	0.99997	22	0.99780	42	0.99147	90	0.96534
3	0.99999	23	0.99757	43	0.99107	95	0.96192
4	1.00000	24	0.99733	44	0.99066	100	0.95838
5	0.99999	25	0.99708	45	0.99025	110	0.9510
6	0.99997	26	0.99682	46	0.98982	120	0.9434
7	0.99993	27	0.99655	47	0.98940	130	0.9352
8	0.99988	28	0.99627	48	0.98896	140	0.9264
9	0.99981	29	0.99598	49	0.98852	150	0.9173
10	0.99973	30	0.99568	50	0.98807	160	0.9075
11	0.99963	31	0.99537	51	0.98762	170	0.8973
12	0.99952	32	0.99506	52	0.98715	180	0.8866
13	0.99940	33	0.99473	53	0.98669	190	0.8750
14	0.99927	34	0.99440	54	0.98621	200	0.8628
15	0.99913	35	0.99406	55	0.98573	210	0.850
16	0.99897	36	0.99371	60	0.98324	220	0.837
17	0.99880	37	0.99336	65	0.98059	230	0.823
18	0.99862	38	0.99300	70	0.97781	240	0.809
19	0.99843	39	0.99263	75	0.97489	250	0.794

4.1.5 Surface Tension of Pure Water as a Function of Temperature

Table 4 lists the surface tension of pure water in contact with air. The reference gives the values in terms of dynes/cm. This was converted to J/m^2, by applying the conversion factor 1 J/m^2 = 1000 dynes/cm.

Table 4. Surface Tension of Pure Water as a Function of Temperature (Weast and Astle 1981, p. F-36)

Temperature (°C)	Surface Tension (dynes/cm)	Surface Tension (J/m^2)
20	72.75	0.07275
25	71.97	0.07197
30	71.18	0.07118
40	69.56	0.06956
50	67.91	0.06791
60	66.18	0.06618
70	64.40	0.06440
80	62.60	0.06260
100	58.90	0.05890

4.1.6 Atomic and Molecular Weights of Various Elements and Molecules

Table 5 is a list of the atomic weights of various elements and the molecular weights of various species.

Table 5. The Atomic and Molecular Weights of Selected Elements and Molecules (Weast and Astle 1981, pp. B-73 - B-166)

Element	Atomic Weight (g/mol)	Molecule	Molecular Weight (g/mol)
H	1.0079	$CaCO_3$	100.09
Na	22.98977	$CaCl_2$	110.99
K	39.0983	$Ca(OH)_2$	74.09
Mg	24.305	CaF_2	78.08
Ca	40.08	$CaSO_4$	136.14
C	12.011	$Ca(NO_3)_2$	164.09
Si	28.0855	H_2O	18.0153
N	14.0067	$MgCO_3$	84.32
O	15.9994	$MgCl_2$	95.22
S	32.06	MgF_2	62.31
F	18.998403	$Mg(NO_3)_2 \cdot 2H_2O$	184.35
Cl	35.453	$MgSO_4$	120.37
		K_2CO_3	138.21
		$KHCO_3$	100.12
		KCl	74.56
		KF	58.10
		KNO_3	101.11
		K_2SO_4	174.27
		KOH	56.11
		Na_2CO_3	105.99
		$NaHCO_3$	84.00
		NaCl	58.44
		NaF	41.99
		$NaNO_3$	84.99
		Na_2SO_4	142.04
		NaOH	40.00
		O_2	31.9988

4.1.7 Ionization Constant for Water, K_w

Table 6 lists the ionization constant for water, K_W, as a function of temperature, where:

$K_W = [OH][H]$ and

$[OH]$ and $[H]$ are the molar concentrations of the hydroxyl and hydronium ions.

Table 6. Water Ionization Constant as a Function of Temperature (Weast and Astle 1981, p. D-145)

Temperature (°C)	$-\log_{10}(K_W)$
0	14.9435
5	14.7338
10	14.5346
15	14.3463
20	14.1669
24	14.0000
25	13.9965
30	13.8330
35	13.6801
40	13.5348
45	13.3960
50	13.2617
55	13.1369
60	13.0171

4.1.8 Boiling Points of Saturated Solutions of Some Pure Salts

Table 7 lists the boiling points at sea level of the saturated aqueous solutions of several pure salts. The boiling point is defined as the temperature at which the water vapor pressure is equal to the ambient pressure. At sea level, the ambient pressure is 101.32 kPa (760 Torr).

Table 7. Boiling Points of Aqueous Solutions of Pure Salts (Kracek 1928, pp. 351-373)

Salt	Boiling Point (°C)
K_2SO_4	101.4
Na_2SO_4	102.84
KCl	108.6
NaCl	108.67
KNO_3	115.5
$NaNO_3$	120.59
$Ca(NO_3)_2$	151
$CaCl_2$	164.27*

* from interpolation of given data (see text)

The value for the boiling point of $CaCl_2$ was calculated by interpolation of the handbook data. Data given for water vapor pressures of saturated $CaCl_2$ solutions at 160 and 170°C are 719 and 815 Torr, respectively. The boiling point for 760 Torr was calculated from the following equation:

$$\text{Boiling Point}(760\,Torr) = \frac{(170-160)}{(815-719)} \times (760-719) + 160$$

4.1.9 Equilibrium *RH* of Selected Saturated Salt Solutions from 0 to 100°C

Table 8 lists the equilibrium relative humidities of selected saturated salt solutions. These equilibrium relative humidities are also called the deliquescence points. The deliquescence points may also be described as the minimum relative humidities at which these salts will absorb water from the atmosphere and form aqueous solutions. The data in Table 8 was taken from a literature article in *Journal of Research of the National Bureau of Standards – A. Physics and Chemistry* (Greenspan 1977). A subset of the data is part of the ASTM Standard "Maintaining Constant Relative Humidity by Means of Aqueous Solutions" (ASTM 1999b). Included in the ASTM Standard are the data for magnesium chloride, potassium carbonate, magnesium nitrate, sodium chloride, potassium chloride, potassium nitrate, and potassium sulfate.

4.1.10 Solubilities of Ca, Mg, Na, and K Salts in Water

Table 9 is a list of solubilities of the salts of calcium, magnesium, sodium, and potassium (Weast and Astle 1981, pp. B-73 - B-166).

Table 8. Equilibrium *RH* of Saturated Aqueous Solutions of Various Pure Salts (Greenspan 1977, Table 2)

Temp (°C)	KF	$MgCl_2$	K_2CO_3	$MgNO_3$	$NaNO_3$	NaCl	KCl	KNO_3	NaOH	KOH	K_2SO_4
0		33.66	43.13	60.35		75.51	88.61	96.33			98.77
5		33.60	43.13	58.86	78.57	75.65	87.67	96.27		14.34	98.48
10		33.47	43.14	57.36	77.53	75.67	86.77	95.96		12.34	98.18
15		33.30	43.15	55.87	76.46	75.61	85.92	95.41	9.57	10.68	97.89
20		33.07	43.16	54.38	75.36	75.47	85.11	94.62	8.91	9.32	97.59
25	30.85	32.78	43.16	52.89	74.25	75.29	84.34	93.58	8.24	8.23	97.30
30	27.27	32.44	43.17	51.40	73.14	75.09	83.62	92.31	7.58	7.38	97.00
35	24.59	32.05		49.91	72.06	74.87	82.95	90.79	6.92	6.73	96.71
40	22.68	31.60		48.42	71.00	74.68	82.32	89.03	6.26	6.26	96.41
45	21.46	31.10		46.93	69.99	74.52	81.74	87.03	5.60	5.94	96.12
50	20.80	30.54		45.44	69.04	74.43	81.20	84.78	4.94	5.72	95.82
55	20.60	29.93			68.15	74.41	80.7		4.27	5.58	
60	20.77	29.26			67.35	74.50	80.25		3.61	5.49	
65	21.18	28.54			66.64	74.71	79.85		2.95	5.41	
70	21.74	27.77			66.04	75.06	79.49		2.29	5.32	
75	22.33	26.94			65.56	75.58	79.17		1.63		
80	22.85	26.05			65.22	76.29	78.90				
85	23.20	25.11			65.03		78.68				
90	23.27	24.12			65.00		78.50				
95		23.07									
100		21.97									

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Table 9. Solubilities of Ca, Mg, Na, and K Salts in Water (Weast and Astle, 1981, pp. B-73 - B-166)

			Low Temperature			High Temperature		
Compound	Formula		Temp (°C)	Solubility (g/100 cm^3)	Solubility (mg/L)	Temp (°C)	Solubility (g/100 cm^3)	Solubility (mg/L)
Calcium sulfate	$CaSO_4$	Natural anhydrite	30	0.2090	2090	100	0.1619	1619
Calcium sulfate dihydrate	$CaSO_4 \cdot 2H_2O$	Natural gypsum		0.241	2410	100	0.222	2220
Calcium nitrate	$Ca(NO_3)_2$		18	121.2	1212000	100	376	3760000
Calcium chloride	$CaCl_2$		20	74.5	745000	100	159	1590000
Calcium fluoride	CaF_2	Natural fluorite	18	0.0016	16	26	0.0017	17
Calcium carbonate	$CaCO_3$	Natural calcite	25	0.0014	14	76	0.0018	18
Calcium hydroxide	$Ca(OH)_2$		0	0.185	1850	100	0.077	770
Calcium metasilicate	$CaSiO_3$	Natural pseudo-wollastonite	17	0.0095	95			
Sodium Sulfate	Na_2SO_4	Natural thenardite	0	4.76	47600	100	42.7	427000
Sodium nitrate	$NaNO_3$	Soda niter	25	92.1	921000	100	180	1800000
Sodium chloride	NaCl	Natural halite	0	35.7	357000	100	39.12	391200
Sodium fluoride	NaF	Natural villiaumite	18	4.22	42200			
Sodium carbonate	Na_2CO_3		0	7.1	71000	100	45.5	455000
Sodium bicarbonate	$NaHCO_3$		0	6.9	69000	60	16.4	164000
Sodium hydroxide	NaOH		0	42.0	420000	100	347	3470000
Sodium metasilicate	Na_2SiO_3			Soluble			Soluble	
Magnesium sulfate	$MgSO_4$		0	26	260000	100	73.8	738000
Magnesium nitrate, hexahydrate	$Mg(NO_3)_2 \cdot 6H_2O$			125	1250000		Very soluble	
Magnesium chloride	$MgCl_2$		20	54.25	542500		72.7	727000
Magnesium fluoride	MgF_2	Natural sellaite	18	0.0076	76		Insoluble	
Magnesium carbonate	$MgCO_3$	Natural magnesite		0.0106	106			
Magnesium carbonate trihydrate	$MgCO_3 \cdot 3H_2O$	Natural nesquehonite	16	0.179	1790		Decomposes	
Magnesium hydroxide	$Mg(OH)_2$	Natural brucite	18	0.0009	9	100	0.004	40
Magnesium metasilicate	$MgSiO_3$			Insoluble			Insoluble	
Potassium sulfate	K_2SO_4	Natural arcanite	25	12	120000	100	24.1	241000
Potassium sulfate, hydrogen	$KHSO_4$	Natural mercallite, misenite	0	36.3	363000	100	121.6	1216000
Potassium nitrate	KNO_3	Saltpeter	0	13.3	133000	100	247	2470000
Potassium chloride	KCl	Natural sylvite	20	23.8	238000	100	56.7	567000
Potassium fluoride	KF		18	92.3	923000		Very soluble	
Potassium carbonate	K_2CO_3		20	112	1120000	100	156	1560000
Potassium carbonate, hydrogen	$KHCO_3$			22.4	224000	60	60	600000
Potassium hydroxide	KOH		15	107		100	178	1780000
Potassium metasilicate	K_2SiO_3			Soluble			Soluble	

4.1.11 Decomposition Temperatures of Some Bicarbonate/Carbonate Species

Table 10 is list of the decomposition temperatures of sodium and potassium bicarbonate species.

Table 10. Decomposition Temperatures of Bicarbonate and Carbonate Species (Weast and Astle 1981, pp. B-87, B-115, B-131, B-147)

Species	Decomposition Temp (°C)	Decomposition Product
K_2CO_3	>891	Not given
$KHCO_3$	100-200	Not given
Na_2CO_3	>851	Not given
$NaHCO_3$	270	CO_2
$MgCO_3$ (magnesite)	350	Not given
$CaCO_3$ (aragonite)	825	Not given
$CaCO_3$ (calcite)	898.6	Not given

4.1.12 Partial Pressure of HCl over Aqueous Solutions of HCl

Tables 11a and 11b list the partial pressure of HCl over aqueous solutions with varying concentrations of HCl up to temperatures of 110°C. The values of vapor pressure are given in

Table 11a. Vapor pressures of HCl and H_2O over aqueous solutions of HCl (Perry and Chilton 1973, p. 3-62, Table 3-10, p. 3-63, Table 3-11)

Temp (°C)	Concentration of HCl (wt.%)						
	2		6				
	HCl		HCl		H_2O		
	mm Hg	kPa	mm Hg	kPa	mm Hg	kPa	RH
0	---	---	6.60E-06	8.80E-07	4.18	0.56	91.1
5	---	---	1.25E-04	1.67E-05	6.04	0.81	92.2
10	1.17E-05	1.56E-06	2.34E-04	3.12E-05	8.45	1.13	91.7
15	2.30E-05	3.07E-06	4.25E-04	5.67E-05	11.7	1.56	91.5
20	4.40E-05	5.87E-06	7.60E-04	1.01E-04	15.9	2.12	90.6
25	8.40E-05	1.12E-05	1.31E-03	1.75E-04	21.8	2.91	91.7
30	1.51E-04	2.01E-05	2.25E-03	3.00E-04	29.1	3.88	91.4
35	2.75E-04	3.67E-05	3.80E-03	5.07E-04	39.4	5.25	93.3
40	4.70E-04	6.27E-05	6.20E-03	8.27E-04	50.6	6.75	91.4
45	8.30E-04	1.11E-04	1.02E-02	1.36E-03	66.2	8.83	92.0
50	1.40E-03	1.87E-04	1.63E-02	2.17E-03	86.0	11.47	92.9
60	3.80E-03	5.07E-04	4.00E-02	5.33E-03	139	18.53	93.0
70	1.00E-02	1.33E-03	9.40E-02	1.25E-02	220	29.33	94.1
80	2.45E-02	3.27E-03	2.06E-01	2.75E-02	333	44.39	93.7
90	5.80E-02	7.73E-03	4.40E-01	5.87E-02	492	65.59	93.5
100	1.32E-01	1.76E-02	9.20E-01	1.23E-01	715	95.32	94.1
110	2.80E-01	3.73E-02	1.78E+00	2.37E-01			

mm Hg as in the original source and in terms of kPa. The conversion factor is 760 mm Hg = 101.32 kPa. The *RH* is also calculated:

$$RH = P/P^0 \qquad \text{(Eq. 1)}$$

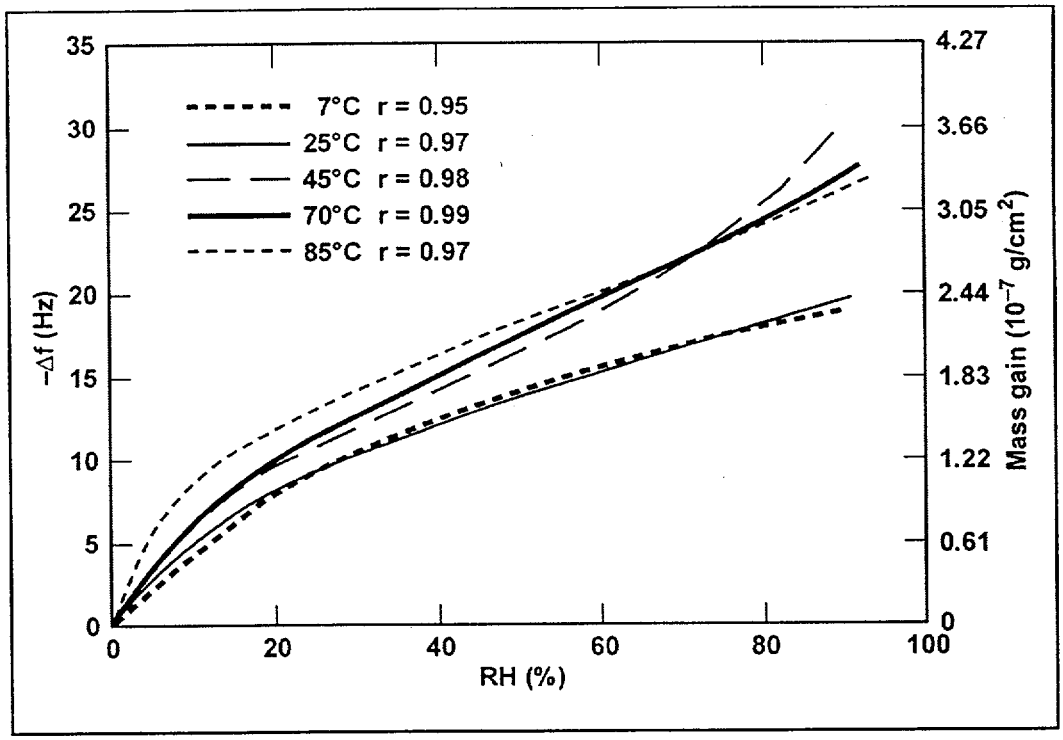
where P is the water partial pressure and P^0 is the saturated water vapor pressure at the same temperature. The saturated water vapor pressure is taken from Table 2.

