General and Localized Corrosion of the Drip Shield

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by

Joseph C. Farmer, John C. Estill, and R. Daniel McCright

August 1999

**Lawrence Livermore National Laboratory
Livermore, California**

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ABBREVIATIONS AND ACRONYMS

AFM	Atomic Force Microscope
AMR	Analyses and Models Report
CP	Cyclic Polarization
DOX	Dry Oxidation
DS	Drip Shield
DTN	Data Tracking Number
EBS	Engineered Barrier System
FW	Formula Weight
GC	General Corrosion
HAC	Humid Air Corrosion
LC	Localized Corrosion
LLNL	Lawrence Livermore National Laboratory
LTCTF	Long Term Corrosion Test Facility
M&O	Management and Operating Contractor
NHE	Normal Hydrogen Electrode
PMR	Process Model Report
RH	Relative Humidity
SCC	Stress Corrosion Cracking
SCE	Saturated Calomel Electrode
SAW	Simulated Acidic Concentrated Water
SCW	Simulated Concentrated Water
SDW	Simulated Dilute Water

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SSW	Simulated Saturated Water
WF	Waste Form
WP	Waste Package
WPOB	Waste Package Outer Barrier
XRD	X-ray diffraction

1. PURPOSE

1.1 ANALYSES AND MODELS REPORT

The purpose of the process-level model is to account for both general and localized corrosion of the Drip Shield (DS), which is assumed to be a titanium alloy. This model will include several sub-models, which will account for dry oxidation, humid air corrosion, general corrosion in the aqueous phase, and localized corrosion in the aqueous phase. This Analyses and Models Report (AMR) serves as a feed to the Waste Package Degradation Process Model Report (PMR) and Model Abstraction for WAPDEG.

1.2 BACKGROUND ON ALLOY 22

Titanium alloys are now being considered for construction of the DS. The current recommendation is to use Ti Gr 7 [UNS R52400; 0.03% N (max.), 0.10% C (max.), 0.015% H (max.), 0.25% O (max.), 0.30% (max.) Fe, 0.12-0.25% (max.) Pd, 0.1% Residuals (max.), 0.4% Residuals (total), and Ti (bal.)]. A similar material used in the testing program is Ti Gr 16, which has 0.04 to 0.08 % Pd. These materials are reviewed elsewhere (Pasupathi 1999; Gdowski 1991). The unusual corrosion resistance of these titanium alloys is apparently due to the formation of a passive film of TiO_2 , which is stable over a relatively wide range of potential and pH (Pourbaix 1974). Corrosion tests of Ti Gr 16 have been conducted in the Project's Long Term Corrosion Test Facility (LTCTF) (Estill 1998). Test media used in this facility include Simulated Acidic Concentrated Water (SAW), which is about one-thousand times more concentrated than the ground water at Yucca Mountain (J-13 well water), and has been acidified to a pH of approximately 2.7. The rates of general corrosion and oxidation of this material have been shown to be very low.

1.3 ENVIRONMENT

The DS will experience a wide range of conditions during its service life. Initially, the underlying high-level waste containers will be relatively hot. The DS surface may be kept dry by the heat generated from radioactive decay. However, the temperature will eventually drop to levels where both humid air and aqueous phase corrosion will be possible. Crevices will be formed between the DS and its support structure on the invert. Crevices may also form between the DS and mineral precipitates, corrosion products, dust, rocks, cement and biofilms. If the DS settles or collapses, crevices may even form with the WP. There has been concern that the crevice environment may be more severe than the near field environment (NFE). The hydrolysis of dissolved metal can lead to the accumulation of H^+ and a corresponding decrease in pH. Field-driven electromigration of various anions into the crevice must occur to balance cationic charge associated with H^+ ions (Gartland 1997; Walton et al. 1996; Shoesmith 1995). These exacerbated conditions can set the stage for subsequent attack of this corrosion resistant material (CRM) by passive corrosion, pitting (initiation & propagation), hydrogen induced cracking (HIC), stress corrosion cracking (initiation & propagation), or other mechanisms.

1.4 RELATIONSHIP TO PRINCIPAL FACTORS

Degradation of the DS is key to understanding one of the most important *principal factors* in repository performance. This principal factor is the amount water transmitted through openings in the DS to the outer surface of the WP. This flux of water will ultimately determine the rate of release of radionuclides out. Once water contacts (touches) the surface of the WP, its fate becomes intertwined with that of the WP. The models and supporting experimental data to account for both DS and WP degradation, as well as the evolution of water involved in the various degradation processes, have been developed by Waste Package Operations (WPO). These models and supporting experimental data are reported in two Process Model Reports (PMRs), one for the WP and another for the WF (Waste Form). The Analyses and Models Reports (AMRs) comprising the WP PMR address the development of realistic models to account for the degradation of the outer barrier of both the DS and WP, based upon data generated by the Project.

2. QUALITY ASSURANCE

2.1 PROCEDURE FOR ANALYSES AND MODELS (AP-3.10Q)

This work has been accomplished in accordance with Quality Assurance Requirements and Description (QARD) requirements as implemented by the Lawrence Livermore National Laboratory (LLNL) Yucca Mountain Project (YMP) Quality Procedures (QPs). This Analysis of Model Report (AMR) has been developed in accordance with Yucca Mountain Site Characterization Project Procedure entitled, "Analyses and Models" (AP-3.10Q, Revision 0, ICN 0).

2.2 ACTIVITY PLANS (E-20-43/44, E-20-50, E-20-69, E-20-70 AND E-20-81)

Threshold potentials were determined in accordance with Activity Plan AP-E-20-43/44. General corrosion rates in environments relevant to the repository were determined in accordance with Activity Plan AP-E-20-50. Activities E-20-43/44 and 50 are described in greater detail in the Scientific Investigation Plan (SIP) for Metal Barrier Selection and Testing (SIP-CM-01, Rev. 3). The procedures are compliant to the Office of Civilian Radioactive Waste Management (OCWRM) Quality Assurance (QA) Requirements.

3. COMPUTER SOFTWARE AND MODEL USAGE

3.1 SOFTWARE APPROVED FOR QA WORK

No such software was required in support of the model presented here.

3.2 SOFTWARE ROUTINES

Calculations used to manipulate raw data were performed electronically in spreadsheets created with Microsoft Excel 97. The Microsoft Excel 97 that was used was bundled with Microsoft Office 97 Professional Edition for Windows 95/NT or Workstation 4.0 (SN # 269-056-174). All spreadsheets have been assigned data tracking numbers, as shown in the Data Inventory provided as an attachment as per Section 9.0. Electronic copies of these spreadsheets and supporting data are provided on a 100 megabyte IBM-formatted ZIP disk provided as an attachment as per Section 9.0.