Table 11b. Vapor pressures of HCl and H_2O over aqueous solutions of HCl (Perry and Chilton 1973, p. 3-62, Table 3-10, p. 3-63, Table 3-11)

Temp (°C)	Concentration of HCl (wt.%)									
	18					26				
	HCl		H_2O			HCl		H_2O		
	mm Hg	kPa	mm Hg	kPa	RH	mm Hg	kPa	mm Hg	kPa	RH
0	0.135	0.02	2.87	0.38	62.5	0.41	0.05	1.76	0.23	38.3
5	0.0225	0.00	4.21	0.56	64.3	0.64	0.09	2.60	0.35	39.7
10	0.037	0.00	5.92	0.79	64.3	0.98	0.13	3.71	0.49	40.3
15	0.060	0.01	8.26	1.10	64.6	1.47	0.20	5.21	0.69	40.7
20	0.095	0.01	11.3	1.51	64.4	2.17	0.29	7.21	0.96	41.1
25	0.148	0.02	15.4	2.05	64.8	3.20	0.43	9.95	1.33	41.9
30	0.228	0.03	20.6	2.75	64.7	4.56	0.61	13.5	1.80	42.4
35	0.345	0.05	27.5	3.67	65.2	6.5	0.87	18.0	2.40	42.6
40	0.515	0.07	36.4	4.85	65.7	9.2	1.23	24.0	3.20	43.3
45	0.77	0.10	47.9	6.39	66.6	12.7	1.69	31.7	4.23	44.1
50	1.11	0.15	62.5	8.33	67.5	17.5	2.33	41.5	5.53	44.8
60	2.3	0.31	102	13.60	68.2	32.5	4.33	69.0	9.20	46.2
70	4.55	0.61	162	21.60	69.3	58.5	7.80	112	14.93	47.9
80	8.6	1.15	248	33.06	69.8	100	13.33	173	23.06	48.7
90	15.7	2.09	374	49.86	71.1	169	22.53	261	34.80	49.6
100	28	3.73	550	73.32	72.4	276	36.80	387	51.59	50.9
110	48	6.40	793	105.72	73.8	436	58.13	555	73.99	51.7

4.1.13 Adsorbed Water Films as a Function of Relative Humidity and Temperature

Figures 1 and 2 show the amount of water adsorbed on nickel as a function of temperature and *RH* (Lee and Staehle 1997). Data was obtained for atmospheres of humidified air and humidified nitrogen. The temperature range was 7 to 85°C. The lowest relative humidity was at least 20% and the highest was at least 90%.



Note: "r" is the regression coefficient for the curve fit to the experimental data

Figure 1. Water adsorption on nickel under humidified N_2 (Lee and Staehle 1997, Figure 5)

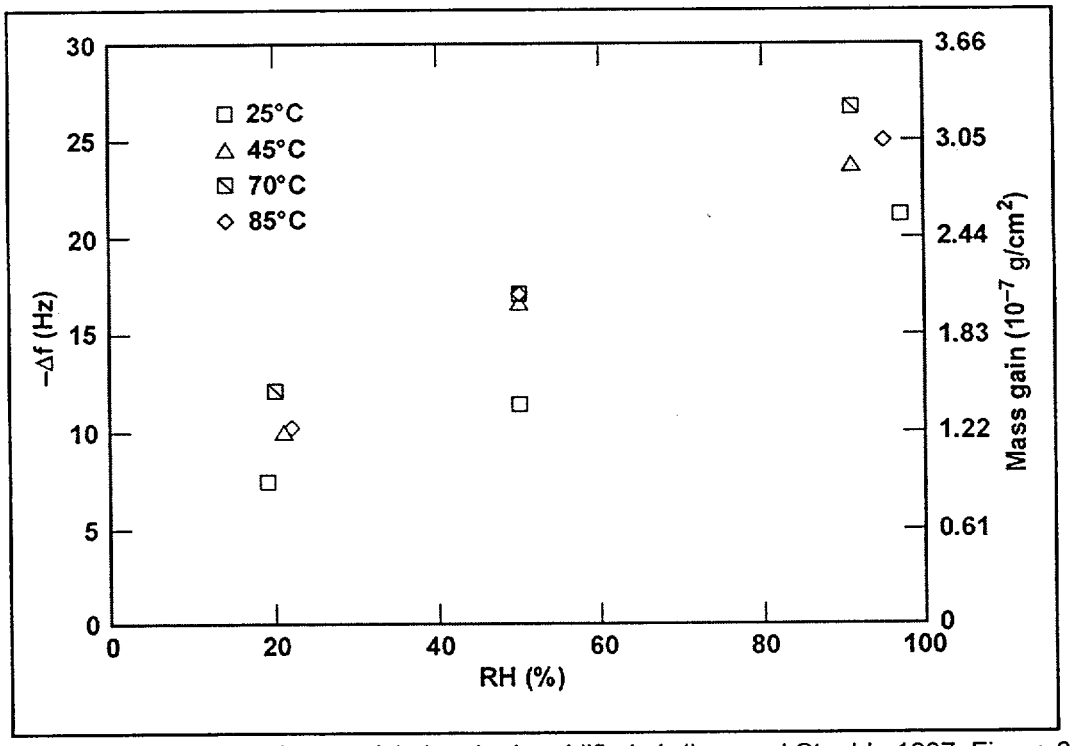


Figure 2. Water adsorption on nickel under humidified air (Lee and Staehle 1997, Figure 8)

4.1.14 Vapor Pressure Lowering of Aqueous NaCl Solutions

Table 12 shows the water vapor pressure lowering of aqueous solutions by NaCl solutions at temperatures from 20 to 100°C (Frazier 1928). The experimental data were reported in terms of two parameters, m and $100R$, where:

m is molality (gram-formula weights (moles) of solute per 1000 g H_2O)

and

$$100R = 100(P^0 - P)/mP^0 \qquad \text{(Eq. 2)}$$

Table 12. Experimental Data on the Vapor Pressure Lowering of Aqueous NaCl Solutions as a Function of Temperature (Frazier 1928)

20-25°C		80°C		100°C	
M	100*R*	M	100*R*	M	100*R*
0.1	3.29	4.0	3.65	2.5	3.47
0.2	3.28	5.0	3.79	3.5	3.57
0.4	3.27	6.0	3.91	4.0	3.62
0.6	3.27			5.0	3.76
0.8	3.28			6.3	3.91
1.0	3.30			6.7	3.89
2.0	3.42				
2.8	3.53				
5.0	3.87				
6.0	3.99				

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From the vapor pressure lowering data of aqueous NaCl solutions (see Table 12), the RH as a function of concentration (both molality and ppm) is calculated:

$$100R = 100(P^0 - P)/mP^0 \qquad \text{(Eq. 3)}$$

where:

P^0 vapor pressure of pure solvent (water) (Table 2)

P partial vapor pressure of the solvent (water) from the solution

Rearranging the above equation in terms of P gives:

$$P = P^0 - m \times P^0 \times (100R/100) \qquad \text{(Eq. 4)}$$

The RH is calculated from: (Eq. 1)

$$RH = P/P^0$$

From the molality data the concentration in terms of ppm (mass) is calculated from the following equation:

$$C(ppm) = 1 \times 10^6 \times \left(m \times MW \Big/ (1000 g_{H2O} + m \times MW) \right) \qquad \text{(Eq. 5)}$$

where:

MW = molecular weight of solute (58.44 g/mole of NaCl) (Table 5), and $1000 g_{H2O}$ is the weight of one liter of water.

In Table 13, the calculated values for solute concentration in ppm, water vapor partial pressure, and *RH* are listed for the data in Table 12.

Table 13. NaCl Molality as a Function of Relative Humidity at Various Temperatures

Temp (°C)	m (molality)	100*R*	Concentration (ppm)	*P* (kPa)	*RH* (%)
20–25[a]	0.1	3.29	5810	3.16	99.7
(P^0=3.17 kPa)	0.2	3.28	11553	3.15	99.4
	0.4	3.27	22842	3.13	98.7
	0.6	3.27	33876	3.11	98.0
	0.8	3.28	44664	3.09	97.4
	1.0	3.30	55213	3.07	96.7
	2.0	3.42	104649	2.95	93.2
	2.8	3.53	140622	2.86	90.1
	5.0	3.87	226126	2.56	80.7
	6.0	3.99	259610	2.41	76.1
80					
(P^0=47.37 kPa)	4.0	3.65	189470	40.45	85.4
	5.0	3.79	226126	38.39	81.1
	6.0	3.91	259610	36.26	76.5
100					
(P^0=101.32 kPa)	2.5	3.47	127476	92.53	91.3
	3.5	3.57	169808	88.66	87.5
	4.0	3.62	189470	86.65	85.5
	5.0	3.76	226126	82.27	81.2
	6.3	3.91	269098	76.36	75.4
	6.7	3.89	281376	74.91	73.9

NOTE: [a] calculation performed for T = 25°C.

4.1.15 Composition of J-13 Well Water

Two types of waters are characteristic of those in volcanic units at Yucca Mountain region (CRWMS M&O 1998). One type is saturated zone water and perched water in the unsaturated zone, and the other type is pore water in the unsaturated zone. The first type of water is dominated by rock/mineral interaction and is sodium-bicarbonate base water. J-13 well water is typical of this type of water and its composition is listed in Table 14. (See section 4.1.16 for discussion of the pore water.)

Table 14. Composition of J-13 Well Water* (Harrar et al. 1990 Table 4.1)

Species	Concentration (mg/L)
Ca^{++}	13.0 ± 0.99
Cl^-	7.14 ± 0.61
F^-	2.18 ± 0.29
HCO_3^- **	128.9 ± 8.6
K+	5.04 ± 0.61
Mg^{++}	2.01 ± 0.21
NO_3^-	8.78 ± 1.03
Na^+	45.8 ± 2.29
SO_4^{--}	18.4 ± 1.03
Si(aq)***	28.5 ± 1.85
pH****	7.41 ± 0.44

DTN: LL980711104242.054

* These values represent the mean concentration values of water collected from this well over the course of about 20 years of sampling. These values represent the mean value of 15-20 analyses, each of which is the mean of replicate sampling in many cases.

** Alkalinity is expressed as mg/L HCO_3^-

*** The conversion from Si to SiO_2 is: 1 mg/L Si is 2.14 mg/L SiO_2.

**** The range reported is 6.8-8.3. This value represents the mean pH values of water collected from this well over the course of about 20 years of sampling.

4.1.16 Composition of Porewaters from Topopah Springs welded unit (TSw)

Two types of waters are characteristic of those in volcanic units at Yucca Mountain region (CRWMS M&O 1998). One type is saturated zone water and perched water in the unsaturated zone, and the other type is pore water in the unsaturated zone. Table 15 lists the concentrations of the major ions in two pore waters that were collected from the Topopah Springs welded (TSw) unit at Yucca Mountain. The data for the pore waters does not list the concentrations for the bicarbonate component. See section 4.1.15 for discussion of the perched and saturated zone waters.

Table 15. Major ion concentrations reported for TSw pore water at ambient temperature.

Ions	ESF-HD PERM-2	ESF-HD PERM-1
	Concentration (mg/L)	Concentration (mg/L)
Na^+	61	62
K^+	7	9
Mg^{++}	16.6	17.4
Ca^{++}	106	97
$SiO_2(aq)$	66	75
HCO_3^-		
SO_4^{--}	111	120
Cl^-	110	123
NO_3^-	3	10
pH	8.32	8.31

DTN: LL990702804244.100

4.1.17 Henry's Law Constants for the Solubility of Oxygen in Several Aqueous Solutions

Table 16 lists parameters for calculating the Henry's Law Constant for oxygen solubility in pure water and three aqueous NaCl solutions. The Henry's Law constant, k, in MPa, was determined experimentally, and the variation with temperature fit to the following equation:

$$\ln k = a_0 + a_1/T + a_2/T^2 + a_3/T^3 + a_4/T^4 \qquad \text{(Eq. 6)}$$

where a_0, a_1, a_3, and a_4 are experimentally determined constants, and T is temperature in Kelvin.

Also included in Table 16 are the characteristics of the fluids for which the k values were determined.

Table 16. Coefficients for Henry's Law Constants for the Oxygen Solubility in the NaCl Solutions and Demineralized Water (Cramer 1980, Tables I & V)

Solution	Molality	Molarity	Coefficients					
	(moles/ 1,000 g)	(moles/ L)	a_0	$a_1(10^4)$	$a_2(10^7)$	$a_3(10^9)$	$a_4(10^{11})$	Std dev (%)
Deminer-alized water	0	0	-35.4408	5.58970	-2.67211	5.80947	-4.91667	5.6
NaCl-1	0.87	0.85	-23.8312	4.05434	-1.89188	4.02544	-3.35511	4.5
NaCl-2	2.97	2.78	-14.7705	2.95905	-1.38197	2.97589	-2.51663	5.3
NaCl-3	5.69	5.09	18.7594	-2.02638	1.38823	-3.75034	3.52602	4.9

DTN: LL000202705924.115

Table 17 lists the Henry's Law constants that were calculated using the coefficients in Table 16.

Table 17. Calculated Henry's Law Constants for Oxygen Solubility in Four Aqueous Solutions

	Henry's Law Constants, k (MPa)			
Temp (°C)	Demineralized Water	NaCl-1	NaCl-2	NaCl-3
0	2427.81	3948.40	9404.30	21073.80
5	2863.54	4464.37	10208.99	21453.07
10	3297.81	4963.39	10938.31	21966.03
15	3722.91	5440.21	11591.48	22565.62
20	4132.95	5891.19	12170.10	23213.24
25	4523.66	6313.95	12677.33	23876.50
30	4892.07	6707.11	13117.18	24528.06
35	5236.23	7069.92	13494.07	25144.91
40	5554.97	7402.14	13812.51	25708.11
45	5847.63	7703.84	14076.89	26202.50
50	6113.91	7975.28	14291.32	26616.56
55	6353.75	8216.84	14459.60	26942.21
60	6567.23	8428.99	14585.22	27174.52
65	6754.52	8612.21	14671.31	27311.44
70	6915.85	8767.04	14720.70	27353.44
75	7051.50	8894.05	14735.98	27303.16
80	7161.78	8993.82	14719.45	27165.00
85	7247.07	9067.00	14673.26	26944.75
90	7307.78	9114.26	14599.38	26649.23
95	7344.41	9136.37	14499.63	26285.95
100	7357.55	9134.14	14375.74	25862.82
105	7347.86	9108.45	14229.36	25387.88
110	7316.12	9060.26	14062.06	24869.08
115	7263.18	8990.61	13875.36	24314.14
120	7190.02	8900.61	13670.75	23730.39
125	7097.72	8791.44	13449.69	23124.66
130	6987.44	8664.34	13213.58	22503.24
135	6860.44	8520.59	12963.84	21871.86
140	6718.03	8361.53	12701.82	21235.62

DTN: LL000202805924.116
NOTE: T(K) = T(°C) + 273.15

4.1.18 Effect of Boiling on the Solubility of Gases

In the process of boiling of aqueous solutions, absorbed gases are stripped from aqueous solutions by steam formation. In other words, the solubility of volatile gases is negligible under boiling conditions. The effect on the *pH* of boiling of bicarbonate/carbonate base solution is discussed later in Section 6.2.6.

4.1.19 Silica Solubility in High pH Aqueous Solutions

It is known that the solubility of silica increases with increasing pH. In particular there is a very large increase in the solubility of amorphous silica in the region of pH 10 (Iler 1979).

4.1.20 Evaporative/Boiling Concentrating of a Simulated J-13 Well Water Near the Boiling Point of the Concentrated Water (DTN: LL000202905924.117)

Table 18 lists the composition of waters that result from the evaporative/boiling concentrating of a simulated concentrated J-13 well water. The initial water that is to be concentrated by evaporation/boiling has an ionic content which is nominally 100 times the ionic content of J-13 well water, except for Ca, Mg, Si, and carbonate. Samples of the solutions were taken after nominally concentrating 1 liter, 2 liters, etc., of solution to approximately 100 to 200 ml. The water was dripped onto heated crushed tuff. Heat was supplied to the system in order to keep the temperature of the water at or near its boiling point. The testing is continuing in order to obtain the compositions and boiling points of aqueous solutions that result from progressively more evaporative concentrating.

Table 18. Compositions for the Evaporative Concentration of Simulated 100x J-13 Well Water.

Species	Starting Solution (mg/L)	Solution Compositions (mg/L) and the Estimated Boiling Point (°C)					
Sample #	Initial J-13 Batch 3	ECBP 042399-0	ECBP 050699-0	ECBP 051899-0	ECBP 060199-0	ECBP 061099-0	ECBP 061499-0
Boiling Point (°C)		101	Not available	Not available	Not available	Not available	108
Ca	6	735	0	0	48	0	62
K	535	3885	7985	15878	21180	24510	21532
Mg	0	0	0	0	0	0	0
Na	4360	43317	106465	177301	202726	226721	190711
Si	13	7461	30875	79388	118912	121020	90741
F	210	2230	4392	4393	0	843	0
Cl	729	7446	16130	32814	38125	49021	49831
NO_3	846	9370	14905	34402	40243	51165	50443
SO_4	1790	19326	38594	53455	41150	48408	32913
HCO_3[a]	4773	28921	53990	79599	98307	97053	91637

DTN: LL000202905924.117
Note: [a] Total inorganic carbon given as bicarbonate.

In Table 18, boiling point measurements were not obtained for all the solutions sampled. Measurements of solution pHs were made after dilution of the sampled solutions by factors of 10 to 1000, and were in the range pH 10.5 to 12. The concentrated solution pHs were not measured.

4.1.21 Evaporative Concentrating of Simulated J-13 Well Water at Temperatures Below the Boiling Point (DTN: LL000202905924.117)

At temperatures below the ambient boiling point of pure water, concentration of aqueous solutions will occur solely by evaporation for $RH < 100\%$. At temperatures above the ambient boiling point of water, concentration of aqueous solutions will occur by evaporation at a given T

when the *RH* is below the maximum accessible *RH* as discussed in Section 6.2.2 (see Figure 3). A series of tests are being performed to characterize the aqueous solutions that will evolve because of evaporation under these conditions. The intent of the testing is to determine the solution compositions and *pHs* that develop at various *RH*s due to evaporation.

The tests are being performed in an environmental chamber where the *T* and *RH* can be controlled. Initially, tests are being performed at *T* above 85°C and *RH* above 50%. The upper temperature is limited to temperatures less than 120°C by the requirement of *RH* above 50% (see Figure 3). The *RH* limit of 50% was chosen because aqueous solutions are not expected to exist at lower *RH* values. If aqueous solutions do exist under these conditions, then testing will be performed at lower *RH* values. The lower temperature limit of 85°C is arbitrary, and testing may be conducted at lower *T* if deemed appropriate later.

Shown in Table 19 are the initial results for the evaporative concentration of a simulated well J-13 water at 85% *RH* and 95°C. Testing is continuing at other *T*s and *RH*s.

Table 19. Results of the Evaporative Concentration of a Simulated J-13 Well Water Under Conditions of Constant Temperature and *RH*

Species	Starting Solution (mg/L)	Final Solution 85%*RH*/90°C (mg/L)
Sample #	Initial J-13 Batch A(1)	J-13-01
Cl	730	14419
NO_3	732	14085
SO_4	1632	29783
F	208	3630
HCO_3[a]	4142	54614
Na	4032	76314
K	513	10832
Ca	5.0	36
Mg	2.0	0

DTN: LL000202905924.117
Note: [a] Total inorganic carbon given as bicarbonate.