4. INPUTS

4.1 PARAMETERS

4.1.1 Definition of Parameters

a	dimension of weigh loss sample
b	dimension of weight loss sample
c	dimension of weight loss sample
b_0	coefficient in regression equation
b_1	coefficient in regression equation
b_2	coefficient in regression equation
$f(y)$	probability density function
i_{corr}	corrosion current density
i_{pass}	passive current density
k	parabolic rate constant in dry oxidation model
p	wall penetration due to corrosive attack
t	exposure time during weight loss measurement
t	time in dry oxidation model
u_i	mobility of the i^{th} ion
w	measured weight loss
w_{oxide}	formula weight of oxide formed during dry oxidation
x	independent variable in regression equation
x	oxide thickness in dry oxidation model
x_i	measured parameter in sensitivity (error) analysis
y	dependent variable in regression equation
y	computed value in sensitivity (error) analysis
z_i	valence (charge) of the i^{th} ion
$C_i(\alpha)$	molar concentration of the i^{th} ion in alpha phase
$C_i(\beta)$	molar concentration of the i^{th} ion in the beta phase
D_{oxide}	diffusivity of reacting species through protective oxide
E_{corr}	corrosion potential
$E_{critical}$	critical potential – threshold for localized attack
E_j	junction potential – correction for reference electrode junction
F	Faraday's constant
J_{oxide}	flux of reacting species through protective oxide
R	universal gas constant
R^2	regression coefficient
RH	relative humidity
$RH_{critical}$	threshold relative humidity for humid air corrosion
T	temperature

σ	standard deviation
μ	mean
ρ	density of Alloy 22
ρ_{oxide}	density of oxide formed during dry oxidation
ζ_{oxide}	stoichiometric coefficient for dry oxidation reaction

4.1.2 Determination of Input Parameters

Input for this AMR includes bounding conditions for the local environment on the DS and WP surfaces, which include temperature, relative humidity, wetness (whether or not liquid phase water is present), electrolyte concentration in the liquid phase (chloride, buffer and pH), and oxidant level. The detailed evolution of the environment on the DS surface is defined by a companion AMR entitled "Environment on the Surface of Drip Shield and Waste Package Outer Barrier" (Gdowski 1999). This work has been used to define the threshold relative humidity for humid air and aqueous phase corrosion, as well as a medium for testing Waste Package (WP) materials under what is now believed to be a worst-case scenario. This test medium is presented here as Simulated Saturated Water (SSW), and has a boiling point of approximately 120°C.

As discussed in Section 6.4.1 of the AMR on environment (Gdowski 1999), hygroscopic salts may be deposited by aerosols and dust, and may be introduced with the backfill. They will be contained in seepage water that enters the drifts and the episodic water that flows through the drifts. Such hygroscopic salts enable aqueous solutions to exist at relative humidities below 100%. The threshold relative humidity (RH_{critical}) at which an aqueous solution can exist is defined as the deliquescence point. This threshold defines the condition necessary for aqueous electrochemical corrosion processes of a metal with salt deposits to occur at a given temperature. The deliquescence point of NaCl is relatively constant with temperature, and varies from 72 to 75%. In contrast, the deliquescence point of NaNO_3 has a strong dependence on temperature, ranging from an RH of 85% at 20°C to 70% at 90°C. The implied equilibrium RH is 50.1% at 120.6°C. The primary uncertainty in the threshold RH for humid air and aqueous phase corrosion is due to the presence of nitrate. For the time being, this threshold will be assumed to obey the following quadratic in temperature, which is a fit of the data deliquescence point data for NaNO_3 .

$$RH_{\text{critical}} = -0.0045 \times T(^{\circ}\text{C})^2 + 0.2797 \times T(^{\circ}\text{C}) + 81.203 \quad (4-1)$$

As discussed in Section 6.5.2 of the AMR on environment (Gdowski 1999), the evaporative concentration of J-13 water results in the concentration of Na^+ , K^+ , Cl^- , and NO_3^- . The concentration of HCO_3^- reaches a constant level, while the concentrations of F^- and SO_4^{2-} initially increase, but eventually fall due to precipitation. Ultimately, the F^- drops below the level of detection. The Simulated Saturated Water (SSW) used for testing is an abstract embodiment of this observation. The SSW formulation is based upon the assumption that evaporation of J-13 eventually leads to a sodium-potassium-chloride-nitrate solution. The absence of sulfate and carbonate in this test medium is believed to be conservative, in that carbonate would help buffer pH in any occluded geometry such as a crevice.

Experimental data from the scientific and technical literature, the Long Term Corrosion Test Facility (LTCTF) and Cyclic Polarization (CP) measurements and crevice corrosion experiments at both LLNL are used as a basis for this process level model.

4.2 CRITERIA

The DS is intended to extend the life of the WP so that necessary performance requirements can be met. The applicable requirements reproduced below are from Section 1.2, "System Design Criteria" of Uncanistered Spent Nuclear Fuel Disposal Container System Description Document (CRWMS 1999).

"The disposal container shall be designed such that no more than 1 percent of all waste packages breach during the first 1,000 years after emplacement (breaching is defined as an opening through the wall of the waste package through which advective or diffusive transport of gas or radionuclides can occur)." (Section 1.2.1.1)

"The disposal container shall be designed such that for 10,000 years after permanent closure of the repository the release rate of any radionuclide from all waste packages shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1 percent of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay." (Section 1.2.1.4)

The analyses contained in this AMR serve as a basis to determine whether or not the performance requirements for the DS can be met. The performance requirements of the DS are dependent upon the requirements for systems in the repository.

4.3 CODES AND STANDARDS

4.3.1 Standard Test Media

G. E. Gdowski, Formulation and Make-up of Simulated Dilute Water (SDW), Low Ionic Content Aqueous Solution, Yucca Mountain Project, Lawrence Livermore National Laboratory, Livermore, CA, TIP-CM-06, Revision CN TIP-CM-06-0-2, April 4, 1997, Table 1, p. 3.

G. E. Gdowski, Formulation and Make-up of Simulated Concentrated Water (SCW), High Ionic Content Aqueous Solution, Yucca Mountain Project, Lawrence Livermore National Laboratory, Livermore, CA, TIP-CM-07, Revision CN TIP-CM-07-0-2, April 4, 1997, Table 1, pp. 3-4.

G. E. Gdowski, Formulation and Make-up of Simulated Acidic Concentrated Water (SAW), High Ionic Content Aqueous Solution, Yucca Mountain Project, Lawrence Livermore National Laboratory, Livermore, CA, TIP-CM-08, Revision CN TIP-CM-08-0-2, April 4, 1997, Table 1, p. 3.

4.3.2 Cyclic Polarization Measurements

Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements, Designation G 5-87, 1989 Annual Book of ASTM Standards, Section 3, Vol. 3.02, pp. 79-85.

4.3.3 General Corrosion Measurements

Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, Designation G 1-81, 1987 Annual Book of ASTM Standards, Section 3, Vol. 3.02, pp. 89-94, Subsection 8 – Calculation of Corrosion Rate, Appendix X1 – Densities for a Variety of Metals and Alloys.

5. ASSUMPTIONS

5.1 DRY OXIDATION

Dry oxidation is assumed to occur at any relative humidity (RH) below the threshold for humid air corrosion (HAC):

$$RH < RH_{critical} \quad (5-1)$$

This threshold RH for HAC ($RH_{critical}$) is assumed obey Equation 4-1, which is based upon the AMR entitled "Environment on the Surface of Drip Shield and Waste Package Outer Barrier" (Gdowski 1999). This process is assumed to result in the formation of an adherent, protective oxide film of uniform thickness. The rate of dry oxidation will be assumed to be limited by mass transport through the growing metal oxide film. Consequently, the oxide thickness will obey the following parabolic growth law (film thickness proportional to the square root of time). Reasonable values of the parabolic rate constant will be assumed, as discussed in Section 6.1.

5.2 HUMID AIR CORROSION

HAC is assumed to occur at any RH above the threshold, provided that there is no dripping:

$$RH \geq RH_{critical} \quad (5-2)$$

This threshold RH for HAC ($RH_{critical}$) is assumed to obey Equation 4-1, which is based upon the AMR entitled "Environment on the Surface of Drip Shield and Waste Package Outer Barrier" (Gdowski 1999). As a bounding worst-case assumption, it will be assumed that the rate of HAC is identical to the largest observed rate for aqueous phase corrosion during the period where HAC is operable. It will also be assumed that the corrosion rate is constant, and does not decay with time. Less conservative corrosion models assume that the rate decays with time.

5.3 AQUEOUS PHASE CORROSION

At a given surface temperature, the existence of liquid-phase water on the DS depends upon the presence of a salt and mineral deposit. In the presence of such a deposit, a liquid-phase can be established at a higher temperature than otherwise possible. In the model discussed here, it is assumed that two conditions must be met for aqueous phase corrosion: dripping water; and RH above the deliquescence point of the deposit at the temperature of the DS surface.

$$RH \geq RH_{critical} \quad (5-3)$$

This threshold RH for HAC ($RH_{critical}$) is assumed obey Equation 4-1, which is based upon the AMR entitled "Environment on the Surface of Drip Shield and Waste Package Outer Barrier" (Gdowski 1999). For the time being, the composition of the electrolyte formed on the DS surface is assumed to be that of SCW below 100°C, and that of Simulated Saturated Water (SSW) above 100°C. It will be assumed that the corrosion rate is constant, and does not decay

with time. Less conservative corrosion models assume that the rate decays with time.

5.4 DRIPPING CONDENSATE FROM INNER SURFACE OF DRIP SHIELD

Once the temperature of the DS drops below the dew point, condensation can occur on the inner surface. While clinging to the underside of the WP, it will be assumed that this electrolyte is essentially pure water. As a worst case scenario, measurements made with SDW will be used as the basis of model predictions. Ultimately, this condensate can then form droplets that fall and impinge the underlying WP surface, provided that the droplets are sufficiently large so that they can fall through the temperature gradient towards the WP without complete evaporation.

5.5 FLOW THROUGH OPENINGS BETWEEN DRIP SHIELDS

It is believed that the final analysis will show that general corrosion does not limit the life of the DS and that no significant LC occurs. However, ground movement may cause displacement of adjacent drip shields along the drift axis, thereby opening pathways that enable dripping water to reach the WP. Such displacement may also lead to sufficient stress to cause either SCC or HIC, and a more catastrophic failure of the DS. For a given mass flow of water contacting the outer surface of the DS, the fraction passing through an opening to the WP is assumed to be proportional to the following multiplication factor (Θ_{shield}):

$$\Theta_{shield} = \frac{A_{opening}}{A_{shield}} \quad (5-4)$$

where $A_{opening}$ is the projected area of the opening on the floor of the drift, and A_{shield} is the projected area of the DS on the floor of the drift. If the DS fails due to SCC, a multiplication factor of one will be assumed.

5.6 THRESHOLD FOR LOCALIZED CORROSION

If the open circuit corrosion potential (E_{corr}) is less than the threshold potential for localized corrosion ($E_{critical}$), it will be assumed that no localized corrosion occurs.

$$E_{corr} < E_{critical} \quad (5-5)$$

Threshold values have been determined for various representative environments, as discussed in Section 6.4.

5.7 EFFECT OF GAMMA RADIOLYSIS ON CORROSION POTENTIAL

It will be assumed that the effects of oxidant can be accounted for through the open circuit corrosion potential (E_{corr}). Based upon published data described in Section 6.5.2, it is believed that the shift in corrosion potential due to gamma radiolysis will be much less than 200 mV.

5.8 MICROBIAL GROWTH

In the present model, it is assumed that the effect of microbial growth on corrosion potential is not significant. In general, titanium is very resistant to microbial influenced corrosion (MIC).

5.9 PHASE INSTABILITY

Pure titanium is an allotropic element, meaning that it has more than one crystallographic form (Gdowski 1997). Above 883°C it has the body-centered cubic (bcc) crystal structure, which is called the beta (β) phase. Below 883°C, it transforms to a hexagonal closed-packed (hcp) structure, which is called the alpha (α) phase. Both Ti Grs 7 and 16 are α -phase alloys and have very small additions of Pd. The solubility of Pd in these materials is about 1 weight percent at 400°C. The nominal concentrations of Pd in both Ti Grs 7 and 16 are well below the solubility limit at this temperature (Gdowski 1997). Titanium-palladium intermetallic compounds capable of being formed in this system have not been reported to occur in Ti Gr 7 and 16 with normal heat treatments.

The temperature of the DS is limited by the temperature of the underlying WP. The transition from α - to β -phase titanium should not occur at these temperatures. As discussed in the companion AMR on general and localized corrosion of the Waste Package Outer Barrier (WPOB), it is assumed that the WP temperature is kept below 300°C. With this constraint, it is further assumed that the impact of aging and phase instability on the corrosion of Ti Gr 7 will be insignificant.

6. ANALYSIS

6.1 DRY OXIDATION

Dry oxidation is assumed to occur at any relative humidity (RH) below the threshold for HAC.

$$RH < RH_{critical} \quad (6-1)$$

This process is assumed to result in the formation of an adherent, protective oxide film of uniform thickness. It will be assumed that the protective oxide film is primarily TiO_2 . The oxidation reaction given as (Welsch et al. 1996):

The rate of dry oxidation will be assumed to be limited by mass transport through this growing metal oxide film. Fick's first law is applied, assuming a linear concentration gradient across the oxide film of thickness x :

$$J_{oxide} = -D_{oxide} \frac{\partial C}{\partial x} \approx -D_{oxide} \frac{\Delta C}{x} \quad (6-3)$$

where J_{oxide} is the molar flux of the reacting species in the oxide, D_{oxide} is the diffusivity of the reacting species in the oxide, ΔC is the corresponding differential molar concentration. Oxide growth is related to the flux by:

$$\frac{dx}{dt} = \frac{\zeta_{oxide} \times w_{oxide} \times J_{oxide}}{\rho_{oxide}} \quad (6-4)$$

where ζ_{oxide} is the stoichiometric coefficient (moles of oxide per mole of diffusing species), w_{oxide} is the formula weight of the oxide, and ρ_{oxide} is the density of the oxide. Integration shows that the oxide thickness should obey the following parabolic growth law (Wagner's Law), where the film thickness is proportional to the square root of time:

$$x = \sqrt{x_0^2 + k \times t} \quad (6-5)$$

where x_0 is the initial oxide thickness, x is the oxide thickness at time t , and k is a temperature-dependent parabolic rate constant. More specifically, k is defined as follows:

$$k = \frac{2 \times \zeta_{oxide} \times w_{oxide} \times D_{oxide} \times \Delta C}{\rho_{oxide}} \quad (6-6)$$