4.1.22 Gas Phase Compositions in the Emplacement Drifts

The composition of the gas phase has a controlling influence on the water chemistry of aqueous solutions. Important parameters include the partial pressures of water (H_2O), oxygen (O_2), and carbon dioxide (CO_2). Other gas phase components such as H_2S and SO_2 will also affect the water chemistry if present in significant quantities. The water chemistry can also be affected by the presence of aerosols and dust particles containing soluble salts. Aerosols and dust particles in the atmosphere can contain chlorides, sulfates, and nitrates.

For the purposes of this report, the maximum water vapor pressure is assumed to be limited to that which corresponds to the ambient boiling point of water. No minimum value of the water vapor pressure is explicitly assumed. The composition of the air excluding water vapor is assumed to be that of normal atmospheric air. In the repository, the atmospheric pressure is

fixed, and the water vapor generated in the potential repository will displace the other components of air. Therefore the partial pressures of oxygen and carbon dioxide are a function of temperature and relative humidity. An analysis is included in Section 6 that discusses the implications of very low partial pressures of CO_2 on the *pH* of bicarbonate/carbonate solutions.

Ventilation of the emplacement drifts is a design feature of EDA II, the design that has been selected by the LADS program team (CRWMS M&O 1999b). Ventilation is required for at least 50 years and may be operative for 200 years. The air flow rate will range from 3 to 10 m^3/s. If the air that is used for ventilation is unfiltered, this will result in deposition of dust and aerosols from the environment outside of the underground repository.

The *Yucca Mountain Site Description Document* addresses the issue of wet and dry deposition of species other than water (CRWM M&O 1998). Analysis of rain water collected at Yucca Mountain (CRWM M&O 1998, Table 6.2.10) indicates the presence of Ca, Mg, Na, SiO_2, Al, HCO_3, Cl, NO_3, and SO_4. A "crude estimate" of the amount of Cl deposition due to dry deposition is about 60% (CRWM M&O 1998, Section 6.2.3.2). These results indicate the presence of hygroscopic salts in the air and rain at Yucca Mountain.

An estimate of the amount of the hygroscopic salts deposited in the drifts cannot be made at this time. However, it is assumed that they will be present on the EBS components in sufficient amounts to result in the formation of aqueous films.

4.1.23 Future Work

At the present time, experimental and theoretical work that characterizes the expected water chemistry on the DS and WPOB surfaces are ongoing or planned. The following is a listing of this work. If deemed appropriate in the future this list may be modified.

The following evaporative/boiling concentration testing will determine the composition of and determine or estimate the pH of the concentrated solutions. These analyses will be performed in order to determine if significant differences exist between the characteristics of these concentrated waters and those of concentrated J-13 well water.

- Evaporative concentration of Yucca Mountain field studies (Drift Scale Test and Single Heater Test) waters at constant *T* and *RH*
- Evaporative concentration of Yucca Mountain pore water at constant *T* and *RH*
- Evaporative concentration of Yucca Mountain perched water at constant *T* and *RH*
- Evaporative concentration of Yucca Mountain field studies (Drift Scale Test and Single Heater Test) waters near the boiling point of the concentrated water
- Evaporative concentration of Yucca Mountain pore water near the boiling point of the concentrated water
- Evaporative concentration of Yucca Mountain perched water near the boiling point of the concentrated water

The pH of aqueous solutions is dependent on the partial pressure of CO_2 and this will have implications for the degradation susceptibility of the EBS components.

- Calculation of pH dependence of aqueous solutions on the partial pressure of CO_2 at elevated temperatures

The EDA II design requires ventilation of the drifts for thermal control. This has the potential to introduce hygroscopic salts into the drifts. It is prudent to characterize the salts that may be deposited on the EBS components.

- Analysis of air-borne salts that could be entrained in ventilation air

4.2 CRITERIA

4.2.1 Uncanistered Spent Nuclear Fuel Disposal Container System Description Document

The applicable requirements reproduced below are from Section 1.2, "System Design Criteria" of *Uncanistered Spent Nuclear Fuel Disposal Container System Description Document* (CRWMS M&O 1999e). For the sake of clarity, the original section numbers appear in parentheses after the text.

4.2.1.1 "System Performance Criteria" (Section 1.2.1)

"The disposal container/waste package shall be designed, in conjunction with the Emplacement Drift System and the natural barrier, such that the expected annual dose to the average member of the critical group shall not exceed 25 mrem total effective dose equivalent at any time during the first 10,000 years after permanent closure, as a result of radioactive materials released from the geologic repository." (Section 1.2.1.3).

The analyses contained in this AMR characterize the range of environments possible on the surfaces of the DSs and WPOBs. The environmental conditions will be considered in evaluating the performance of the candidate materials for the DSs and WPOBs to determine if the performance requirements for the WPs and DSs listed above will be met.

4.2.1.2 System Environment Criteria (Section 1.2.3)

"The waste package shall meet all performance requirements during and after exposure to the emplacement drift external environments identified in Table I-7 (TBD-234)..." (Section 1.2.3.1) These data are reproduced in Table 20.

The analyses contained in this AMR characterize the range of environments possible on the surfaces of the DSs and WPOBs in order that testing may be conducted to determine if the performance requirements for the WPs and DSs will be met.

TBD-234 will have no effect on the analyses since a range of temperatures and relative humidities is being considered for the determination of the water chemistry in contact with the DS and WPOB.

Table 20. "Emplacement Drift External Environment (CRWMS M&O 1999e Table I-7)"

Environment	Range	Duration/Frequency of Occurrence
Microbe Influx	$0–10^{14}$ microbes/yr/m of drift	10,000 yr
pH	8.2-10.2	10,000 yr
Colloid Concentration	$8x10^{-6} – 6x10^{-5}$ mg/ml	10,000 yr
Temperature	TBD-234	TBD-234
Humidity	TBD-234	TBD-234
Radiation	TBD-234	TBD-234
TBD-234	TBD-234	TBD-234

4.2.2 NRC Acceptance Criteria in Issue Resolution Status Reports for Key Technical Issues

The applicable NRC acceptance criteria for this AMR are stated two subissues of two IRSRs: 1) Subissue 2 in the U.S Nuclear Regulatory Commission (NRC) document *Issue Resolution Status Report; Key Technical Issue: Evolution of the Near-Field Environment* (NRC 1999a), and 2) Subissue 1 in the US-NRC document *Issue Resolution Status Report; Key Technical Issue: Container Life and Source Term* (NRC 1999b). In Section 1 PURPOSE of this AMR, the criteria are listed and the responses to these criteria based on information in this AMR are given.

4.3 CODES AND STANDARDS

No codes or standards are currently used in this document.

5. ASSUMPTIONS

The following assumptions were used in Section 6 of this report. The assumptions concern the nature of the water contacting the surfaces of the DSs and the WPOBs and the expected DS and WPOB *T* and *RH* histories.

- The waters in the volcanic units of the Yucca Mountain region can be classified into two types. One type is unsaturated zone perched water and saturated zone water and is characterized by water rock/mineral interaction. The other type of water is pore water of the unsaturated zone. This assumption is based on the analysis in the *Yucca Mountain Site Description Document* (CRWMS M&O 1998). This assumption is used in Section 6.6.

- The characteristics (e.g., compositions) of the waters that develop on the DSs' and WPOBs' surfaces can be bounded by the types of concentrated solutions (brines) that would evolve because of evaporative concentration of waters sampled at Yucca Mountain. As discussed in Section 6.5, it is known that the types of brines in natural systems are limited, and their evolution from dilute waters can be explained by the relative ratios of certain ionic solution species. This assumption is based on the analysis of Drever (1997).

  This analysis assumes that the composition range of water that can develop under the potential repository conditions are characteristic of waters that have been sampled at Yucca Mountain.

- The temperatures of the DSs and WPOBs are less than 350°C. This assumption is based on "System Performance Criteria" that states "The waste package shall maintain SNF zircaloy cladding temperature below 350 degrees C (662 degrees F) (TBV-241) under normal conditions, and below 570 degrees C (1,058 degrees F) (TBV-245) for short-term exposure to fire, as specified by Criterion 1.2.2.1.11." This is from Section 1.2.1.6 of the *Uncanistered Spent Nuclear Fuel Disposal Container System Description Document* (CRWMS M&O 1999e). For post closure purposes the 350°C limit is relevant. This assumption is used in Section 6.11.

- The total pressure in the drifts is limited to the ambient nominal atmospheric at the repository horizon. This assumption is based on information contained in the *Yucca Mountain Site Description Document* (CRWMS M&O 1998). It is used in Section 6.2.

- The gas phase composition of the drift air exclusive of water is nominally that of atmospheric air. This assumption is based in information contained in the *Yucca Mountain Site Description Document* (CRWMS M&O 1998). It is used in Section 6.2.

- The ventilation of the emplacement drifts will result in deposition of dust and aerosols on the EBS components. This assumption is based on the description of EDA II the preferred design selected by the LADS program team (CRWMS M&O 1999b). It is assumed that the air used for ventilation is unfiltered. It is used in Section 6.4.2.

- For the present revision of this report it is assumed that the water which contacts the EBS components is in equilibrium with the T of the component and the effective RH at the component. This is a conservative assumption in that if the evaporation rate is less than the water flux to the surface, less concentrated water would exist on the components. With regards to the water chemistries that develop, the major controlling factor is the precipitation of minerals with limited solubility and hence is assumed to occur quite readily during the evaporative concentration of these waters. The latter assumption is used in Section 6.5 and 6.6 and needs experimental verification.

- For the present revision of this report it is assumed that the composition of the water that contacts the DS and WPOB will not change significantly because of chemical interaction with these materials. This is based on the slow general corrosion of the materials, Alloy 22 and TiGr 7, proposed for the WP outer barrier and the DS, respectively. This allows the evolution of water chemistry to be a function of T and RH. This assumption is used in Section 6.7.

- The testing discussed in this report uses crushed tuff as a media on/through which the evaporative concentration of the Yucca Mountain waters, in particular, simulated J-13 well water, is allowed to occur. The presence of the tuff allows for heterogeneous precipitation of minerals from solution rather than homogeneous nucleation and growth as would occur in bulk liquids. It is assumed that this would more closely simulate processes occurring under repository-like conditions where flow would occur along fractures. This assumption is based the characteristics of the fractured rock as discussed in the Yucca Mountain Site Description report (CRWMS M&O 1998). It is used in Section 6.7. The interaction between the crushed tuff and concentrated solutions is also discussed in Section 6.7.

6. ANALYSIS

6.1 INTRODUCTION

The environments on the DS and WPOB are determined by: the compositions of the waters that contact these components and / or salts that have been deposited on them; the temperature (T) of these components; the effective relative humidity (RH) at these components; and the gas phase composition (in particular, the CO_2 partial pressure). There are several plausible scenarios for aqueous solution formation on the EBS components. These include seepage flow into the drifts, episodic water flow, and water sorption by deposited hygroscopic salts. The hygroscopic salts can be deposited from dust or aerosols entrained in drift air or by complete evaporation of seepage water or episodic water contacting the EBS components.

Considering the waters at Yucca Mountain just in terms of the ionic components, the major cations are sodium, potassium, calcium, and magnesium, and the major anions are chloride, nitrate, sulfate, fluoride, and bicarbonate/carbonate. The aqueous salt solutions that are formed from binary combinations of these cations and anions have significantly different characteristics.

The boiling point is an important consideration for aqueous solutions in contact with the EBS components. Salts whose saturated solutions have boiling points at sea level in excess of 115°C include $CaCl_2$, $NaNO_3$, KNO_3, and $Ca(NO_3)_2$. In contrast, saturated solutions of KCl and NaCl have nominal boiling points at sea level of 109°C, and saturated solutions of K_2SO_4 and Na_2SO_4 have nominal boiling points at sea level of less than 103°C (see Section 4.1.8).

The deliquescence point, which defines the minimum RH where a salt will sorb water from the atmosphere and form its most concentrated aqueous salt solutions, is also an important consideration. Those salts with elevated boiling points tend to have lower deliquescence points at temperatures below their boiling points (see Section 4.1.9 and Section 6.4.1).

Waters that form on the DS and WPOB surfaces at elevated temperatures will be concentrated because the effective RH at these components will be below 100% and at times may be significantly below 100% (CRWMS M&O 1999b). The degree of solute concentration increases with decreasing RH (see Section 6.4.3). As an example, NaCl solutions in equilibrium with air at less than 95% RH, the concentration of NaCl will be greater than 1 M. However, at RHs below the deliquescence point for a salt or salt mixture, liquid water formation does not occur.

The solution pH is another important characteristic of the aqueous solution in contact with the EBS components. Concentrated solutions of $NaHCO_3$ and Na_2CO_3 will have elevated pHs when in contact with normal atmospheric CO_2 partial pressures. When the CO_2 partial pressure is significantly less than the normal atmospheric partial pressure, the pH of these solutions will become more elevated (see Section 6.2.6).

Although there are numerous binary combinations of the cations and anions in Yucca Mountain waters, the concentrated aqueous solutions that evolve due to evaporative concentration of natural dilute waters can be classified into a limited number of types. Studies of natural systems show that dilute waters, such as those at Yucca Mountain, will form specific types of saline

solution (brines) based on relative amounts of calcium, magnesium, carbonate alkalinity, and sulfate contained in the dilute waters (see Section 6.5). It is important to emphasize that it is not the initial ionic strength nor the exact composition of these dilute waters that determines the type of brine which would form. Complete evaporation and then re-wetting of the salts would result in similar type brines. Natural brines can be classified into three types: high pH, Na-CO_3-Cl-SO_4 brines, near neutral pH, Na-Mg-SO_4-Cl brines, and near neutral Na-Ca-Mg-Cl brines.

In terms of solution chemistry, the waters at Yucca Mountain are classified into two types: saturated zone and perched waters (see section 4.1.15), and unsaturated zone pore waters (see section 4.1.16). A saturated zone water, J-13 well water, is theoretically shown to evolve by evaporative concentration into a high pH, Na-CO_3-Cl-SO_4 brine (see Section 6.6.3). Experimentally a simulated J-13 well water was determined to evolve into the same type of brine (see section 6.7). Theoretical analysis of unsaturated zone, porewater showed that these waters evolve by evaporative concentration into near neutral pH, Na-Mg-SO_4-Cl brine (see Section 6.6.4). The results for the porewaters are tentative because the bicarbonate concentration has not been determined experimentally. In the brine that results from J-13 well water, it is assumed that nitrate will be present since it is a component of the dilute waters at Yucca Mountain, and the nitrate salts of the major cations in Yucca Mountain waters are very soluble (see Table 9).

In the experimental study of the evaporative/boiling concentration of simulated J-13 well water, it was found that significant amounts of silica were dissolved from the crushed Yucca Mountain rock which was included in the testing. This is due to the very alkaline pHs of the concentrated solutions. This high solubility of silica in high pH waters is known. Silica base materials are being considered as backfill material. This result indicates the potential for buffering of the very alkaline water by the silica depending on the quantity of backfill and alkaline water. Carbonate base backfill would have no buffering effect.

The existence of aqueous salt solutions on the DS and WPOB surfaces as a function of *T* and *RH* will be determined by the deliquescence points of the hygroscopic salts in contact with the surfaces. It is assumed that the deliquescence point dependence of the salt mixtures will be determined by the $NaNO_3$ component of the mixture (see Section 6.4.2). Sodium nitrate ($NaNO_3$) is assumed to be the salt with the lowest deliquescence point present in significant quantities. At a given temperature if the RH is above the deliquescence point of the salt mixture, the solute concentration will become more dilute and the ionic content of the solution may change due to dissolution of salts that may be in contact with the solution.

Water films of limited thickness can exist on surfaces when water vapor is present with the film thickness increasing with increasing relative humidity. However these films will be lacking in the electrolytes that facilitate the electrochemical corrosion reactions.

Absorbed oxygen, a reducible species, which participates in the electrochemical corrosion reactions, is shown to be soluble in aqueous salt solutions at temperatures above the boiling point of pure water provided that gaseous oxygen is present (see Section 6.2).

Under some conditions aqueous solutions may become acidified due to hydrolysis of metal ions. In Section 6.9, factors, which may limit the extent of the acidification of the solutions, are presented. In brief, the vapor pressure of the acid gases (e.g. HCl and HNO_3) may not be

sustainable at the levels required to maintain very low pH solution on the EBS components at high temperatures. This is because the environment, which surrounds the components, is an open system with respect to removal of these minority gas components.

Under some conditions it is possible that conditions could exist where the rate of water evaporation necessary to obtain equilibrium between the aqueous solution and the RH can not be obtained because of the high water flow rate to the surface. Under low RH conditions it is expected that the brine discussed above will still prevail because mineral precipitation occurs early in the evaporative concentration of the aqueous salt solutions (see Section 6.8). Under high RH conditions where the temperature difference between the EBS components and the surrounding environment is not large, the changes in the water chemistry are not expected to be significant. However, under both conditions aqueous solutions would be present at higher temperature than would be possible under equilibrium conditions.

A discussion of the aqueous solutions that are being used in corrosion testing is then presented (see Section 6.12). The relevance of these solutions with regard to the brines that could form is discussed (see Section 6.13).

6.2 REPOSITORY CONDITIONS AFFECTING AQUEOUS SOLUTION PROPERTIES

Atmospheric conditions can affect the composition and ionic strength, the *pH*, and the electrochemical potential (Eh) of aqueous solutions under equilibrium conditions. The ionic composition and strength of aqueous solutions are functions of the *RH* and *T* under equilibrium conditions. The presence of gaseous components, such as CO_2 and SO_2, affects the solution composition. The partial pressure of CO_2 affects the solution *pH*. The partial pressure of oxygen affects the solution Eh. The presence of aerosols or dust entrained in air (e.g., ventilation air) will affect the characteristics of the aqueous solutions because of their hygroscopic salt content.

The following sections discuss the effect of the various parameters on the characteristics of the aqueous solutions under conditions that are relevant to the potential repository.

6.2.1 Atmospheric Pressure at the Potential Repository Elevation

The atmospheric pressure at the potential repository affects the boiling point of aqueous salt solutions and limits the relative humidities of aqueous solutions for temperatures above the boiling point of pure water.