To facilitate an approximate calculation, published values of k_{pw} can be used (Welsch et al. 1996). From Figure 25 of this reference, it is concluded that all observed values of k_{pw} fall below a line defined by:

$$\log[k_{pw} (mg^2 cm^{-4} min^{-1})] = -4.004384 \times \left(\frac{1}{T(K)} \right) + 4.383507 \times 10^{-3} \quad (6-7)$$

where T is defined as the absolute temperature. This can be converted to the parabolic rate constant, k ($m^2 s^{-1}$), by dividing by the square of the density and multiplying by an appropriate correction factor. The density of TiO_2 is approximately $4.26 g cm^{-3}$ (CRC 1978-79 p. B178). The highest temperature is expected to be approximately $350^\circ C$ (623 K), which corresponds to the limit for the fuel cladding. The value of k_{pw} corresponding to this upper limit is $0.9953 mg^2 cm^{-4} min^{-1}$. The corresponding value of k is $9.14 \times 10^{-14} m^2 s^{-1}$ (2.88×10^6 square microns per year). Thus, a layer of TiO_2 could grow to a thickness of 1698 microns after one year at $350^\circ C$ (about 1698 microns per year). Given how high this rate is, it is recommended that dry oxidation of the Ti Gr 7 be accounted for through application of the parabolic law. The above expression represents a conservative upper bound, based upon the published literature. Actually values of the rate constant may be less by an order of magnitude.

6.2 HUMID AIR CORROSION

HAC is assumed to occur above a threshold RH, provided that there is no dripping:

$$RH \geq RH_{critical} \quad (6-8)$$

This threshold RH for HAC ($RH_{critical}$) is assumed obey Equation 4-1, which is based upon the AMR entitled "Environment on the Surface of Drip Shield and Waste Package Outer Barrier" (Gdowski 1999). The existence of this threshold is due to the dependence of water adsorption on RH.

Despite significant experimental work, there continues to be significant uncertainty in the threshold RH for humid air and aqueous phase corrosion. Furthermore, other sources of data indicate that it may be reasonable to consider HAC at a relative humidity below that predicted with Equation 4-1 at $20^\circ C$. The approximate number of water monolayers on typical metal surfaces as a function of RH is given by Leygraf (1995) and repeated in Table 6-1 of the companion AMR on the general and localized corrosion of the WPOB (Farmer et al. 1999). Based upon this data, it is reasonable to consider the possibility of HAC at only 40% RH. This is the point at which it may be possible for two monolayers of water can exist on the WP surface. It is therefore recommended that a sensitivity analysis be performed. During this analysis, it should be assumed that the threshold is uniformly distributed between 40 to 100% RH, limits corresponding to the 0th and 100th percentiles, respectively.

It will be assumed that HAC can be treated as uniform general corrosion. As a bounding worst-case assumption, it will be assumed that the rate of HAC is identical to the largest observed rate for aqueous phase corrosion during the period where HAC is operable. It will also be assumed that the corrosion rate is constant, and does not decay with time.

6.3 AQUEOUS PHASE CORROSION

At a given surface temperature, the existence of liquid-phase water on the WP depends upon the presence of a salt and mineral deposit. In the presence of such a deposit, a liquid-phase can be established at a higher temperature than otherwise possible. In the model discussed here, it is assumed that two conditions must be met for aqueous phase corrosion: dripping water; and RH above the deliquescence point of the deposit at the temperature of the WP surface.

$$RH \geq RH_{critical} \quad (6-9)$$

This threshold RH for HAC ($RH_{critical}$) is assumed obey Equation 4-1, which is based upon the AMR entitled "Environment on the Surface of Drip Shield and Waste Package Outer Barrier" (Gdowski 1999). For the time being, the composition of the electrolyte formed on the WP surface is assumed to be that of SCW below 100°C, and that of SSW above 100°C. It will be assumed that the corrosion rate is constant, and does not decay with time. Less conservative corrosion models assume that the rate decays with time.

6.4 LOCALIZED CORROSION

6.4.1 Threshold Potential for Ti Gr 7

The localized corrosion model for the titanium DS assumes that localized attack occurs if the open circuit corrosion potential (E_{corr}) exceeds the threshold potential for breakdown of the passive film ($E_{critical}$):

$$E_{corr} \geq E_{critical} \quad (6-10)$$

6.4.2 Cyclic Polarization in Synthetic Concentrated J-13 Waters

The Project has used cyclic polarization (CP) to determine threshold potentials for titanium alloys in various test media relevant to the environment expected in the repository. Relevant test environments are assumed to include Simulated Dilute Water (SDW), Simulated Concentrated Water (SCW) and Simulated Acidic Concentrated Water (SAW) at 30, 60 and 90°C, as well as Simulated Saturated Water (SSW) at 100 and 120°C. The compositions of the first three environments are given in Tables 6-3 and 6-4 of the AMR on general and localized corrosion of the WPOB (Farmer et al. 1999). The compositions of these test media are based upon the work of Gdowski as documented in TIP-CM-06 Rev. 0 (Gdowski 1997a), TIP-CM-07 Rev. 0 (Gdowski 1997b) and TIP-CM-08 Rev. 0 (Gdowski 1997c). The SSW composition has been recently developed and is documented in a companion AMR on the subject of WP surface environment (Gdowski 1999).

Cyclic polarization measurements have been based on ASTM G 5-87 [ASTM 1989a]. Any necessary deviations are noted in the corresponding Scientific Notebooks. Representative cyclic polarization curves are shown in Figures 6-1 through 6-5 of this report. In general, these curves exhibit complete passivity (no passive film breakdown) between the Corrosion Potential and the point defined as Threshold Potential 1. Threshold Potential 1 is in the range where the onset of

oxygen evolution is expected and is defined by a large excursion in anodic current.

6.4.3 Correlation of Potential vs. Temperature Data for Various Test Media

Values of corrosion and threshold potentials have been correlated as a function of temperature for the conditions of interest. These correlated data are shown in Figures 6-6 through 6-9. In general, it has been found that these potential verses temperature data can be represented by the following simple regression equation:

$$y = b_0 + b_1x + b_2x^2 \quad (6-11)$$

where y is either the corrosion or threshold potential (mV vs. Ag/AgCl), and x is the temperature ($^{\circ}\text{C}$). The correlations for E_{corr} and $E_{critical}$ are summarized in Table 6-1.

It is assumed that the specifications for the DS material include allowable values for E_{corr} and $E_{critical}$. Acceptance of the material requires that: (1) the measured value of E_{corr} in a particular environment cannot exceed the value calculated with the corresponding correlation in Table 6-1 by more than 325 mV; and (2) the measured value of $E_{critical}$ in a particular environment cannot be less than the value calculated with the corresponding correlation in Table 6-1 by more than 325 mV.

The correlations given in Table 6-1 were used to calculate the values of E_{corr} and $E_{critical}$ shown in Table 6-2 for SDW, SCW, SAW and SSW. Table 6-2 shows the difference between E_{crit} and E_{corr} (column heading *Diff.*) is never less than 651 mV between 20 and 150 $^{\circ}\text{C}$. Therefore, implementation of the potential-based specification will prevent the use of heats of material that would be prone to passive film instability or localized corrosion. The cost of such performance would be associated with the quantity of rejected material (assumed to be approximately 20%). The specification can be changed to allow more material to be accepted, but with greater risk of localized corrosion.

In an ideal case, the crevice corrosion temperature can be estimated from the intersection of the lines representing the corrosion and threshold potentials at elevated temperature. To force crevice corrosion to occur in the model, E_{corr} and $E_{critical}$ can simply be equated over temperature ranges of uncertainty (90 to 120 $^{\circ}\text{C}$). Additional data is needed to fill this void.

Figure 6 - 1. Titanium Grade 7 in SSW at 120 Centigrade (NEA031s) [DTN #].

Figure 6 - 2. Titanium Grade 7 in SAW at 90 Centigrade (NEA025) [DTN #].

Figure 6 - 3. Titanium Grade 7 in SCW at 90 Centigrade (NEA029) [DTN #].

Figure 6 - 4. Titanium Grade 7 in SCW at 60 Centigrade (NEA019) [DTN #].

Figure 6 - 5. Titanium Grade 7 in SCW at 90 Centigrade (NEA003) [DTN #].

Figure 6 - 6. Corrosion & Threshold Potentials of Titanium Grade 7 in SSW (NEA031s) [DTN #].

Figure 6 - 7. Corrosion & Threshold Potentials for Titanium Grade 7 in SAW [DTN #].

Figure 6 - 8. Corrosion & Threshold Potentials for Titanium Grade 7 in SCW [DTN #].

Figure 6 - 9. Corrosion & Threshold Potentials for Titanium Grade 7 in SDW [DTN #].

Table 6 - 1. Summary of Correlated Corrosion and Threshold Potential Data [DTN #]

Medium	Potential	Parameter	b ₀	b ₁	b ₂	R ²
SDW	Corrosion	E _{corr}	-24.154	-2.9462		0.7964
SDW	Threshold 1	E _{critical}	1161	-4.2111		0.9203
SCW	Corrosion	E _{corr}	14.444	-5.8056		0.8868
SCW	Threshold 1	E _{critical}	1084.3	-3.7278		0.7373
SAW	Corrosion	E _{corr}	-414.3	9.9833	-414.33	0.4127
SAW	Threshold	E _{critical}	1290.3	5	-0.0515	0.2468
SSW	Corrosion	E _{corr}	414	-6.25		None
SSW	Threshold 1	E _{critical}	1461	-5.4		None

Table 6 - 2. Values of E_{corr} and $E_{critical}$ Based on Correlated Cyclic Polarization Data [DTN #].

	SDW	SDW	SDW	SCW	SCW	SCW	SAW	SAW	SAW	SSW	SSW	SSW
T	E_{corr}	$E_{critical}$	Diff.	E_{corr}	$E_{critical}$	Diff.	E_{corr}	$E_{critical}$	Diff.	E_{corr}	$E_{critical}$	Diff.
°C	mV	mV	mV	mV	mV	mV	mV	mV	mV	mV	mV	mV
20	-83	1077	1160	-102	1010	1111	-248	1370	1617	289	1353	1064
30	-113	1035	1147	-160	972	1132	-189	1394	1583	227	1299	1073
40	-142	993	1135	-218	935	1153	-147	1408	1555	164	1245	1081
50	-171	950	1122	-276	898	1174	-121	1412	1533	102	1191	1090
60	-201	908	1109	-334	861	1195	-112	1405	1517	39	1137	1098
70	-230	866	1097	-392	823	1215	-119	1388	1507	-24	1083	1107
80	-260	824	1084	-450	786	1236	-143	1361	1504	-86	1029	1115
90	-289	782	1071	-508	749	1257	-183	1323	1506	-149	975	1124
100	-319	740	1059	-566	712	1278	-240	1275	1515	-211	921	1132
110	-348	698	1046	-624	674	1298	-313	1217	1530	-274	867	1141
120	-378	656	1033	-682	637	1319	-403	1149	1552	-336	813	1149
130	-407	614	1021	-740	600	1340	-509	1070	1579	-399	759	1158
140	-437	571	1008	-798	562	1361	-632	981	1613	-461	705	1166
150	-466	529	995	-856	525	1382	-771	882	1652	-524	651	1175

6.4.4 Correction of Measured Potential for Junction Potential

It is important to understand the error in the potential measurements due to the junction potential. A correction has been performed based upon the Henderson Equation (Bard and Faulkner 1980). Calculated values of the isothermal junction potentials are summarized in Table 6-7 of the AMR on general and localized corrosion of the WPOB (Farmer et al. 1999), which is repeated below at Table 6-3. The thermal gradient across the Luggin probe with saturated KCl should produce no significant potential.

Table 6 - 3. Summary of Junction Potential Corrections for Cyclic Polarization (Volts) [DTN #].

T (°C)	SDW	SCW	SAW	SSW
30	2.650E-03	2.729E-02	-3.550E-03	-2.291E-03
60	2.912E-03	2.999E-02	-3.902E-03	-2.518E-03
90	3.175E-03	3.269E-02	-4.253E-03	-2.745E-03

6.5 RATES OF GENERAL AQUEOUS-PHASE CORROSION

Localized corrosion (LC) rates will be assumed if the open circuit corrosion potential (E_{corr}) exceeds the threshold potential ($E_{critical}$). General corrosion (GC) rates will be assumed if the threshold potential is not exceeded. GC rates will be estimated with weight-loss data from the Long Term Corrosion Test Facility (LTCTF) (Estill 1998). LC rates and failure mode characteristics (e.g., number failure sites and opening size) will be estimated from experimental measurements of crevice corrosion made at LLNL. Since pitting has not been observed in laboratory experiments at LLNL, it will be assumed that the primary mode of LC is crevice corrosion. This APC model will be applied to each patch in the WAPDEG simulation. To the

extent possible, uncertainty will be estimated from available data.

6.5.1 Corrosion Rates Based Upon Electrochemical Measurements

The corrosion potential depends upon environment, and is illustrated by Figure 6-8. The local minima in current observed at the corrosion potential (circled) can be interpreted in terms of a penetration rate, provided that the current is due to dissolution. The corrosion (penetration) rate of an alloy can be calculated from the corrosion current density with the following formula (Jones 1996):

$$\frac{dp}{dt} = \frac{i_{corr}}{\rho_{alloy} n_{alloy} F} \quad (6-12)$$

where p is the penetration depth, t is time, i_{corr} is the corrosion current density, ρ_{alloy} is the density of the alloy, assumed to be approximately 4.54 g cm^{-3} , n_{alloy} is number of gram equivalents per gram of alloy, and F is Faraday's constant. The value of n_{alloy} can be calculated with the following formula:

$$n_{alloy} = \sum_j \left(\frac{f_j n_j}{a_j} \right) \quad (6-13)$$

where f_j is the mass fraction of the j -th alloying element in the material, n_j are the number of electrons involved in the anodic dissolution process, which is assumed to be congruent, and a_j is the atomic weight of the j -th alloying element. These equations have been used to calculate the penetration rate for Ti Gr 7 as a function of corrosion current density. The results of these calculations are shown in Tables 6-4 and 6-5. The penetration rate for this material is linearly proportional to current density and is estimated to be between 11.55 and 11.51 microns per year at one microamp per square centimeter. If the corrosion current is due to oxidation rather than dissolution, the penetration corresponds to the thickness of titanium metal converted to oxide. From Figures 6-1 through 6-5, it can be seen that typical values of the corrosion current density range from approximately $10^{-9} \text{ A cm}^{-2}$ to approximately $10^{-8} \text{ A cm}^{-2}$ (10^{-3} to $10^{-2} \text{ } \mu\text{A cm}^{-2}$). This corresponds to penetration (or oxidation) rates that range from 0.01 to 0.1 microns per year (10 to 100 nanometers per year). This is in reasonable agreement with the rates given in Section 6.5.2.