The ambient atmospheric pressure at the elevation of the potential repository is a function of elevation, temperature, and the effective molecular weight of the ambient "air." The atmospheric pressure P can be calculated from barometric equation (Fleagle and Businger 1980):

$$P = P(0)\exp\left(-gz/R_m T\right) \qquad \text{(Eq. 7)}$$

where $P(0)$ is atmospheric pressure at sea level, g is acceleration of gravity (9.81 m/s^2) (Weast and Astle 1981, p. F-144), z is elevation in meters, T is the temperature in K, and R_m is gas law constant (R) divided by the molecular weight (MW) of a gas.

Assuming a temperature of 293 K, the effective molecular weight of air equal to 28.964 g/mol (see Section 4.1.2), and an elevation of 1100 m above sea level, the nominal ambient atmospheric pressure at the potential repository elevation is 89.1 kPa.

6.2.2 Accessible Relative Humidity Conditions

In Section 6.2.1, the nominal atmospheric pressure at the potential repository elevation was calculated to be 89.1 kPa; this corresponds to a boiling point between 96 and 97°C for pure water. In the following discussions, it will be assumed that the boiling point is 96°C for which the corresponding water vapor pressure is 87.67 kPa. Figure 3 shows the relative humidities that are accessible as a function of temperature for the fixed total pressure of 87.67 kPa. For comparison, the maximum *RH* values are also plotted for a fixed total pressure of 101.32 kPa, with the corresponding boiling point of water equal to 100°C. For the fixed total system pressure, the relative humidities decrease with increasing temperatures above the boiling point of water.

The following illustrates how the data is plotted in Figure 3. For T $\leq$ BP, RH = 100%. For T > BP, RH = P / P^0 where P = 101.32 kPa (BP = 100°C) and 87.67 kPa (BP = 96°C), and P^0 is taken from Table 2. For example, at T = 150°C, RH(BP = 100°C) = 101.32 kPa / 475.72 kPa = 21% and RH(BP = 96°C) = 87.67 kPa / 475.72 kPa = 18%.

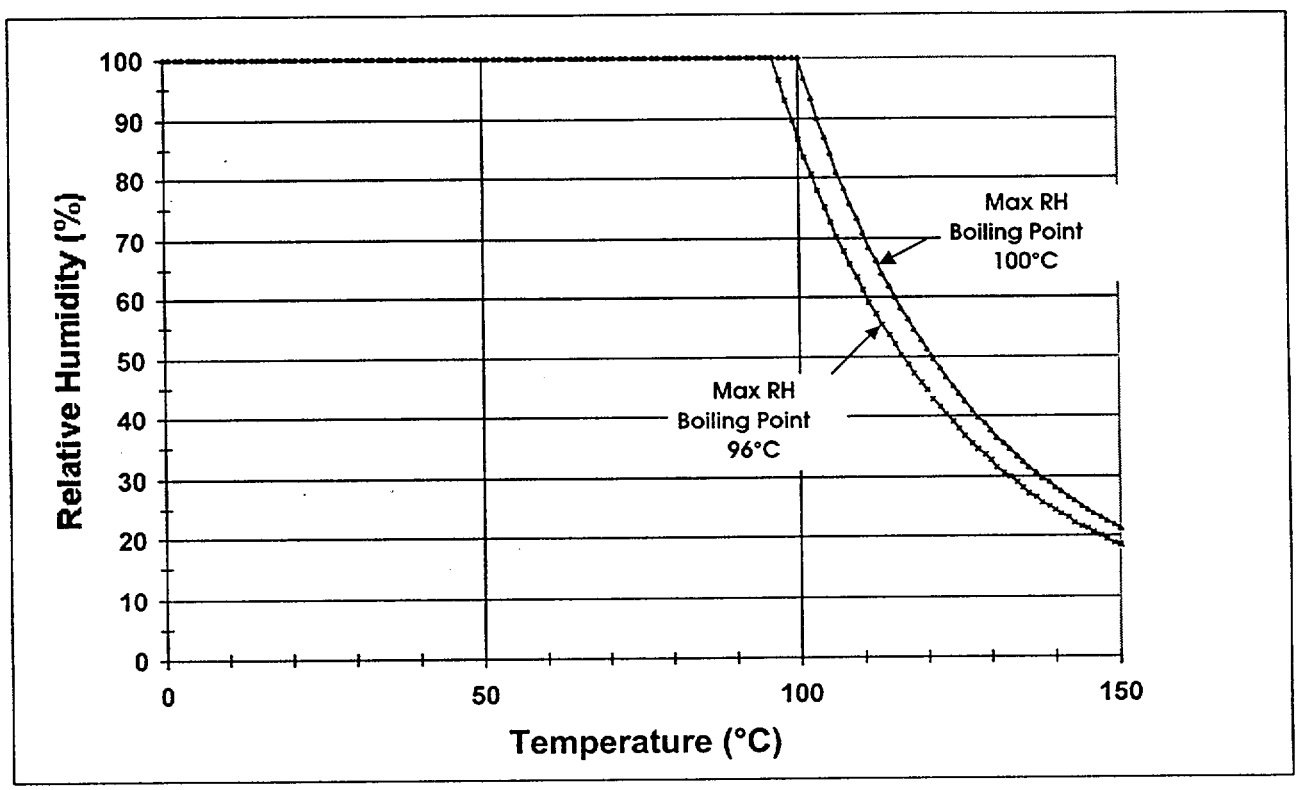

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Figure 3. Maximum RH versus Temperature for Boiling Points of 96°C and 100°C

At the potential repository's elevation the boiling points of aqueous salt solutions are at lower temperatures than those at sea level. The lower atmospheric pressure will decrease the temperature at which aqueous solutions will be present on the EBS component. However, most relevant data on aqueous salt solutions is for sea level atmospheric conditions and coupled with the higher temperatures obtainable for the aqueous solutions at sea level, the discussions in the subsequent sections will assume sea level atmospheric conditions.

6.2.3 Effective RH at the DS and WPOB Surfaces

Because the temperatures of the DSs and the WPOBs are higher than that of the surrounding near-field environment, the RH at the DSs and the WPOBs will be lower than that of the surrounding near-field environment. Note that the WPOB will be at higher temperatures than the DS. The RH difference is a result of the water partial pressure in the drift being constant and no higher than the equilibrium water vapor pressure at the temperature of the drift wall (DW). Hence,

$$P_{H2O}(WP) = P_{H2O}(DW)\text{, but} \qquad \text{(Eq. 8)}$$

$$P^0_{H2O}(WP) > P^0_{H2O}(DW)\text{because } T(WP) > T(DW)\text{, and therefore,} \qquad \text{(Eq. 9)}$$

$$RH(WP) < RH(DW)\text{, with } RH = P_{H2O}/P^0_{H2O}\text{,} \qquad \text{(Eq. 10)}$$

where:

P_{H2O} is the partial pressure of water, and

P^0_{H2O} is the equilibrium vapor pressure of water.

Consequently, some of the water that contacts the DSs or WPOBs will necessarily evaporate in order for the remaining aqueous solutions to equilibrate with the local RH. Hence concentrating of the solutes in the aqueous solutions will occur. The effect of this concentrating is discussed in the following sections.

6.2.4 Gas Phase Composition as a Function of *RH*

The following figures show the variation of oxygen (O_2) and carbon dioxide (CO_2) content of the drift air as a function of temperature and RH. Water (P_{H2O}), carbon dioxide (P_{CO2}), and oxygen (P_{O2}) partial pressure were calculated according to the following:

$$P_{H2O} = x_{RH} \times P^0_{H2O} \qquad \text{(Eq. 11)}$$

$$P_{CO2} = x_{CO2} \times \left(P_{total} - x_{RH} \times P^0_{H2O}\right) \qquad \text{(Eq. 12)}$$

$$P_{O2} = x_{O2} \times \left(P_{total} - x_{RH} \times P^0_{H2O}\right) \qquad \text{(Eq. 13)}$$

where:

x_{CO2} carbon dioxide volume fraction of air

x_{O2} oxygen volume fraction of air

P_{total} total atmospheric pressure

x_{RH} fractional RH

P^0_{H2O} water vapor pressure

Figures 4 and 5 are plots of the calculations for the oxygen and carbon dioxide partial pressures for two scenarios. One case assumes that the partial pressure of water is always equal to its vapor pressure. The other scenario assumes that RH = 90% for $T \leq$ 100°C, and $P_{H2O} = 0.90 \times P_{total}$ for T > 100°C. x_{CO2} and x_{O2} are taken from Table 1.

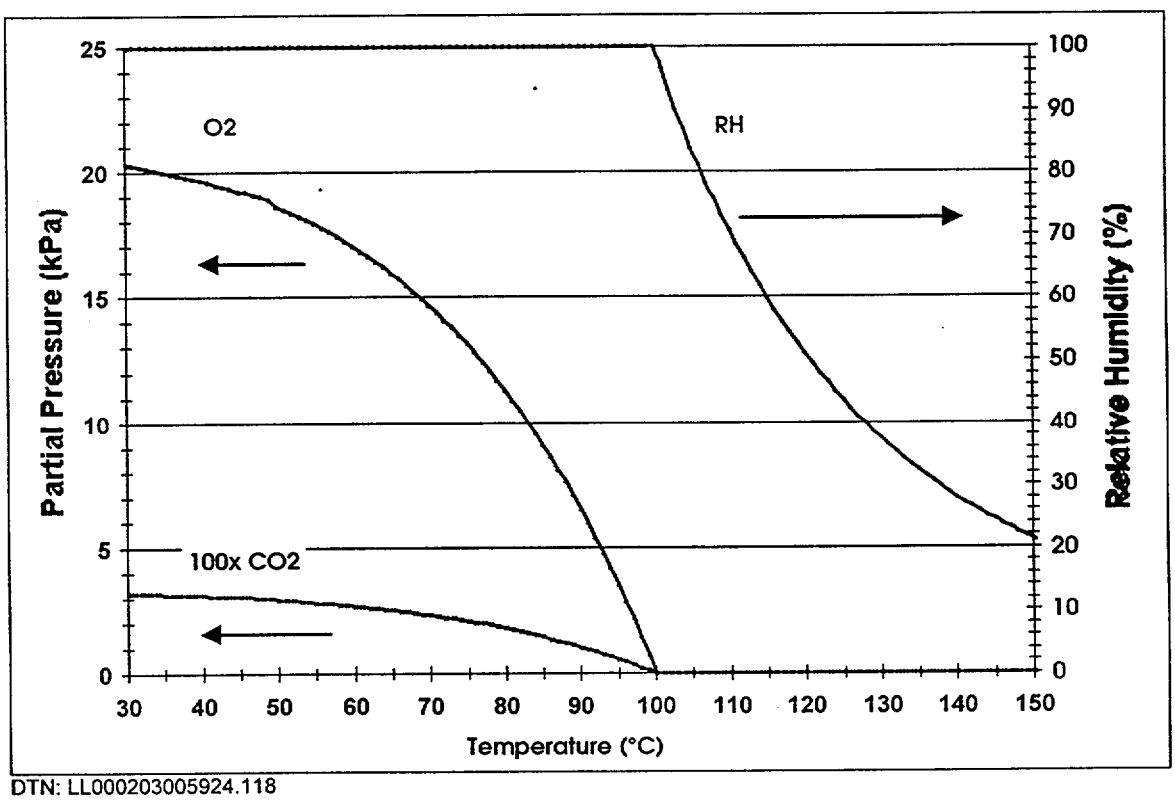

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Figure 4. Calculated Partial Pressure of O_2 and CO_2, Assuming H_2O Partial Pressure is at its Maximum, that is, 100% RH for T ≤ 100°C and 101.32 kPa for T > 100°C

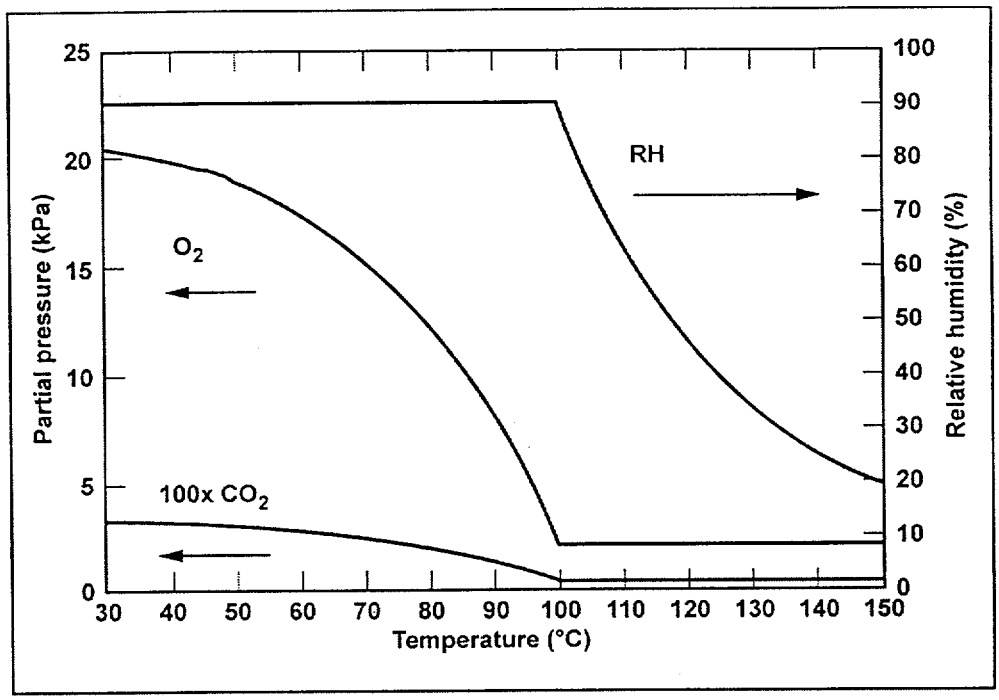

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Figure 5. Calculations of O_2 and CO_2 Partial Pressures, Assuming that RH = 90% for T < 100°C and that the Partial Pressure of Water is Equal to 0.9 Times the Total System Pressure for T > 100°C

6.2.5 Oxygen Solubility

The electrochemical potential of an aqueous solution is a determinant of the corrosion processes that can occur on a metal surface. Dissolved oxygen strongly influences the electrochemical potential of an aqueous solution. Oxygen solubility in pure water and various salt solutions (in particular, NaCl) have been studied by Cramer (1980).

The mole fraction, x_{O2}, of molecular oxygen in the aqueous solution with some simplifying assumption was given by (Cramer 1980):

$$x_{O2} = P_{O2}/k \qquad \text{(Eq. 14)}$$

where P_{O2} is the partial pressure of oxygen in the gas phase, and k is the Henry's Law constant. An analytical expression for k was given as follows:

$$\ln k = a_0 + a_1/T + a_2/T^2 + a_3/T^3 + a_4/T^4 \qquad \text{(Eq. 15)}$$

where k is in MPa and T in K. The constants a_0, a_1, a_2, and a_3 are given in Table 16.

The solubility of oxygen in ppm by weight is given by:

$$D_{O2}(ppm) = 10^6 \times x_{02} \times (1000 g_{H2O} / MW_{H2O} + M_{solute}) \times MW_{O2} / \rho_{soln} \qquad \text{(Eq. 16)}$$

where:

x_{O2} mole fraction of oxygen in the solution ($= P_{O2}/k$) (see above)

$1000 g_{H2O}$ weight in grams of one liter of water (solvent)

MW_{H2O} molecular weight of water (18.0153g/mol) (Table 5)

MW_{O2} molecular weight of O_2 (31.9988g/mol) (Table 5)

M_{solute} molarity of the solute

ρ_{soln} density of the solution in g/L

The term in the parenthesis gives the number of moles in a liter of solution. Multiplying by the mole fraction gives the number of moles of oxygen in a liter of solution. Multiplying by the molecular weight of oxygen gives the number of grams of oxygen in a liter of solution. Dividing by the density of the solution gives the mass fraction.

The density of the fluid is given by (Cramer 1980):

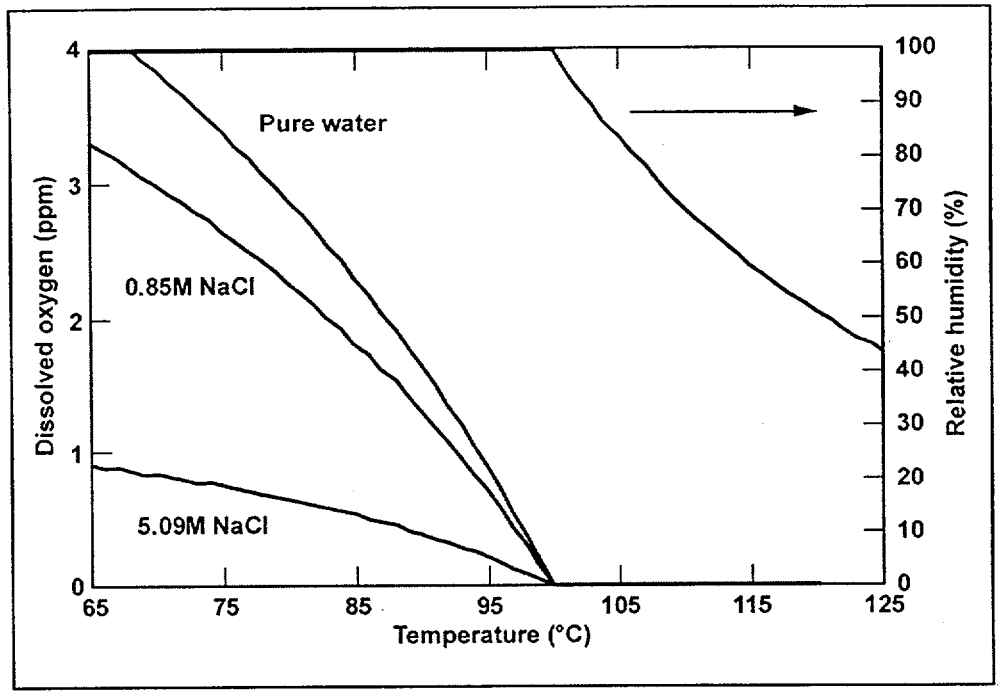
$$\rho_{soln} = \rho_{H2O} + \left(0.03378 + 0.5622 \times 10^{-5} \times \exp(T/66.0)\right) \times \rho_{H2O} \times m_{soln} \qquad \text{(Eq. 17)}$$

where:

ρ_{H2O} density of water

m_{soln} molality of solutions

Plotted in Figures 6 and 7 are the solubilities of oxygen in three aqueous solutions for two cases of different partial pressures of oxygen with a fixed total pressure. In Figure 6, the partial pressure of H_2O is assumed to be at its maximum value, i.e., 100% *RH* below 100°C and 101.32 kPa above 100°C. Above 100°C there is no partial pressure of oxygen—therefore there is no dissolved oxygen in any of the solutions. Below 100°C, the partial pressure of oxygen is steadily increasing with decreasing temperature (see Figure 4), and hence the oxygen solution concentrations are increasing. The curves for the salt solutions in Figure 6 illustrate the "salting out" effect, which is that solutes in solution cause a decrease in the oxygen solubility for a given partial pressure of oxygen. It is worth noting that the salt solutions are *not* in equilibrium with the water vapor pressure under these conditions. Under the condition of 100% *RH*, waters in equilibrium with the surrounding gas phase are infinitely dilute. Therefore, both aqueous salt solutions would tend to become more dilute over time. The equilibrium solute concentration dependence on *RH* is discussed in Section 6.4.3.