The corrosion and passive currents from cyclic polarization measurements in SDW, SCW, SAW and SSW are summarized in Figures 6-10 through 6-13. In general, it has been found that the current versus temperature data can be represented by one of the following linear regression equations. The linear and polynomial forms are both represented by:

$$y = b_0 + b_1 x + b_2 x^2 \quad (6-14)$$

The exponential form is represented by:

$$\ln y = \ln b_0 + b_1 \ln x \quad (6-15)$$

where y is the passive current (A) and x is the temperature ($^{\circ}\text{C}$). This can be rewritten as:

$$y = b_0 \times (x)^{b_1} \quad (6-16)$$

Since the exposed area in these measurements is approximately 0.96 cm^2 , the current density can be obtained by dividing the area into the current. The coefficients based upon the correlation of data for SDW, SCW, SAW and SSW are summarized in Table 6-6. The current density is converted to a corrosion rate based upon the information in Tables 6-4 and 6-5. The corrosion current density should be used as the basis of any corrosion rate estimate. This is the rate that should be experienced at the open circuit corrosion potential. Under actual conditions, even with significant anodic shifts in the corrosion potential, passive current densities are not expected. Clearly, if the passive current density is experienced under repository conditions, unacceptable rates of penetration would be experienced.

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Table 6 - 4. Conversion of Current Density to Corrosion (Penetration) Rate [DTN #].

		Value at Low f_i	Value at High f_i
Faraday Constant	C equiv-1	9.648460E+04	9.648460E+04
Assumed Current Density	A cm ⁻²	1.000000E-06	1.000000E-06
Assumed Mass Density	gm cm ⁻³	4.540000E+00	4.540000E+00
Total $(f_i n_i / a_i) / 100$		6.233572E-02	6.257576E-02
dp/dt	cm sec ⁻¹	3.662260E-11	3.648212E-11
dp/dt	microns per year	1.154930E+01	1.150500E+01

Table 6 - 5. Conversion of Current Density to Corrosion (Penetration) Rate [DTN #].

	a_i	n_i	n_i	n_i	f_i	f_i	$(f_i n_i / a_i) / 100$	$(f_i n_i / a_i) / 100$
					Wt. %	Wt. %		
		Low	High	Calc.	Low	High	Low	High
C	12.011	2	4	4	0.000	0.080	0.000000E+00	2.664224E-04
Ni	58.69	2	3	2	0.000	0.000	0.000000E+00	0.000000E+00
Cr	51.9969	3	6	3	0.000	0.000	0.000000E+00	0.000000E+00
Mo	95.94	3	6	3	0.000	0.000	0.000000E+00	0.000000E+00
Fe	55.847	2	3	2	0.300	0.000	1.074364E-04	0.000000E+00
Cu	63.546	1	2	2	0.000	0.000	0.000000E+00	0.000000E+00
P	30.973762	3	5	5	0.000	0.000	0.000000E+00	0.000000E+00
Si	28.0855	4	4	4	0.000	0.000	0.000000E+00	0.000000E+00
S	32.066	2	6	6	0.000	0.000	0.000000E+00	0.000000E+00
Mn	54.93805	2	2	2	0.000	0.000	0.000000E+00	0.000000E+00
W	183.85	2	6	6	0.000	0.000	0.000000E+00	0.000000E+00
Co	58.9332	2	3	2	0.000	0.000	0.000000E+00	0.000000E+00
V	50.9415	2	3	3	0.000	0.000	0.000000E+00	0.000000E+00
Ti	47.88	2	3	3	99.280	99.370	6.220551E-02	6.226190E-02
Pd	105.42	2	2	2	0.120	0.250	2.276608E-05	4.742933E-05
Other	1	0	0	0	0.300	0.300	0.000000E+00	0.000000E+00
Total					100.000	100.000	6.233572E-02	6.257576E-02

Figure 6 - 10. Corrosion & Passive Currents for Titanium Grade 7 in SSW [DTN #].

Figure 6 - 11. Corrosion & Passive Currents for Titanium Grade 7 in SAW [DTN #].

Figure 6 - 12. Corrosion & Passive Currents for Titanium Grade 7 in SCW [DTN #].

Figure 6 - 13. Corrosion & Passive Currents for Titanium Grade 7 in SDW [DTN #].

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Table 6 - 6. Coefficients for Regression Equations Used to Represent Corrosion and Passive Current Data [DTN #].

Medium	Current	Corresponding Potential	Correlation Type	b_0	b_1	b_2	R^2
SDW	Corrosion	E_{corr}	Power	1.0446E-07	-1.5352		0.3858
SDW	Passive	$E_{critical}$	Power	3.5350E-03	-2.2616		0.3806
SCW	Corrosion	E_{corr}	Power	9.7399E-15	3.6966		0.6570
SCW	Passive	$E_{critical}$	Power	9.2993E-08	0.9935		0.2258
SAW	Corrosion	E_{corr}	Polynomial	1.5291E-08	-4.9725E-10	4.1200E-12	0.1014
SAW	Passive	$E_{critical}$	Linear	1.9608E-06	-1.7368E-09		0.0133
SSW	Corrosion	E_{corr}	Linear	-1.2300E-10	1.6020E-08		None
SSW	Passive	$E_{critical}$	Linear	1.1690E-05	-8.4500E-08		None

6.5.2 Corrosion Rates Based Upon Weight Loss Measurements

It will be assumed that the general corrosion rates of Ti Gr 16 measured in the Long Term Corrosion Test Facility (LTCTF) are representative of those for Ti Gr 7. Testing includes a wide range of plausible generic test media, including Simulated Dilute Water (SDW), Simulated Concentrated Water (SCW) and Simulated Acid Water (SAW). The SCW test medium is three orders-of-magnitude (1000X) more concentrated than J-13 well water and is slightly alkaline (pH~8). The SAW test medium is three orders-of-magnitude (1000X) more concentrated than J-13 well water and is acidic (pH~2.7). Two temperature levels (60 and 90°C) are included in this qualified (Q) testing program. It will be further assumed that all drip shields undergo general corrosion at a constant rate corresponding to the maximum observed value. The maximum observed rate, which is much less than 1 micron per year, clearly indicates that the life of the DS will not be limited by general corrosion. It will also be assumed that the corrosion rate is constant, and does not decay with time. Less conservative corrosion models assume that the rate decays with time.

The Long Term Corrosion Test Facility (LTCTF) appears to be the most complete source of corrosion data for Ti Gr 16 in environments relevant to the proposed high-level waste repository at Yucca Mountain. This facility is equipped with an array of nearly cubic fiberglass tanks. Each tank has a total volume of ~2000 liters and is filled with ~1000 liters of aqueous test solution. The solution in a particular tank is controlled at either 60 or 90°C, covered with a blanket of air flowing at approximately 150 cm³ min⁻¹, and agitated. The test environments used in the LTCTF are referred to as: Simulated Dilute Water (SDW); Simulated Concentrated Water (SCW); Simulated Acidic Concentrated Water (SAW); and Simulated Cement-Modified Water (SCMW). The descriptions and compositions of three of these solutions are summarized in Tables 6-3 and 6-4. Four generic types of samples, U-bends, crevices, weight loss samples and galvanic couples, are mounted on insulating racks and placed in the tanks. Approximately half of the samples are submersed, half are in the saturated vapor above the aqueous phase, and a limited number at the water line. It is important to note that condensed water is present on specimens located in the saturated vapor.

As previously discussed, general corrosion measurements have been based upon ASTM G 1-81 (ASTM 1989b). The general corrosion (or penetration) rate of an alloy can be calculated from weight loss data as follows with the following general formula:

$$\text{Corrosion Rate} = \frac{(K \times W)}{(A \times T \times D)} \quad (6-17)$$

where K is a constant, T is the time of exposure in hours, A is the exposed area of the sample in square centimeters, W is the mass loss in grams, and D is the density in grams per cubic centimeter. The value of K used for the LTCTF data was 8.76×10^7 microns per year. This formula for corrosion rate can be rewritten in the following form:

$$\frac{dp}{dt} = \frac{w}{\rho \times t} \frac{1}{[2(a \times b) + 2(b \times c) + 2(a \times c)]} \quad (6-18)$$

6.5.3 Uncertainty in Weight Loss Measurements

The best representation of the uncertainty in the measured corrosion rate of Ti Gr 16 in the LTCTF appears to be normal distribution. It is assumed that the measured corrosion rate is a random variable with a mean μ and a standard deviation σ . As discussed by Burr (1974), the density function is:

$$f(y) = \frac{\exp\left[-\frac{(y-\mu)^2}{2\sigma^2}\right]}{\sigma\sqrt{2\pi}} \quad (\pm \infty) \quad (6-19)$$

The properties of this function are well known. First, the curve is symmetrical about the mean value, and the area underneath the curve is one. The following standard areas fall between the specified low and high limits:

Table 6 - 7. Standard Areas Under Density Function for Normal Distribution

Low Limit	High Limit	Area Under Curve
$\mu-1\times\sigma$	$\mu+1\times\sigma$	0.6827
$\mu-2\times\sigma$	$\mu+2\times\sigma$	0.9545
$\mu-3\times\sigma$	$\mu+3\times\sigma$	0.9973
$\mu-1.960\times\sigma$	$\mu+1.960\times\sigma$	0.9500
$\mu-2.576\times\sigma$	$\mu+2.576\times\sigma$	0.9900

The cumulative probability is obtained by integration of the density function. Figures 6-18 and 6-20 represent the cumulative probabilities for general corrosion rates measured in the LTCTF, based upon weight loss and crevice samples, respectively. The mean and standard deviation of these curves are first determined by inspection, with the results given in Tables 6-8 and 6-9.

Table 6 - 8. Mean and Standard Deviation of General Corrosion Rates – Weight Loss

Parameter	All Data (nm y ⁻¹)	No Outlier (nm y ⁻¹)
μ	-143.80	-16.51
σ	+391.90	+72.70

Table 6 - 9. Mean and Standard Deviation of General Corrosion Rates – Crevice Samples

Parameter	All Data (nm y ⁻¹)	No Outlier (nm y ⁻¹)
μ	-11.83	
σ	+93.25	

The distributions of corrosion rates are centered around negative mean values. The negative corrosion rates that are significant correspond to cases where the samples actually appear to have gained weight during exposure, due to oxide growth or the formation of silica deposits. To substantiate these interpretations, atomic force microscopy has been used to inspect a number of samples removed from the LTCTF.

6.5.4 Error Analysis for Weight Loss Measurements

The general method used in the formal error analysis is now presented. Consider the dependent variable y defined by the following generic function:

$$y = f(x_1, x_2, x_3, x_4 \cdots x_n) \quad (6-20)$$

where x_i is the i^{th} independent variable. The total derivative of y is then defined as:

$$dy = \frac{\partial y}{\partial x_1} dx_1 + \frac{\partial y}{\partial x_2} dx_2 + \frac{\partial y}{\partial x_3} dx_3 + \frac{\partial y}{\partial x_4} dx_4 + \cdots + \frac{\partial y}{\partial x_n} dx_n \quad (6-21)$$

Based upon this definition, the maximum error in y can then be defined as:

$$\Delta y = \left| \frac{\partial y}{\partial x_1} \Delta x_1 \right| + \left| \frac{\partial y}{\partial x_2} \Delta x_2 \right| + \left| \frac{\partial y}{\partial x_3} \Delta x_3 \right| + \left| \frac{\partial y}{\partial x_4} \Delta x_4 \right| + \cdots + \left| \frac{\partial y}{\partial x_n} \Delta x_n \right| \quad (6-22)$$

where Δx_i is the error in the i^{th} independent variable. Let the dependent variable y be the general corrosion rate measured in the LTCTF:

$$y = \frac{dp}{dt} = \frac{w}{\rho \times t} \frac{1}{[2(a \times b) + 2(b \times c) + 2(a \times c)]} \quad (6-23)$$

The total derivative of the corrosion rate is:

$$dy = \frac{\partial y}{\partial w} dw + \frac{\partial y}{\partial \rho} d\rho + \frac{\partial y}{\partial t} dt + \frac{\partial y}{\partial a} da + \frac{\partial y}{\partial b} db + \frac{\partial y}{\partial c} dc \quad (6-24)$$

The maximum error in the corrosion rate is:

$$\Delta y = \left| \frac{\partial y}{\partial w} \Delta w \right| + \left| \frac{\partial y}{\partial \rho} \Delta \rho \right| + \left| \frac{\partial y}{\partial t} \Delta t \right| + \left| \frac{\partial y}{\partial a} \Delta a \right| + \left| \frac{\partial y}{\partial b} \Delta b \right| + \left| \frac{\partial y}{\partial c} \Delta c \right| \quad (6-25)$$

The partial derivatives are:

$$\frac{\partial y}{\partial w} = \frac{1}{\rho \times t} \frac{1}{[2(a \times b) + 2(b \times c) + 2(a \times c)]} \quad (6-26)$$

$$\frac{\partial y}{\partial \rho} = \frac{w}{\rho^2 \times t} \frac{1}{[2(a \times b) + 2(b \times c) + 2(a \times c)]} \quad (6-27)$$

$$\frac{\partial y}{\partial t} = \frac{w}{\rho \times t^2} \frac{1}{[2(a \times b) + 2(b \times c) + 2(a \times c)]} \quad (6-28)$$

$$\frac{\partial y}{\partial a} = \frac{w}{\rho \times t} \frac{[2b + 2c]}{[2(a \times b) + 2(b \times c) + 2(a \times c)]^2} \quad (6-29)$$

$$\frac{\partial y}{\partial b} = \frac{w}{\rho \times t} \frac{[2a + 2c]}{[2(a \times b) + 2(b \times c) + 2(a \times c)]^2} \quad (6-30)$$

$$\frac{\partial y}{\partial c} = \frac{w}{\rho \times t} \frac{[2a + 2b]}{[2(a \times b) + 2(b \times c) + 2(a \times c)]^2} \quad (6-31)$$