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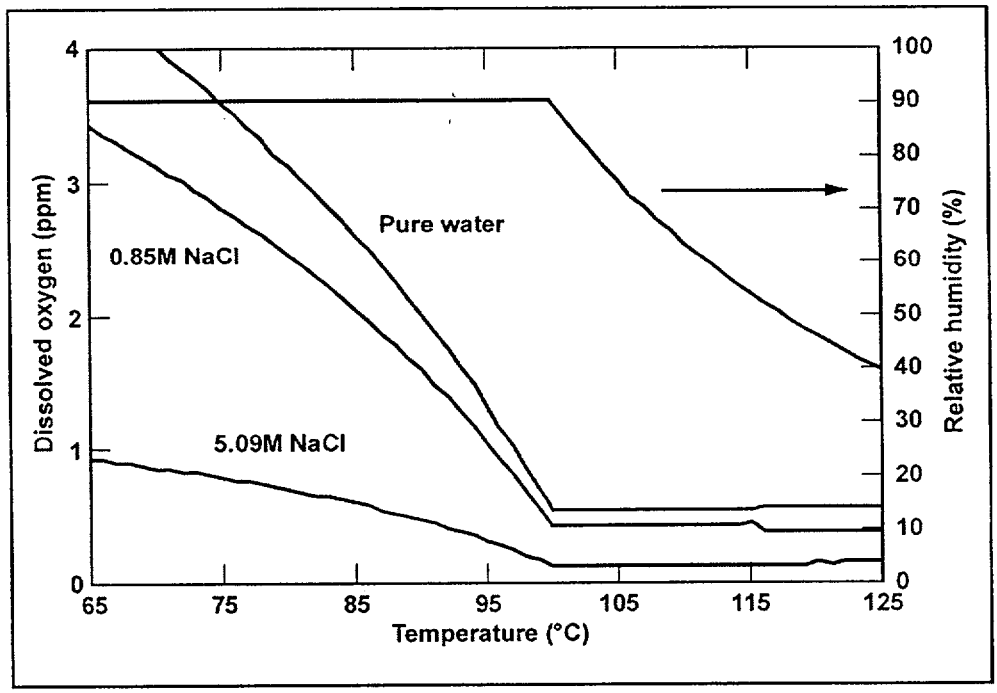
NOTE: Water Partial Pressure, 100% RH for T ≤ 100°C and 101.32 kPa for T > 100°C

Figure 6. Dissolved Oxygen Concentration (ppm) for Three Aqueous Solutions



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NOTE: Partial Pressure of Water Determined by 90% RH for T ≤ 100°C and 87.67 kPa for T > 100°C

Figure 7. Dissolved Oxygen Concentration (ppm) for Three Aqueous Solutions

In Figure 7 the dissolved oxygen content is calculated for the three aqueous solutions assuming that the water partial pressure is determined by the following conditions: 90% RH for $T \leq 100°C$ and 87.67 kPa for $T > 100°C$. For all the solutions, a significant dissolved oxygen concentration is evident above 100°C. As in the previous example, for at least a portion of the T and RH, the aqueous solutions are not in thermodynamic equilibrium with the environmental conditions. Bulk pure water is not in equilibrium with the vapor conditions at any temperature and would evaporate. The 5.09 M NaCl solution would be in equilibrium with the vapor only when the *RH* is approximately 75%. At lower RH values, it would tend to concentrate, and at still lower, it would form a dry salt. At higher RH values, it would tend to form more dilute solutions. The 0.85 M NaCl solution is approximately in equilibrium with the 90% RH conditions. A solution, which is in equilibrium with the specified vapor, would form an aqueous solution at approximately 109°C with some dissolved oxygen. With decreasing temperature (and hence, increasing *RH*) the solution will become more dilute with a consequent rise in the dissolved oxygen content. At temperatures below 100°C the oxygen solubility curve would approximately follow the curve for the 0.85 M NaCl solution.

6.2.6 The Effect of CO_2 Partial Pressure on Aqueous Solution pH

J-13 well water is a sodium bicarbonate water. The pH of well J-13-type waters is strongly influenced by the gas phase CO_2 in contact with the water. The exact relationship between gas phase CO_2 and pH is a function of several parameters, including the partial pressure of CO_2, temperature, the ionic content of the water, and minerals phases in contact with the water. However, all other parameters remaining constant, the pH of aqueous solutions will decrease with increasing partial pressure of CO_2 (Stumm and Morgan 1981). Boiling water is stripped of volatile gases such as CO_2, in effect a condition with no CO_2 partial pressure.

6.3 WATER ADSORPTION ON SURFACES IN THE ABSENCE OF HYGROSCOPIC SALTS

6.3.1 Water Adsorption on Flat Surfaces as a Function of Temperature and RH

In the absence of hygroscopic salts, only limited amounts of water will adsorb on transition metal or metal oxide surfaces. The data of Lee and Staehle (1997) show that the amount of water adsorbed is a function of RH but is also a weak function of temperature (see Figures 1 and 2). Estimates of water film thickness have been made from this data by assuming microscopically flat surfaces in their tests and a water density of 1 to 0.96 g/cm^3. For the purposes of this analysis, the assumptions are reasonable. From the plots, the water film thickness can be estimated to range from about 0.0006 μm at 20% RH to approximately 0.004 μm at 90 to 95% RH.

It is important to note that bulk water condensation can occur only when $RH \geq 100\%$, that is, where the atmosphere is supersaturated with water vapor.

6.3.2 Capillary Condensation as a Function of RH and Temperature

The condensation of water vapor in crevices in contact with the metal barrier surfaces is of concern when considering corrosion under humid air conditions (see Table 21). The Thomson

equation is used to estimate the conditions under which water vapor condensation occurs in crevices in contact with the surface or in defects (e.g. cracks) in corrosion products on the surface.

Table 21. Calculation of the Radius of a Pore in which Water Condensation will Occur

			Pore Radius r, (Å) or (10^{-10}m)			
RH	100°C	80°C	70°C	60°C	50°C	40°C
0.99	710.2	786.5	827.6	871.2	917.1	965.3
0.98	353.3	391.3	411.7	433.4	456.2	480.2
0.97	234.3	259.5	273.1	287.5	302.6	318.5
0.96	174.8	193.6	203.8	214.5	225.8	237.7
0.95	139.2	154.1	162.2	170.7	179.7	189.1
0.94	115.4	127.8	134.4	141.5	149.0	156.8
0.93	98.4	108.9	114.6	120.7	127.0	133.7
0.92	85.6	94.8	99.8	105.0	110.5	116.4
0.91	75.7	83.8	88.2	92.8	97.7	102.9
0.90	67.7	75.0	78.9	83.1	87.5	92.1
0.85	43.9	48.6	51.2	53.9	56.7	59.7
0.80	32.0	35.4	37.3	39.2	41.3	43.5
0.75	24.8	27.5	28.9	30.4	32.0	33.7
0.70	20.0	22.2	23.3	24.5	25.8	27.2
0.65	16.6	18.3	19.3	20.3	21.4	22.5
0.60	14.0	15.5	16.3	17.1	18.0	19.0
0.55	11.9	13.2	13.9	14.6	15.4	16.2
0.50	10.3	11.4	12.0	12.6	13.3	14.0
0.45	8.9	9.9	10.4	11.0	11.5	12.1
0.40	7.8	8.6	9.1	9.6	10.1	10.6
0.35	6.8	7.5	7.9	8.3	8.8	9.2
0.30	5.9	6.6	6.9	7.3	7.7	8.1
0.25	5.1	5.7	6.0	6.3	6.6	7.0
0.20	4.4	4.9	5.2	5.4	5.7	6.0
0.15	3.8	4.2	4.4	4.6	4.9	5.1
0.10	3.1	3.4	3.6	3.8	4.0	4.2

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The RH at which condensation occurs in a pore of radius r is given by Fyfe (1994):

$$x_{RH} = \exp\left(P_c MW_{H2O} / \rho RT\right) \text{ with } P_c = 2\gamma / r \qquad \text{(Eq. 18)}$$

Rearranging the equation to define the radius as a function of temperature and RH gives:

$$r = -2\gamma MW / \left(\rho RT \times \ln(x_{RH})\right) \qquad \text{(Eq. 19)}$$

where:

x_{RH} fractional RH

MW_{H2O} molecular weight (kg/mole)

ρ mass density of water (kg/m^3)

R gas constant (8.31433 J/K-mole) (Weast and Astle 1981, p. F-96)

γ surface tension of water-air (J/m^2)

T temperature (K)

Sample calculation for T = 353.15 K (80°C) and x_{RH} = 0.91:

$$r = -2 \cdot 0.0626\ \text{J/m}^2 \cdot (18.0153/1000)/[0.97183\text{g/cm}^3 \cdot (1\text{kg}/1000\text{g}) \cdot (1000000\text{cm}^3/\text{m}^3) \cdot (8.31433\ \text{J/K-mole}) \cdot 353.15\ \text{K} \cdot \ln(0.91)] \quad \text{(Eq. 20)}$$

$$r = 8.38 \times 10^{-9}\ \text{m} \quad \text{(Eq. 21)}$$

The results shown in Table 21 indicate that capillary condensation will increase the amount of water "adsorbed" relative to adsorption on free surfaces. However this is still a very small amount of water in contact with the surface.

6.3.3 Eh and pH in Aqueous Films in the Absence of Hygroscopic Salts

The aqueous films that form in the absence of hygroscopic salts are expected to have similar properties to bulk water under similar environmental conditions. Because of the limited thickness of the films, constant concentrations of absorbed gases are expected. Oxygen that may be consumed in electrochemical reactions is expected to be rapidly replenished from the gas phase. Likewise, steady-state concentration of carbon dioxide should also be maintained; CO_2 may be "consumed" because of precipitation of carbonate minerals with which it is in equilibrium.

Similar to bulk water solutions, the solution *pH* of thin films will be dependent on the partial pressure of CO_2. For example, the *pH* of de-ionized water solutions in contact with normal atmospheric CO_2 partial pressure at room temperature is about 5.6.

At the present time it is not know if acid gases, such as SO_2, will be present in the drift environments. If present in sufficient quantity they could lower the pH below those which would result from gas phase CO_2.

The adsorbed water layer may facilitate the electrochemical reduction of oxygen when it is present. Assuming a fixed partial pressure of oxygen, steady-state amounts of oxygen in the films are expected because of the limited thickness of the films and the fast diffusion of the oxygen in water.

6.4 CHARACTERISTICS OF AQUEOUS SALT SOLUTIONS

Aqueous solutions of hygroscopic salts on the DSs and WPOBs can occur as a result of several processes. The hygroscopic salts enable aqueous solutions to exist at relative humidities below

100%. Hygroscopic salts may be deposited by aerosols and dust, and introduced with the backfill. They will be contained in the seepage water that enters the drifts and the episodic water that flows through the drifts.

The following sections describe the *RH* dependence of aqueous solutions of pure salts. An argument is present for considering $NaNO_3$ as the salt that determines the minimum *RH* at which aqueous salt solutions will form.

6.4.1 Deliquescence Points and Boiling Points for Pure Salts

As stated in Section 6.1, it is the deliquescence point of a particular salt that defines the *RH* condition necessary for aqueous electrochemical corrosion processes of a metal with salt deposits to occur at a given temperature. Similarly, salt mixtures will have a characteristic deliquescence point that is dependent on the ions in the mixture.

The deliquescence points have been determined for a limited number of pure salts over a limited temperature range (Greenspan 1977). The data for various pure salts given in Table 8 are plotted in Figure 8. Included in the figure are plots for the maximum *RH* obtainable for pure water with boiling points of 96°C (P_{total} = 87.67 kPa) and 100°C (P_{total} = 101.32 kPa). Also included in the figure are the boiling points at sea level (P_{total} = 101.32 kPa) for some salts (Kracek 1928).

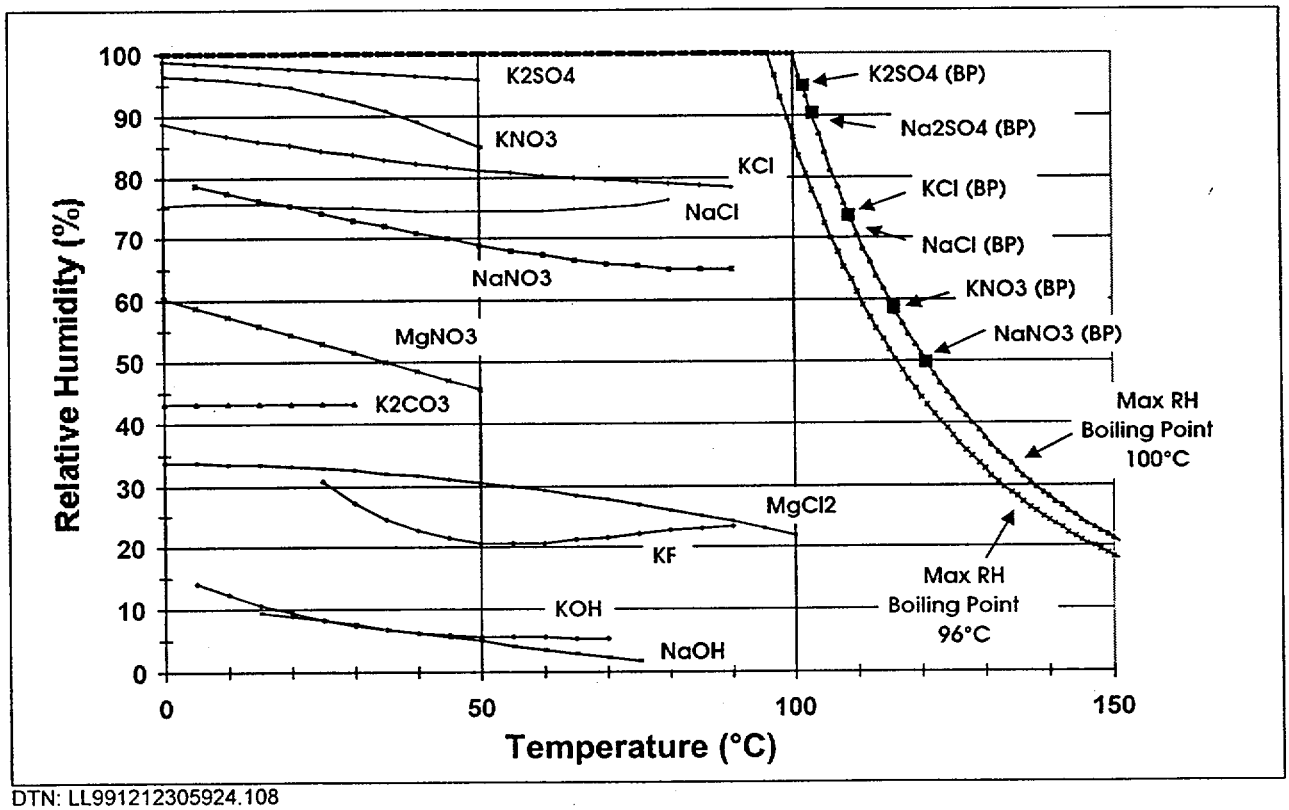

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Figure 8. Deliquescence Points (Greenspan 1977) and Boiling Points for Several Pure Salts (Kracek 1928)

The boiling point for an aqueous salt solution is the temperature at which the equilibrium water vapor pressure of the salt solution is equal to the atmospheric pressure. The aqueous salt solution concentration is also at its maximum. Hence, the *RH* value at the boiling point is its deliquescence point.

For pure salts whose solubilities change little with temperature, the deliquescence points also change little with temperature. For NaCl, whose solubility changes from 35.7 g/100 cm^3 of water at 0°C to 39.12 g/100 cm^3 of water at 100°C (see Table 9), the deliquescence points (see Table 8) are nearly constant with temperature (75% *RH*). At the boiling point of NaCl, the *RH* is 73.15%. Similar behavior is seen for KCl and K_2SO_4.

In contrast, for pure salts whose solubility changes significantly with temperature, the deliquescence points also change significantly with temperature. For $NaNO_3$, whose solubility changes from 92 g/100 cm^3 of water at 25°C to 180 g/100 cm^3 of water at 100°C (see Table 9), the deliquescence points change significantly with temperature from 75.4% at 20°C to 65.0 at 90°C (see Table 8). At the sea-level boiling point (120.6°C), the *RH* is 50.1%.

6.4.2 Minimum RH for Aqueous Solution Formation Under the Potential Repository Conditions

As a bounding condition for the formation of aqueous salt solution on the DS and WPOB, it is assumed that hygroscopic salts are present on these components. The deposition of the hygroscopic salts could result from evaporation of waters infiltrating the drifts after emplacement or from the ventilation of the drifts with air from outside of the Yucca Mountain. The LADS program team has selected the EDA II design, which requires ventilation for times ranging from 50 to 300 years (CRWMS M&O 1999b). See Section 4.1.22 for a more detailed discussion.

The theoretical analyses presented in Section 6.6 and the experimental analyses presented in Section 6.7 show that the concentrated solutions (brines) that would form from evaporative/boiling concentration of well J-13 type waters would be lacking in significant quantities of calcium (Ca) and magnesium (Mg) ions. The Ca and Mg would be precipitated as carbonates, sulfates, and silicates. Considering porewaters the resulting concentrating is assumed to result in chloride and sulfate salts of Mg, Na, and K. However, at the present time complete experimental analysis of the solutions, in particular, the bicarbonate content has not been done, and the analysis is tentative. At the present time it is also assumed that the salts, which would be deposited by the ventilation system, have similar characteristics to those in Yucca Mountain waters.

At the present time, it is assumed that the predominant feature of concentrated Yucca Mountain waters is that sodium and, possibly, potassium will be the major cations. In addition, sodium ions are generally in excess of the potassium ions in these waters. The implication is that the type of hygroscopic salts on the WPOB and DS are limited to either sodium or potassium salts. For a bounding condition, it is assumed that sodium nitrate ($NaNO_3$) - the salt with lowest deliquescence points at elevated temperatures (see Section 6.4.1) - will determine the minimum *RH* at which aqueous films will form on the DS and WPOB. The possibility of aqueous solution formation at a particular temperature is determined by the salt's deliquescence point at that temperature.

The deliquescence points of $NaNO_3$ (equilibrium RH for a saturated solution) as a function of temperature are given in Table 8. The deliquescence point at the boiling point (Table 7) is equal to the sea level atmospheric pressure (101.32kPa) divided by the water vapor pressure at the boiling point (see Table 2). At the present time, this threshold for aqueous film formation is assumed to obey the following polynomial in temperature, which is a fit of the deliquescence point data for $NaNO_3$:

$$RH_{critical} = -3.5932 \times 10^{-5} \times T(°C)^3 + 5.9649 \times 10^{-3} \times T(°C)^2 - 0.45377 \times T(°C) + 81.701 \quad \text{(Eq. 22)}$$

$$R^2 = 0.9854,$$

where R^2 is the coefficient of correlation for the curve fit to the experimental data. The equation is plotted with the data in Figure 9 below.

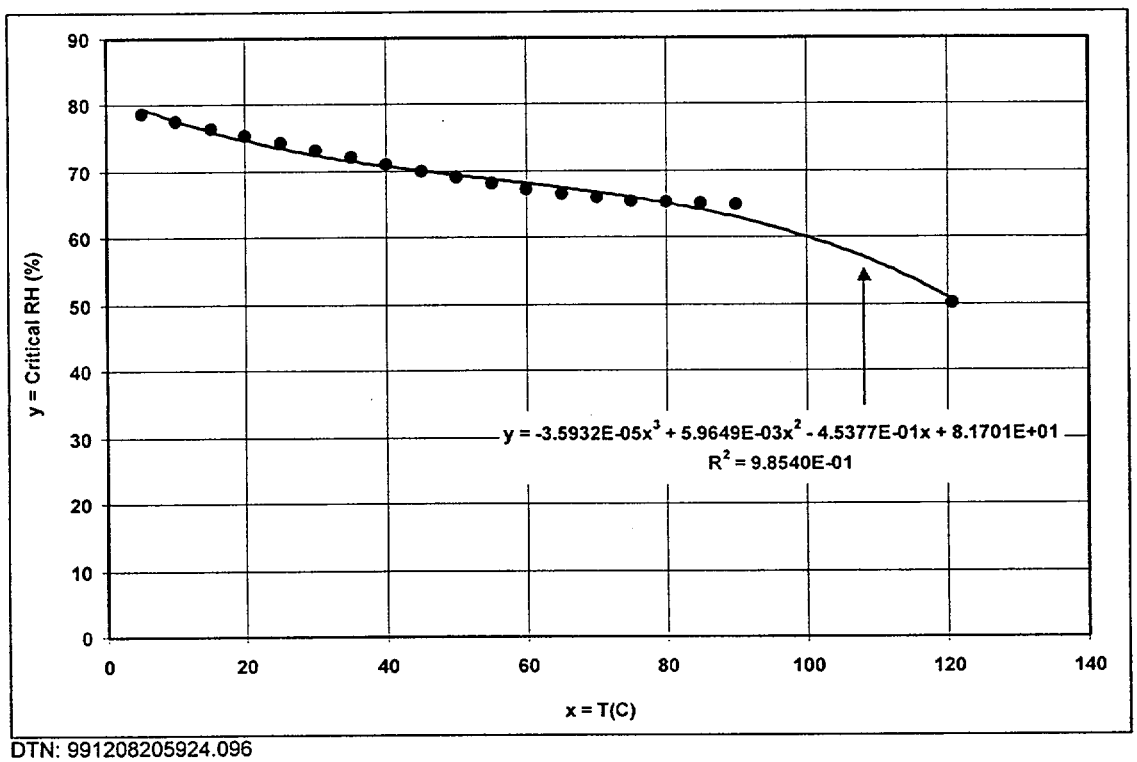

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Figure 9. Deliquescence Points for $NaNO_3$ and a Curve Fit to the Data.

6.4.3 RH Effect on Aqueous Solution Composition

Decreasing the RH of the atmosphere in contact with an aqueous solution of a pure salt will lead to the evaporative concentrating of the aqueous solution. Decreasing the *RH* below a certain value (the deliquescence point) will result in the precipitation of the salt. The molality of sodium chloride aqueous solutions in equilibrium with given relative humidities is shown in Figure 10. It is important to note that the equilibrium concentrations of solutions with *RH* less than 95% are greater than 1 molal.

For mixed salt solutions, decreasing the *RH* of the atmosphere will concentrate some of the ion in solution and cause the precipitation of some species. For instance, as discussed below, the initial concentrating of J-13 water causes the precipitation of calcium and magnesium species.

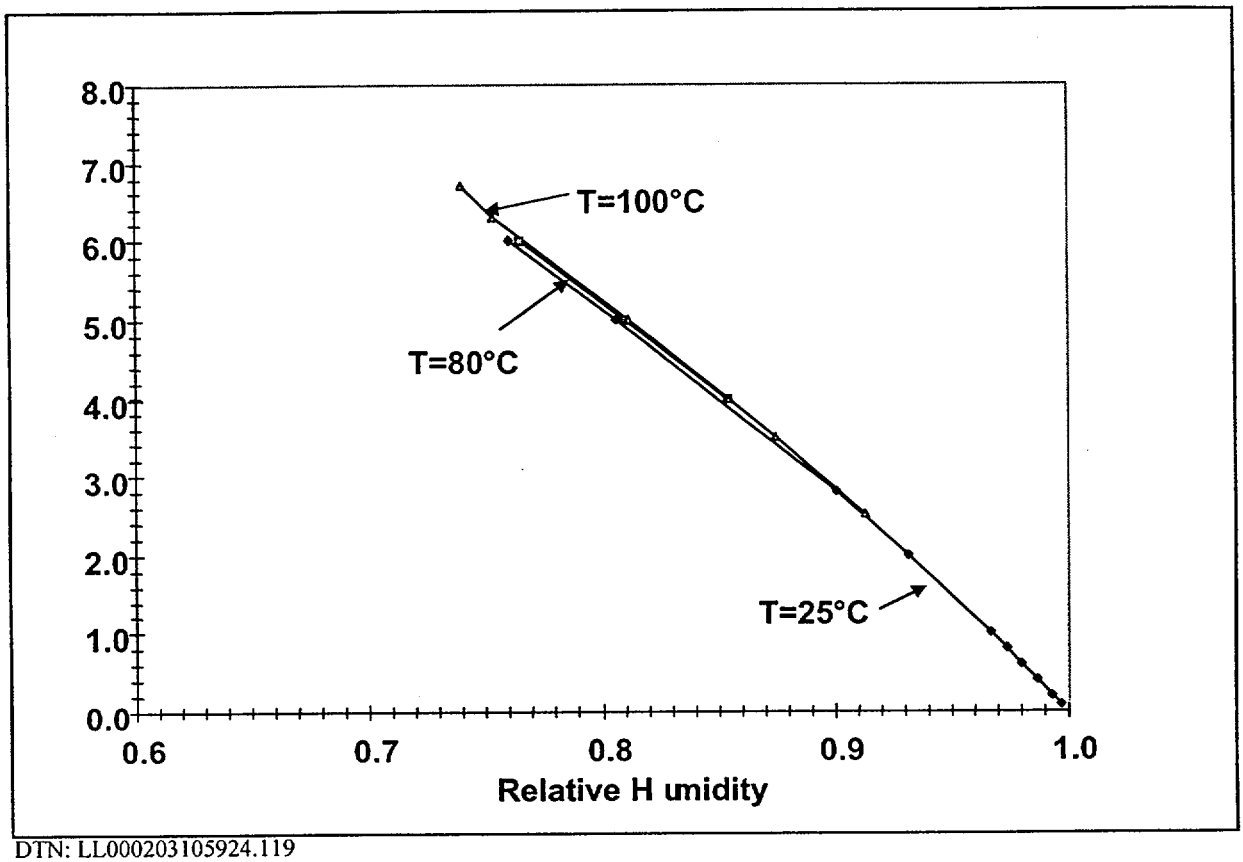

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Figure 10. Aqueous NaCl Molality as a Function of Fractional *RH* (Frazier 1928)

6.5 THE EVOLUTION OF DILUTE NATURAL WATERS TO CONCENTRATED BRINES

As discussed in Section 6.1 it is expected that the aqueous solutions that evolve on the DS and WPOB surfaces will be concentrated aqueous solutions, i.e. brines, because of the low effective *RH* at these surfaces. In the discussion that follows, brines found in natural systems can be categorized into three general types, high pH Na-CO_3-Cl-SO_4 brines, near-neutral pH Na-Mg-SO_4-Cl brines, and near-neutral pH Na-Ca-Mg-Cl brines.

The evaporative concentration of natural waters into brines can be conceptualized as a series of chemical divides, as discussed in Drever (1997) and is based on earlier work by Eugster and Hardie (1978). The main point of this approach is that brines are generally chemically simple systems containing relatively few major ions and that brine evolution can to a large extent be determined from knowing certain characteristic of the initial dilute water, in particular, relative concentration of certain cations and anions.

The concept of chemical divides is straightforward. When a binary salt such as NaCl is precipitated from solution during evaporation, the concentration of one of the ions in solution (e.g., Na or Cl) will increase relative to the other unless, at the start, the molal ratio of the two ions in solution was exactly

identical to the molal ratio in the binary salt. With most natural waters, the first minerals to precipitate, and therefore the first chemical divide, are calcium carbonates ($CaCO_3$). The path from there is determined based on whether the molal concentrations of Ca is greater than or less than the carbonate alkalinity.

If the Ca concentrations are less than the carbonate alkalinity, all the Ca will be removed from the solution as carbonates during evaporation and, if the Mg concentration is also less than the remaining alkalinity, the solution will evolve toward a sodium carbonate (Na_2CO_3) alkaline brine. Dilute sodium carbonate groundwaters are common in volcanic and metamorphic terrains. In many closed basins, such as Owens Lake in southeastern California, shallow Na_2CO_3 groundwater has been concentrated by evaporation, producing a calcium and magnesium-free, high pH, high alkalinity brine and evaporative minerals such as trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) and halite (NaCl). If instead, the remaining Mg concentration is greater than the remaining carbonate alkalinity, then a Na-Mg-SO_4-Cl brine will result.

If the Ca concentration is greater than the carbonate alkalinity, all the carbonate species are removed from solution followed by gypsum precipitation. If the Ca concentration remaining is greater than the SO_4 concentration, the resulting solution will be a Na-Ca-Mg-Cl brine. If the converse is true and the SO_4 concentration is greater than the remaining Ca, the resulting solution will be a near neutral pH, Na-Mg- SO_4-Cl brine, as was the case for one of the systems described above.

It is worth discussing the precipitation of magnesium minerals from the dilute solutions. The above approach assumes that the calcium carbonate is precipitated with the complete exclusion of the magnesium. In reality some of the magnesium may be precipitated as magnesium containing calcium carbonate. For carbonate alkalinity in excess to precipitate the calcium component, the magnesium may precipitate as either carbonate or silicate. However, the magnesium silicate precipitation requires an equivalent amount of carbonate alkalinity as the carbonate precipitation for the reaction to occur.

Additionally potassium does not remain in the natural brines to a significant extent; this may be due to the ion exchange with clays. Also nitrates do not appear as a major anion in brines even though they are a component of the inflow waters. Nitrates are hygroscopic (Table 8), and saturated aqueous solutions of nitrate salts have high boiling points (Table 7).

In Section 6.6.3, the approach discussed in this section has been applied to the saturated zone groundwater (J-13 well water) at Yucca Mountain and it predicts that J-13 well water evolves into a high pH, Na-CO_3-Cl-SO_4 brine. Experimental studies have also shown that a simulated J-13 well water evolves into the same type of brine (see section 6.7). In Section 6.6.4, this approach has been applied to pore waters sampled in the unsaturated zone, TSw hydrogeologic unit and it predicts that they would evolve into near neutral pH, Na-Mg-SO_4-Cl.

6.6 ESTIMATE OF BRINE FORMATION FROM YUCCA MOUNTAIN WATERS

6.6.1 Introduction

The effective RH at the DSs and WPOBs will always be less than 100% because of the temperature differences between these EBS components and the surrounding environment (See Section 6.2.3). The actual values of *RH* at these components will be a function of thermal-hydrological-chemical characteristics of the potential repository. Concentration of the aqueous solutions will occur when the *RH* is less than 100% (see Section 6.4.3).

The analysis performed in this section predicts the types of very concentrated waters that may form on the DS and WPOB surfaces by understanding the sequence of mineral precipitation of the relatively dilute waters that are characteristic of the Yucca Mountain region. This is based on the approach presented in Section 6.5 that described the evolution of saline lakes (brines) from dilute inflow waters.

The analysis is performed to determine if there is sufficient carbonate alkalinity present in the waters to precipitate Ca as carbonate and then Mg as either carbonate or silicate. If there is insufficient carbonate alkalinity to precipitate all the Ca, then the analysis is performed to determine if there is sufficient sulfate to precipitate the calcium as sulfate minerals. The type of brine is determined from this analysis.

The analysis consists of calculating the equivalents for the ions in solution, then comparing the quantities for Ca and Mg with those for bicarbonate and sulfate, and finally determining the type of brine that would form based on the relative ratio of the ions, as discussed in the Section 6.5.

The equivalents, the amount of electronic charge associated with a particular ion, are defined as:

$$Eq = C*EC/MW \qquad \text{(Eq. 23)}$$

where C is the concentration (mg/L)

EC is the electronic charge of the ion

and MW is the molecular weight of the ionic species (Table 5)

6.6.2 Types of Water at Yucca Mountain

According to the Yucca Mountain Site Description report (CRWMS M&O 1998): "The available data on the chemistry of waters at Yucca Mountain indicate the existence of two basic types of waters in volcanic units in the Yucca Mountain region. Type I is found as pore water above the Calico Hills nonwelded hydrogeologic unit. Type II is found as perched water and saturated-zone groundwater. The pore waters in the Calico Hills nonwelded unit appear to be mixtures of these two waters." Note that the Calico Hills are below the proposed repository horizon.

6.6.3 Saturated Zone Water; J-13 Well Water

J-13 well water is assumed to be typical of the saturated zone and perched water from unsaturated zone (Table 14). Table 22 is a calculation of the milli-equivalents of ions in J-13 well water. The equivalents associated with the Ca, Mg, HCO_3/CO_3, and SO_4 are shown at the bottom of the table.

Table 22. Composition of J-13 Well Water (Harrar et al. 1990) and Calculation of Equivalents

Species	Concentration (mg/L)	Milli-Equivalent (10^{-3} x charge/L)
Na	45.8	1.992
Si	28.5	
Ca	13.0	0.649
K	5.04	0.129
Mg	2.01	0.165
F	2.18	0.115
Cl	7.14	0.201
NO_3	8.78	0.142
SO_4	18.4	0.383
HCO_3	128.9	2.112
Ca		0.649
Mg		0.165
HCO_3		2.112
SO_4		0.383

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For J-13 well water the calculation shows that the bicarbonate concentration is well in excess of that necessary to precipitate the calcium and magnesium content as carbonates. It is expected that this type of water would form a high pH Na-CO_3-Cl-SO_4 brine (see Section 6.5). In Sections 6.7 experimental studies of the evaporative/boiling concentration of simulated J-13 well water are shown to form this type of brine.

6.6.4 Composition of Porewaters from Topopah Springs welded unit (TSw)

Table 23 lists the concentrations of the major ions in two porewaters that were collected from the Topopah Springs welded (TSw) unit at Yucca Mountain (Table 15). It also lists the milli-equivalents for each ionic component.

The data for the porewaters does not give concentrations for the bicarbonate component. Therefore the milli-equivalent for the bicarbonate component was calculated to balance the charge of the waters, i.e. cation charge = anion charge. The bicarbonate concentration was then calculated from the above equation. The contribution to the ionic charge due to the silicic acid component ($Si(OH)_4$) was not included in the calculation. The contributions of H^+ and OH^- components are negligible.

The results in Table 23 show that the carbonate alkalinity is not sufficient to precipitate all the calcium as carbonate. However there is sufficient sulfate concentration to remove the remaining calcium as calcium sulfate. It is expected that these types of dilute waters would form Na-Mg-SO_4-Cl type brines. These results are tentative until experimentally determined value for the bicarbonate/carbonate concentrations are obtained.

Table 23. Major ion concentrations reported for TSw pore water at ambient temperature and Calculation of Equivalents.

Ions	ESF-HD PERM-2		ESF-HD PERM-1	
	Concentration (mg/L)	Milli-Equivalent (10^{-3} x charge/L)	Concentration (mg/L)	Milli-Equivalent (10^{-3} x charge/L))
Na^+	61	2.65	62	2.70
K^+	7	0.18	9	0.23
Mg^{2+}	16.6	1.37	17.4	1.43
Ca^{2+}	106	5.29	97	4.84
$SiO_2(aq)$	66		75	
HCO_3^-	246*	4.03*	187*	3.07*
SO_4^{2-}	111	2.31	120	2.50
Cl^-	110	3.10	123	3.47
NO_3^-	3	0.05	10	0.16
Ca^{2+}		5.29		4.84
Mg^{2+}		1.37		1.43
HCO_3^-		4.03		3.07
SO_4^{2-}		2.31		2.50

DTN: LL000203705924.125
* calculated value see text for explanation.

6.7 BOILING/EVAPORATIVE CONCENTRATING OF A SIMULATED J-13 WELL WATER

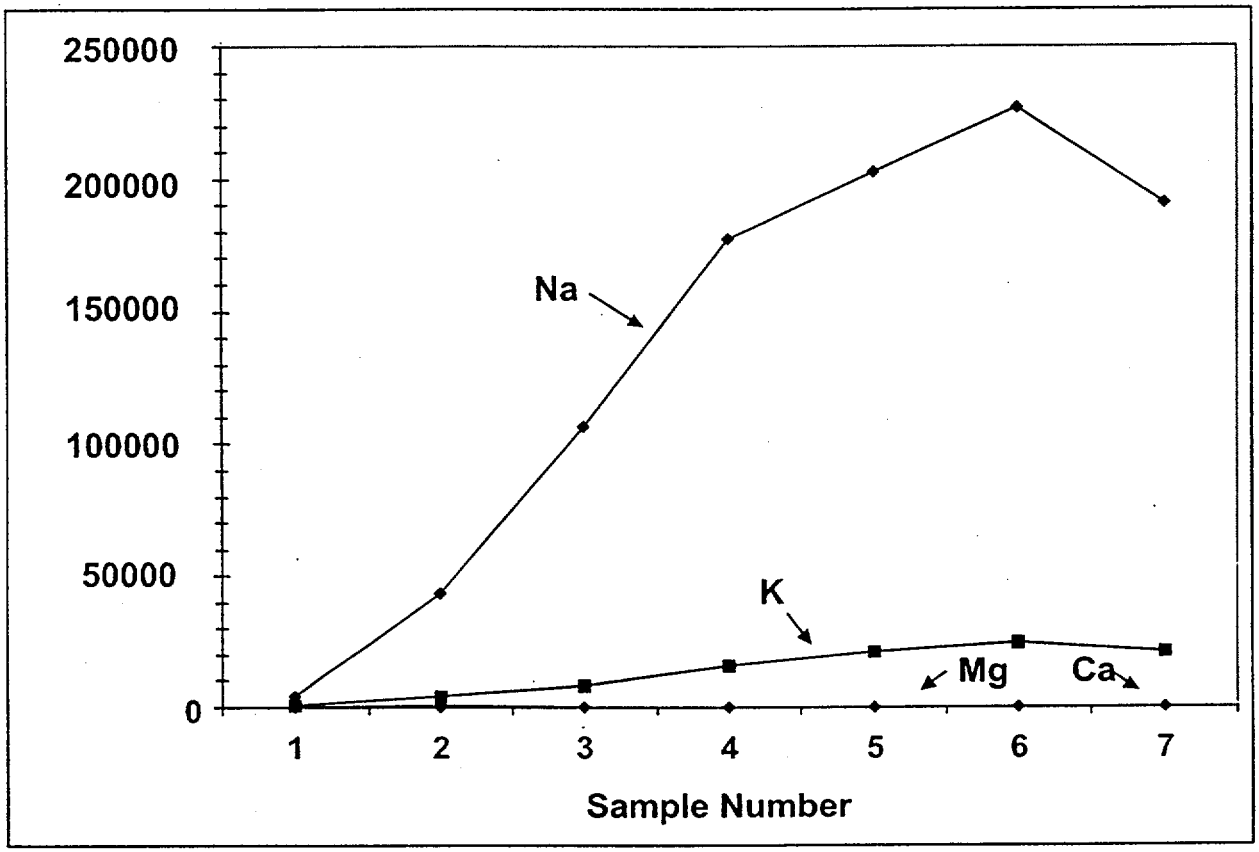
The testing program has assumed that that a well J-13 type water will contact the DSs and WPOBs. If a different composition of water is later deemed more appropriate, then an analysis will be performed to determine if that composition has a significant effect on the results presented in this section.

As discussed in Section 6.4.3, it is inevitable that the waters in contact with the DSs and WPOBs will be more concentrated than the ambient waters at Yucca Mountain or the seepage water that enters the drifts. Several tests are ongoing to characterize the changes that occur upon boiling/evaporative concentrating of simulated J-13 well water and slightly concentrated, simulated J-13 well water. These tests include the evaporative concentrating of simulated well J-13 water that is dripped onto heated crushed tuff that is at or near the boiling point of the concentrated solution and evaporative concentrating of simulated J-13 well water that is dripped onto crushed tuff under conditions of constant temperature and *RH*.

6.7.1 Initial Concentrating of J-13 Well Water

It is expected that the initial concentrating of J-13 well water will lead to the precipitation of Ca- and Mg-based salts/minerals because of the very low solubility of the Ca and Mg in high bicarbonate/carbonate waters in neutral/alkaline aqueous solutions (see Section 4.1.10). The

composition of J-13 well water is given in Table 14. The largest anionic component of the water is the carbonate/bicarbonate couple (total bicarbonate concentration of 128.9 ppm). Calcium and magnesium concentrations are 13 and 2 ppm respectively. Evaporative concentrating of the aqueous solutions will exceed the solubility limits for the calcium and magnesium carbonates. The removal of Mg and Ca ions from solution by concentrating simulated J-13 well waters has been documented experimentally (see Section 6.7.2). The magnesium seems to be removed to a greater extent than the calcium; however, both are removed to a much greater extent than the Na and K ions. In the discussions that follow, particular emphasis is placed on the water chemistry of sodium (Na) and potassium (K) salts because these are expected to be the dominant cation species in concentrated solutions.



DTN: LL000202905924.117

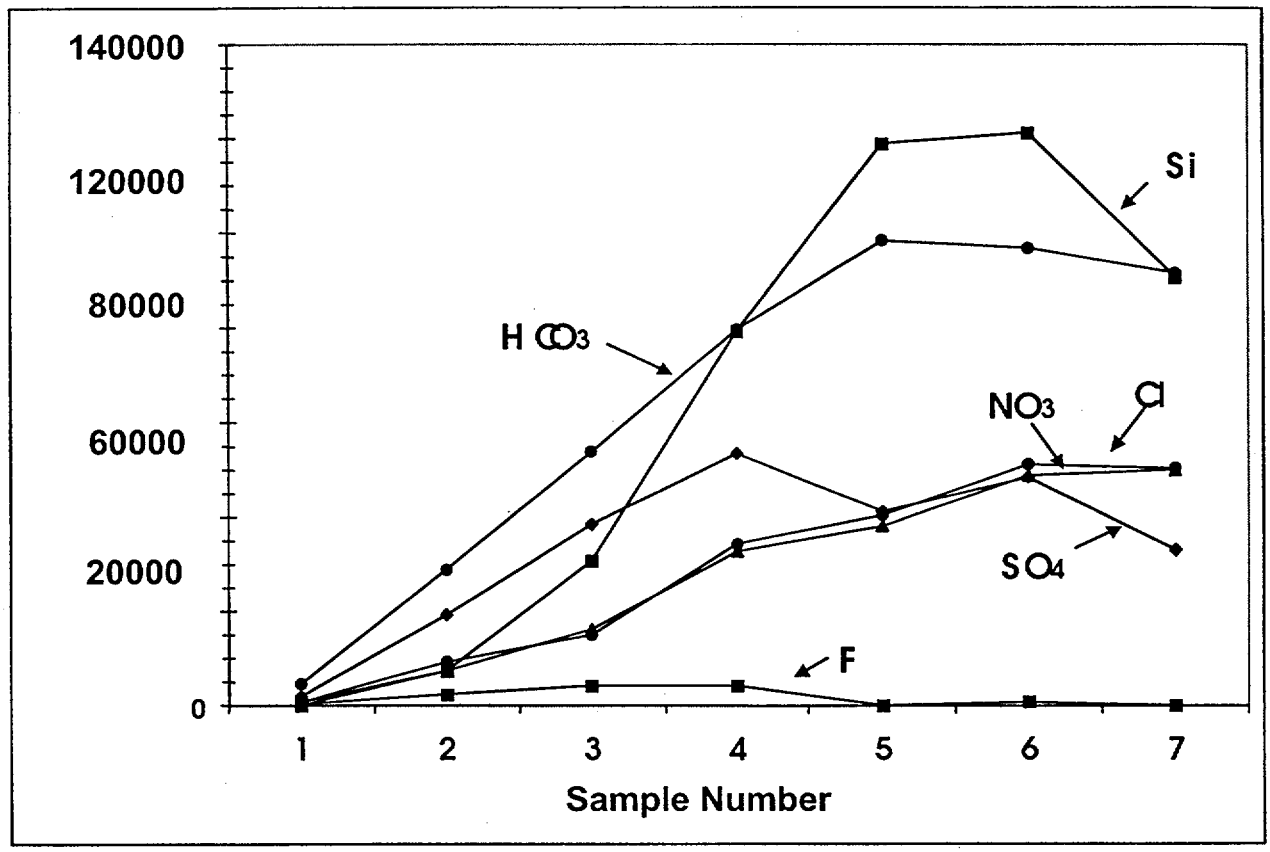
NOTE: The First Sample Corresponds to the Initial Solution. Data from Table 18.

Figure 11. Concentration of Cations Resulting from the Evaporative Concentration of Simulated J-13 Well Water Near the Boiling Point

6.7.2 Evaporative Concentrating of a Simulated J-13 Well Water by Boiling

The results of evaporative concentrating of a simulated J-13 well water by boiling are presented in Section 4.1.20. Figures 11 and 12 are plots of the experimentally determined cation and anion concentrations as a function of the sequential sampling of the aqueous solutions. Figure 13 is a plot of the concentration factors for the anions as a function of the sequential sampling of the aqueous solutions. Each sample number after Sample # 1 was taken after evaporation of

between one and two liters of the simulated solution. Sample #1 was the original starting solution.



DTN: LL000202905924.117

NOTE: The First Sample Corresponds to the Initial Solution. Data from Table 16.

Figure 12. Concentration of Anions Resulting from the Evaporative Concentration of Simulated J-13 Well Water Near the Boiling Point

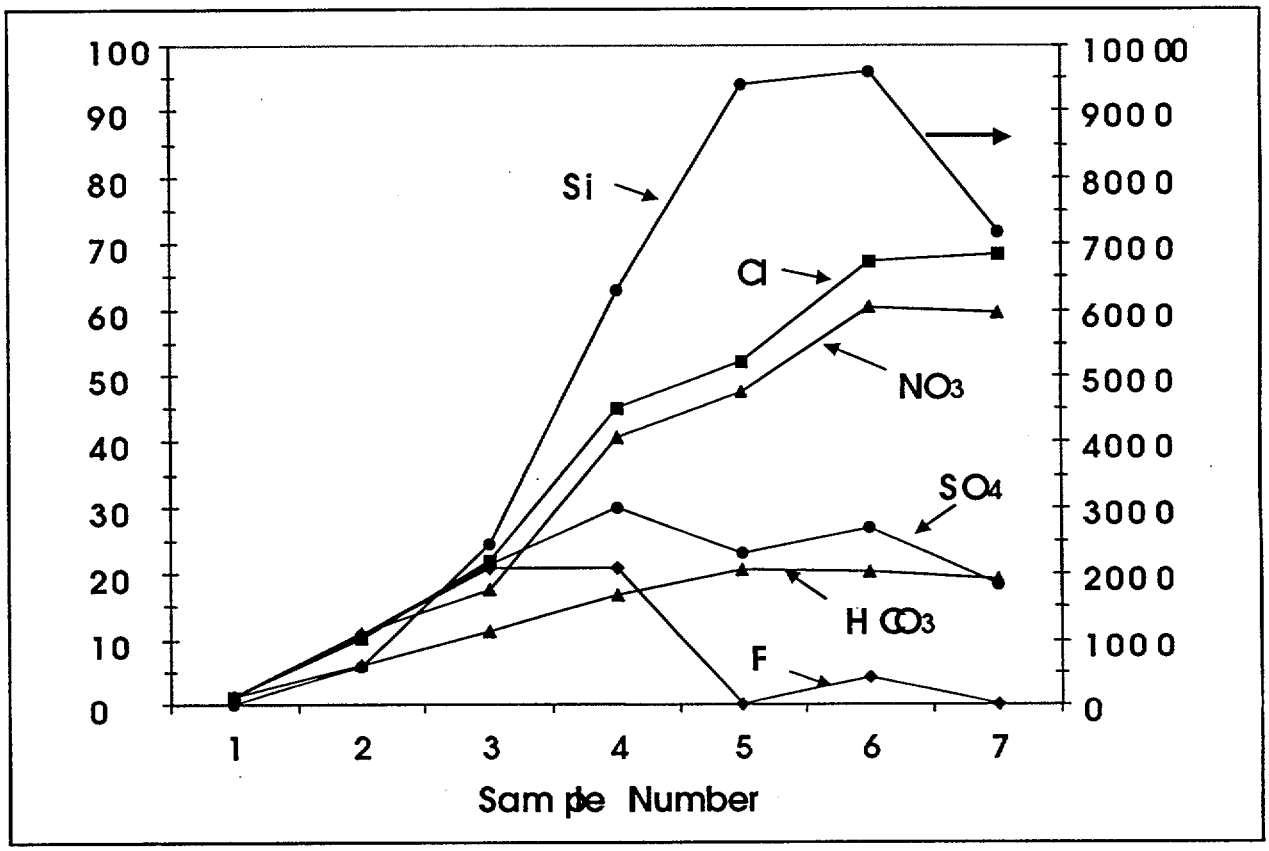
The trend for the solution concentrations of Na and K are that they are increasing with increasing evaporative concentration. In contrast the solution concentrations of Ca and Mg are very small relative to the Na and K concentrations. This behavior is consistent with the precipitation of Ca and Mg as carbonates due to their low solubility in concentrated bicarbonate/carbonate solutions.

The solution concentration data for the anions is a bit more complicated than that for the cations. The bicarbonate/carbonate is very high in all the solutions sampled, however relative to the other anions it is not concentrated in the solutions as much as the other anions. The pH of such solutions is controlled by the bicarbonate/carbonate concentration and is very alkaline.

Fluoride is initially concentrated as much as the other anions, but its concentration and concentration factor decrease as the total solution concentration becomes very large. The least soluble fluoride salts are CaF_2, NaF, and MgF_2 (see Table 9). The amounts of calcium and magnesium ions in solution are low, so direct precipitation from the solution is unlikely. Although the solubility of NaF at 18°C is 42200 mg/L, the great excess of Na in solution would

cause the precipitation of NaF. There appears to be some small amount of fluoride that remains in solutions even for the very concentrated solutions.

Sulfate is also initially concentrated as much as the other anions, but its concentration and concentration factor decrease as the total solution concentration becomes very large. However its concentration remains significant. The least soluble sulfate salts are $CaSO_4$ and K_2SO_4 (see Table 9). The amount of calcium ions in solution is low, so direct precipitation from solution is unlikely. The solubility of K_2SO_4 is 241,000 mg/L at 100°C. This exceeds the amount of potassium and sulfate in solution. At present, the reason for the sulfate removal from solution can not be easily explained. However, it is noted that burkeite, $Na_6CO_3(SO_4)_2$, is a major mineral in sodium carbonate brines containing sulfate (Eugster and Hardie 1978).



DTN: LL000202905924.117

NOTE: The First Sample Corresponds to the Initial Solution. Data from Table 18.

Figure 13. Concentration Factors for Anions Resulting from the Evaporative Concentration of Simulated J-13 Well Water Near the Boiling Point

The trend for the chloride and nitrate concentrations is that they are continuously increasing with increasing evaporative/boiling concentration. This is expected due to the very high solubility of the chloride and nitrate salts of potassium and sodium.

The amount of silicate species in solution greatly exceeds the amount in the starting solution. A probable explanation of this large quantity is that the high pHs of the solutions results in the dissolution of the crushed tuff that is in contact with the aqueous solutions.

6.7.3 Water Composition as a Function of RH at Fixed Temperatures (DTN: LL990703005924.083)

The objective of this work is to characterize the waters that would result from the evaporative concentration of waters contacting the WPOBs and the DSs in the range of temperature/*RH* where candidate materials might be susceptible to corrosion. Testing has begun at 90°C and will continue at regular temperature intervals. The results are reported for evaporation at 85% *RH*. The starting solution was simulated, 100-times concentrated J-13 well water. The aqueous solution dripped through a column of crushed tuff was collected in a beaker at the outlet of the column. Additional evaporation of the aqueous solution occurred in the beaker.

In Table 24 a concentration factor, which is the ratio of a specific ion concentration of the sample solution to the specific ion concentration of the initial solution, is presented. The data show that under these conditions calcium, magnesium, bicarbonate (as an indicator of total carbonate), and possibly fluoride are not concentrated to the extent that chloride, nitrate, sulfate, sodium, and potassium are. This result is consistent with the expected precipitation of carbonate species and with the initial precipitation of some fluoride-containing salts/minerals.

Table 24. Results of the Evaporative Concentration of Simulated J-13 Well Water Under Conditions of Constant Temperature and RH

Species	Starting Solution (mg/L)	Final Solution 85%RH/90°C (mg/L)	Concentration Factor
Sample #	**Initial J-13 Batch A**	**J-13-01**	
Cl	730	14419	19.8
NO_3	732	14085	19.2
SO_4	1632	29783	18.2
F	208	3630	17.5
HCO_3[a]	4142	54614	13.2
Na	4032	76314	18.9
K	513	10832	21.1
Ca	5	36	7.2
Mg	2	0	0

DTN: LL000202905924.117
NOTE: [a]Total inorganic carbon expressed as bicarbonate.

6.8 THE EXISTENCE OF AQUEOUS SOLUTIONS ON THE EBS COMPONENTS UNDER NONEQUILIBRIUM CONDITIONS

Aqueous solutions may exist on the EBS components where the evaporation rate is slower than the seepage flow of additional water. Under these conditions, aqueous solutions may exist at

higher temperatures or lower relative humidities than would normally support those solutions. The extent to which this may occur is being investigated to understand if there would be an increase in the aggressiveness of the aqueous solutions contacting the EBS components.

6.9 EFFECT OF BACKFILL ON THE WATER CHEMISTRY CONTACTING THE DS AND WPOB

At least three materials are being considered for backfill, which at the present time is optional. The three potential backfill materials identified in the LADS EDA II design were sand, tuff, or marble ($CaCO_3$). The sand and tuff are both silica base materials.

Tuff, which is crushed Yucca Mountain rock, was included in the evaporative/boiling concentration of J-13 well water. It was found that significant amounts of silica were dissolved from the crushed Yucca Mountain rock which was included in the testing. This is due to the very alkaline pHs of the concentrated solutions. This high solubility of silica in high pH waters is known (Iler 1979). This result indicates the potential for buffering of the very alkaline water by the silica. However, this would depend on the quantity of backfill and alkaline water. Carbonate base backfill would have no buffering effect on high pH aqueous solutions.

If the waters that are in contact with the DS and WPOB are near neutral pH aqueous solutions, then there is the possibility of acidification of these solutions due to hydrolysis of metal ions released during electrochemical corrosion processes. Under this scenario the carbonate base material would have a buffering effect, that is, it would keep the pH from becoming very acidic. This also would depend on the quantity of backfill and water contacting the DS and WPOB.

6.10 CONSIDERATION OF pH CONTROL OF AQUEOUS SOLUTIONS IN "OPEN SYSTEMS"

The aqueous salt solutions that form on the EBS components can be considered to be in an "open system." What this means is that gas phase composition of the minority components will probably be affected significantly by environmental considerations other than the aqueous solutions on the EBS components. On the other hand the water vapor in the drift is assumed to be in equilibrium with the aqueous solutions, that is, the *RH* can be considered fixed. Likewise the oxygen and carbon dioxide contents can be considered fixed for the purposes of this discussion.

For practical purposes the volatile components of aqueous salt solutions tend to be the acid gas components, e.g. HCl and HNO_3. The equilibrium vapor pressure of these components is a function of the solution temperature and pH. For a given pH, the vapor pressure increases with increasing temperature. For a given temperature, the vapor pressure increases with decreasing pH. Hydroxyl species do not have significant vapor pressures even at high pH and elevated temperatures (e.g. 100°C).

Acidic aqueous salt solutions under "open system" conditions will probably be limited in the extent that acidification can occur. In equilibrium with aqueous solutions in the neutral and acidic pH range there is a partial pressure of an acidic gas. For instance, above aqueous chloride solutions there is a partial pressure of HCl required to maintain a given pH. Likewise in nitrate

and sulfate solutions there is a partial pressure of HNO_3 and H_2SO_4 required to maintain a given pH. The equilibrium partial pressure of the acidic gases is a function of temperature and pH.

For the case of acidic aqueous chloride solutions, the equilibrium partial pressures of HCl are given in Tables 11a and 11b. For these very acidic solutions the HCl partial pressures are substantial. It would seem unlikely that the HCl partial pressures could be sustained for substantial periods of time at these levels within the drifts for several reasons. There is expected to be air movement through the drifts and gas phase diffusion, both processes would dilute the gas phase partial pressure of the acidic gas. Absorption of HCl gas by aqueous films on other surfaces within the drifts will also occur. Some of these solutions will be alkaline (e.g. sodium bicarbonate or calcium carbonate base solutions), therefore causing neutralization of the acid gas. The net effect of these processes is to remove HCl from the gas phase which will cause the further net removal of HCl from the low pH solution until a steady state condition is met at some elevated pH.

The volatility of HCl from a nominally pH 3.1 NaCl-saturated solution has been shown experimentally at ambient temperature (22-25°C) by Oplia et al. (1989). These same authors performed theoretical calculations to determine the vapor pressure in equilibrium with several saturated aqueous salt solutions at 25°C and pH 7, 5.6, and 3.15. The calculated vapor pressures for HCl were small but significant, $2x10^{-10} - 4x10^{-6}$ torr or $2.7x10^{-11} - 5.3x10^{-7}$ kPa (calculated for this report using 760 torr = 101.32 kPa). While these values are small at 25°C, the values in Table 11a and 11b indicate that the HCl vapor pressure can be quite high under acidic and elevated temperature conditions.

6.11 CHARACTERIZATION OF MINERAL/SALT SCALE FORMATION ON DS AND WPOB SURFACES

Common scale minerals in natural waters are calcium (magnesium) carbonate, calcium sulfate, and silica (Cowan and Weintritt 1976). The tendency for carbonate scale formation is greatly enhanced by the concentration of the ions by water evaporation, provided the aqueous solution remains alkaline. Silica deposition will also be enhanced by water evaporation, provided that the solution's *pH* does not reach alkaline values where the silica solubility is greatly enhanced.

Scale can protect the underlying material if it forms a dense adherent layer. However, scale can have a deleterious effect on the underlying material if it forms a porous layer or a crevice with the underlying material.

The objective of this study is to characterize the scale that forms on the candidate materials for the DS and the WPOB under conditions simulating the repository environment.

Another important aspect of the scale that forms at very high temperatures is the possibility of decomposition of the some of the dry salts which form due to complete evaporation of the water. In Table 10 the decomposition temperatures of various Na, K, Mg, and Ca carbonate and bicarbonate species are listed. The dissolution of the decomposition products by either seepage water or high *RH* condition would result in alkaline aqueous solutions.

The WP upper temperature limit of less than 350°C (CRWMS M&O 1999e) means that there is the possibility of $KHCO_3$ and $NaHCO_3$ decomposition (see Table 10) under some scenarios.

6.12 COMPOSTIONS OF AQUEOUS SOLUTIONS USED FOR CORROSION TESTING

This section discusses the types of waters that have been formulated for solutions used for corrosion testing of the EBS component materials and the rational for their use. The compositions of these aqueous test solutions are listed in Tables 25 and 26. In Table 25, the ionic compositions of the solutions are given, while in Tables 26 the recipes for solutions are given. The following sections discuss the solutions individually.

Table 25. The Composition of Several Aqueous Solutions used for Corrosion Testing (UCRL-ID-132285, UCRL-ID-132286, UCRL-ID-132287)

	Concentration (mg/L)			
Ion	Simulate Dilute Water (SDW)	Simulated Concentrated Water (SCW)	Simulated Acidified Water (SAW)	Simulated Saturated Water (SSW)
	60 & 90°C	60 & 90°C	60 & 90°C	100°C
K	34	3400	3400	141600
Na	409	40900	40900	48700
Mg	1	<1	1000	0
Ca	0.5	<1	1000	0
F	14	1400	0	0
Cl	67	6700	24250	128400
NO_3	64	6400	23000	1310000
SO_4	167	16700	38600	0
HCO_3	947	70000	0	0
Si	27 (60°C); 49 (90°C)	27 (60°C); 49 (90°C)	27 (60°C); 49 (90°C)	---

Table 26. Recipe for carbonate and silicate containing BSW solution (LLNL 2000, TIP-CM-28)

Chemical	BSW-CS
KCl	9.7 g
NaCl	8.8 g
NaF	0.2 g
$NaNO_3$	13.6 g
Na_2SO_4 (anhydrous)	1.4 g
H_2O (de-ionized)	56 ml
Na_2CO_3	10.6 g
$Na_2SiO_3 \cdot 9H_2O$	4.0 g

Table 27. Recipes for carbonate and silicate-free BSW solutions (LLNL 2000, TIP-CM-28)

Chemical	BSW-13	BSW-12	BSW-11
KCl	8.7 g	8.7 g	8.7 g
NaCl	7.9 g	7.9 g	7.9 g
NaF	0.2 g	0.2 g	0.2 g
$NaNO_3$	13.0 g	13.0 g	13.0 g
Na_2SO_4 (anhydrous)	1.4 g	1.4 g	1.4 g
H_2O (de-ionized)	66 ml	66 ml	66 ml
10N NaOH	2 ml	---	---
1N NaOH	---	2 ml	---
0.1N NaOH	---	---	2 ml
CO_2 partial pressure	0	0	0
Nominal pH	13	12	11

6.12.1 Simulated Concentrated Water

The simulated concentrated water (SCW) was formulated to simulate the concentrating of well J-13 type water, i.e. a bicarbonate base water, by a factor of 1000. The concentration factor is the ratio of the volume of water in the "initial" solution to that in the "concentrated" solution. The resulting solution is depleted in Ca and Mg, and has a moderately high pH (9-10). The carbonate/bicarbonate concentration is depleted to accommodate to calcium and magnesium carbonate precipitation. The anions, Cl, F, NO_3, and SO_4, and the cations, Na and K, are concentrated to the full extent. This type of water is meant to simulate evaporatively concentrated waters.

6.12.2 Simulated Dilute Water

The simulated dilute water (SDW) was formulated to simulate the concentrating of well J-13 type water, i.e. a bicarbonate base water, by a factor of 10. This type of water might exist on the DS and WPOB under conditions where the temperature difference between the EBS components and their surrounding environment is small or where the evaporation rate of the water contacting the DS and WPOB is less than the flux to the surfaces.

6.12.3 Simulated Acidic Water

The simulated acidic water (SAW) was formulated to have an ionic content similar to the SCW solutions, but to be acidic (pH 2.7). It was initially meant to simulate conditions where the bicarbonate water had become acidified. Under this condition the bicarbonate would be removed as gaseous CO_2 and the fluoride ion removed as gaseous HF. In effect it also simulates waters that form a non-bicarbonate/carbonate base brine with sodium and potassium as the major cations. According to the analysis in Sections 6.5 and 6.6 this type of water is plausible at Yucca Mountain.

6.12.4 Simulated Saturated Water

To estimate the upper bound for the boiling point of waters that might contact the DS and WPOB surfaces, the following scenario is postulated. In the near field, refluxing of water along the

fractures will result in the chromatographic separation of the salts by their hygroscopic and solubility characteristics. That is, the salts will separate with the most soluble and hygroscopic salts migrating to the regions of lowest *RH*, while the least soluble and hygroscopic will remain in the regions of highest *RH*.

In terms of the salts present in the waters at Yucca Mountain, it is expected that the chloride and nitrate salts of sodium and potassium are the most likely to be the most soluble and hygroscopic salts remaining in solution upon concentrating Yucca Mountain type water. During the initial concentrating of the Yucca Mountain water, the calcium and magnesium ions are expected to form rather insoluble carbonate and silicate precipitates. With the calcium and magnesium ions removed from solution, it is the chloride, fluoride, sulfate, and nitrate salts of sodium and potassium that will remain in solution. As shown in Table 9, NaF has very limited solubility, and the sulfate salts of Na and K also have limited solubilities.

It is expected that further concentration of the aqueous solution would ultimately result in nitrate-based solution with small amounts of other ions, most notably the chloride ions. In order for the solution to remain aggressive toward corrosion, it was decided that the solution, in addition to being a high-temperature boiling solution, must also contain an aggressive ion, such as chloride. It was decided that the aggressive high-boiling solution would be a mixture of chloride and nitrate salts of potassium and sodium. In the formulation of this solution, the total salt content was chosen to be below the saturation limit in order to maintain an oxygen content that would contribute to aggressiveness of the solution. The oxygen solubility in this type of solution has not been characterized as a function of salt content.

At 100°C, the solution was made by formulating a saturated solution of $NaNO_3$ and then adding an additional amount of KCl. The amount of KCl added corresponded to a Cl ion concentration of 3.6 M. Similarly, at 120°C, the solution was made by increasing the $NaNO_3$ nearly to its saturation limit and then adding the amount of KCl that produces a Cl ion concentration of 4.3 M.

6.12.5 Basic Saturated Water (BSW)

The Basic Saturated Water solutions were formulated to simulate the extreme concentrating of bicarbonate/carbonate base waters. The BSW formulation with carbonate and silicate, BSW-CS (Table 26), is based on experimental evaporative concentration results. The major anions in this test solution are chloride, nitrate, and carbonate, and the major cations are sodium and potassium. The pH of this solution is determined by the sodium carbonate addition.

In order to simulate conditions where the solution pH is very high due to the very low partial pressure of CO_2, BSW solutions were formulated without carbonate and silicate, and with various amounts of NaOH for pH determination (Table 27). The boiling points of these solutions are nominally 111-112°C. High values of pH were used in order to simulate very alkaline conditions. Gaseous CO_2 is excluded so that pH remains stable. At pH > 10 there is a direct reaction of CO_2 with OH^- with the consequent decrease in pH (Cotton and Wilkinson 1988):

$$CO_2 + OH^- \Rightarrow HCO_3^-$$

$$HCO_3^- + OH^- \Rightarrow CO_3^{2-} + H_2O$$

In addition other anions, HCO_3/CO_3 and the various forms of silica, which may affect the solution pH are excluded.

6.13 REPRESENTATIVENESS OF PROPOSED WATER CHEMISTRIES

It is expected that the aqueous solution chemistry of the waters that contact the DS and WPOB will vary throughout the potential repository. No attempt has been made to understand how this chemistry variation in terms of specific compositions or ionic strengths of the solutions would affect the solutions that develop on the EBS components. Instead a characterization of the general type of solution chemistry that would develop on the DS and WPOB surfaces was made in terms of the concentrated solutions (brines) that would develop on these surfaces. It is the relative ratios of specific cations and anions that determine the type of brine that would form. The brines would form due to the temperature differences between the EBS components and their surroundings.

The types of brines that would form based on the types of waters at Yucca Mountain were postulated in Section 6.6. Examples of the two "representative" waters at Yucca Mountain were used in the analysis.

In this AMR, bounding aqueous solution chemistries and less concentrated solution chemistries were postulated and have been used in experimental corrosion testing. The characterization of the responses of these solutions to environmental parameters, such as, the partial pressure of CO_2 was given.

7. CONCLUSIONS

This AMR presents analysis to determine the types of concentrated aqueous solutions that will evolve on these EBS components based on the types of waters which are characteristic of the Yucca Mountain region. The characteristics of the brines that will evolve on the DS and WPOB are determined by: the relative ratios of the ionic species of the waters that contact these components and / or of the salts that have been deposited on them; the temperature (T) of these components; the effective *RH* at these components; and the gas phase composition (in particular, the CO_2 partial pressure).

There are several plausible scenarios for aqueous solution formation on the EBS components. These include seepage flow into the drifts, episodic water flow, and water sorption by deposited hygroscopic salts. Hygroscopic salts may be deposited either by complete evaporation of water that contacts the EBS components, or from dust or aerosols entrained in the drift air (for example, in the ventilation air).

Waters that form on the DS and WPOB at elevated temperatures will be concentrated because the effective *RH* at these components will be below 100% and at times may be significantly below 100%. The degree of concentration increasing with decreasing *RH* until the deliquescence point is reached. At *RH*s below the deliquescence point, aqueous salt solutions are not thermodynamically stable therefore only precipitated salts are present.

The waters at Yucca Mountain are classified into two types: 1) saturated zone water and perched water in the unsaturated zone, and 2) unsaturated zone porewater. A saturated zone water, J-13 well water, was theoretically shown to evolve by evaporative concentration into a high pH, Na-CO_3-Cl-SO_4-(NO_3) brine. Experimentally, a simulated J-13 well water was determined to evolve into the same type of brine. Theoretical analysis of unsaturated zone, pore water showed that these waters evolve by evaporative concentration into near neutral pH, Na-Mg-SO_4-Cl brine. However this latter analysis is tentative because of the incomplete experimental analysis of the porewaters. For this type of analysis it is worth noting that neither the initial ionic strength of these waters nor their exact composition is critical to assessing the type of brine that forms. What is critical is the relative amounts of calcium, magnesium, carbonate alkalinity, and sulfate which determine the characteristics of the brines that would form.

With extensive boiling/evaporative concentrating, a simulated J-13 well water forms an alkaline brine with high chloride and nitrate content. This type of aqueous solution is expected to form whenever the environmental conditions (low *RH*) exist such that the solutions become so concentrated that other less soluble salts precipitate out of solution. As the RH increases at a given temperature the solutions will become more dilute and the less soluble salts (sulfates and fluorides) will begin to dissolve.

The partial pressure of CO_2 will strongly influence the pH of the aqueous solutions. Under very low CO_2 partial pressure sodium carbonate solutions will become very alkaline. Similarly under boiling conditions, volatile gases, such as CO_2, will be stripped from the aqueous solution and high pH solutions can evolve from sodium carbonate solutions. However, boiling will result in complete evaporation of the water and deposition of salt scale.

This report describes bounding types of aqueous solution chemistries for waters that will contact the EBS components. These are bounding in terms of ionic strength and boiling point. The variation in alkaline pH with the partial pressure of CO_2 is also considered a bounding case. This report also describes several other types of aqueous solutions chemistries of waters that will contact the EBS components under non-bounding but expected conditions. These aqueous solutions used in corrosion testing of candidate materials for the DS and WPOB.

From the evaporative concentration of well J-13 type waters, the hygroscopic salts with the lowest deliquescence points that are formed are nitrate salts of potassium and sodium. The deliquescence points for both of these salts decrease with increasing temperature. For the purposes of these analyses it is conservatively assumed that hygroscopic salts will be present on the surfaces of the DS and WPOB in the post closure period regardless of whether there is dripping water or not. It is also assumed that aqueous solution formation is determined by the deliquescence of $NaNO_3$. The presence of backfill is not expected to significantly effect the relative humidity at which the formation of aqueous films occurs on the EBS components. The temperature-dependent, deliquescence points of $NaNO_3$ are recommended to set the conditions where aqueous electrochemical corrosion processes will occur on the EBS components. The DTN associated with the curve fit of the literature data is LL991208205924.096.

The presence of certain backfill material may influence the aqueous solution chemistry. The dissolution of silica may limit the alkaline pHs caused by concentration of sodium carbonate solutions. Carbonate buffers may limit the acidification of near neutral pH aqueous solutions

caused by hydrolysis of metal ions, which result from corrosion. To understand the extent that these effects will occur, further investigation under expected repository conditions is required.

7.1 TBVs AND TBDs

The analysis presented in this report is not effected by TBD-234. This TBD specifies the EBS component temperatures and the corresponding relative humidity at the EBS components. This report considers the temperature-relative humidity conditions that are physically accessible under the potential repository conditions. Bounding conditions were considered. The deliquescence points of hygroscopic salts determine when aqueous solutions will be present on the EBS components. The boiling point elevation of aqueous salt solution was presented along with the corresponding solution composition. Aqueous solution characteristics under non-bounding conditions were also presented.

7.2 UNCANISTERED SPENT NUCLEAR FUEL DISPOSAL CONTAINER SYSTEM DESCRIPTION DOCUMENT CRITERIA

The "System Environment Criteria" in *the Uncanistered Spent Nuclear Fuel Disposal Container System Description Document* (CRWMS M&O 1999e) specifies "the waste package shall meet all performance requirements during and after exposure to emplacement drift external environments identified in Table I-7." Table I-7 is reproduced in Section 4.2 CRITERIA. A pH range of 8.2-10.2 is specified for the environment. This AMR theoretically and experimentally investigated the evolution of brines from dilute waters that have been sampled at Yucca Mountain. The pH of the evolved brines was determined to vary from near neutral to very alkaline. The near neutral pH brines evolve from porewater type waters. The very alkaline brines evolve from sodium carbonate waters. Perched waters in the unsaturated zone are sodium carbonate base. The pH of these brines is determined by the sodium carbonate/bicarbonate content. A 0.1N Na_2CO_3 solution has pH 11.6 (Weast and Astle 1981, p. D-127). Carbonate concentrations in excess of 0.1N have been determined experimentally during the evaporative concentration of the sodium carbonate base water. Based on this AMR the solution pH of the brines that evolve on the EBS components are expected to be outside of the range specified by the "System Environment Criteria" in *the Uncanistered Spent Nuclear Fuel Disposal Container System Description Document* (CRWMS M&O 1999e).

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