The maximum error in the corrosion rate is estimated by calculating numeric values of the partial derivatives from expected values of the independent variables, multiplication of each partial derivative by the corresponding error in independent variable (Δw , $\Delta \rho$, Δt , Δa , Δb and Δc), and summation of the resulting products. The error based upon this method is shown in Tables 6-10 through 6-14. From the estimated errors given in Table 6-11, it is concluded that the typical uncertainty observed in weight loss and dimensional measurements prevent determination of corrosion rates less than 46 nanometers per year (crevice sample worst case). This estimate of error is believed to correspond to about one standard deviation (1σ). Therefore, any measured corrosion rate less than 184 nanometers per year (4σ) will not be distinguishable from measurement error.

General corrosion rates determined from measurements of weight loss in the LTCTF are shown in Figures 6-15 and 6-16. The LTCTF and results from that facility are described in detail previous publications by the Project (Estill 1998). The maximum rates shown in Figure 6-16 appear to be less than about 350 nanometers per year, slightly greater than the estimated 4σ value. Any rate less than 350 nm per year guarantees that the DS (wall thickness of 2 cm) will not fail by general corrosion. Note that the impact of the hole in the crevice samples on the error analysis was believed to be relatively small, and therefore neglected.

Table 6 - 10. Summary of Error Analysis for Corrosion Rates Based Upon Weight Loss Measurements

	Assumed Wt. Loss		0.0001 gm	0.0010 gm	0.0100 gm
			Δy	Δy	Δy
Case	Sample Configuration	Exposure Time	nm y ⁻¹	nm y ⁻¹	nm y ⁻¹
1	Crevice	6 month	23.64	25.72	46.47
2	Weight Loss	6 month	44.89	48.94	89.41
3	Crevice	12 month	11.58	12.50	21.70
4	Weight Loss	12 month	22.00	23.79	41.78

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Table 6 - 11. Error Analysis for LTCTF Corrosion Rates – Definitions.

Parameter	Parameter Definition	Units
W	Weight loss	gm
ρ	Density	gm cm ⁻³
T	Exposure time	hr
A	Length	in
B	Width	in
C	Thickness	in
A	Length	cm
B	Width	cm
C	Thickness	cm
$\partial y / \partial w$	Partial derivative or rate with respect to weight loss	cm gm ⁻¹ h ⁻¹
$\partial y / \partial \rho$	Partial derivative of rate with respect to density	cm ⁴ gm ⁻¹ h ⁻¹
$\partial y / \partial t$	Partial derivative of rate with respect to exposure time	cm h ⁻²
$\partial y / \partial a$	Partial derivative of rate with respect to length	h ⁻¹
$\partial y / \partial b$	Partial derivative of rate with respect to width	h ⁻¹
$\partial y / \partial c$	Partial derivative of rate with respect to thickness	h ⁻¹
Δw	Error in weight loss	gm
$\Delta \rho$	Error in density	gm cm ⁻³
Δt	Error in exposure time	hr
Δa	Error in length	cm
Δb	Error in width	cm
Δc	Error in thickness	cm
$(\partial y / \partial w) \times (\Delta w)$	Weight loss product	cm
$(\partial y / \partial \rho) \times (\Delta \rho)$	Density product	cm
$(\partial y / \partial t) \times (\Delta t)$	Exposure time product	cm
$(\partial y / \partial a) \times (\Delta a)$	Length product	cm
$(\partial y / \partial b) \times (\Delta b)$	Width product	cm
$(\partial y / \partial c) \times (\Delta c)$	Thickness product	cm
Δy	Sum of all products	cm h ⁻¹
Δy	Sum of all products	$\mu\text{m y}^{-1}$
Δy	Sum of all products	nm y ⁻¹

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Table 6 - 12. Error Analysis for LTCTF Corrosion Rates – Assume Weight Loss of 0.0001 Grams

Parameter	Crevice 6 mo.	Wt. Loss 6 mo.	Crevice 12 mo.	Wt. Loss 12 mo.
w	0.0001	0.0001	0.0001	0.0001
ρ	4.52	4.52	4.52	4.52
t	4296	4296	8760	8760
a	2.0000	2.0000	2.0000	2.0000
b	2.0000	1.0000	2.0000	1.0000
c	0.1200	0.1200	0.1200	0.1200
a	5.0800	5.0800	5.0800	5.0800
b	5.0800	2.5400	5.0800	2.5400
c	0.3048	0.3048	0.3048	0.3048
$\partial y / \partial w$	8.9089E-07	1.6912E-06	4.3690E-07	8.2937E-07
$\partial y / \partial \rho$	1.9710E-11	3.7415E-11	9.6659E-12	1.8349E-11
$\partial y / \partial t$	2.0738E-14	3.9366E-14	4.9874E-15	9.4677E-15
$\partial y / \partial a$	1.6598E-11	3.1598E-11	8.1397E-12	1.5496E-11
$\partial y / \partial b$	1.6598E-11	5.9811E-11	8.1397E-12	2.9332E-11
$\partial y / \partial c$	3.1316E-11	8.4638E-11	1.5358E-11	4.1507E-11
Δw	0.0003	0.0003	0.0003	0.0003
$\Delta \rho$	0.1	0.1	0.1	0.1
Δt	24	24	24	24
Δa	0.00254	0.00254	0.00254	0.00254
Δb	0.00254	0.00254	0.00254	0.00254
Δc	0.00254	0.00254	0.00254	0.00254
$(\partial y / \partial w) \times (\Delta w)$	2.6727E-10	5.0735E-10	1.3107E-10	2.4881E-10
$(\partial y / \partial \rho) \times (\Delta \rho)$	1.9710E-12	3.7415E-12	9.6659E-13	1.8349E-12
$(\partial y / \partial t) \times (\Delta t)$	4.9770E-13	9.4479E-13	1.1970E-13	2.2722E-13
$(\partial y / \partial a) \times (\Delta a)$	4.2158E-14	8.0259E-14	2.0675E-14	3.9360E-14
$(\partial y / \partial b) \times (\Delta b)$	4.2158E-14	1.5192E-13	2.0675E-14	7.4503E-14
$(\partial y / \partial c) \times (\Delta c)$	7.9543E-14	2.1498E-13	3.9009E-14	1.0543E-13
Δy	2.6990E-10	5.1249E-10	1.3224E-10	2.5109E-10
Δy	2.3643E-02	4.4894E-02	1.1584E-02	2.1996E-02
Δy	2.3643E+01	4.4894E+01	1.1584E+01	2.1996E+01

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Table 6 - 13. Error Analysis for LTCTF Corrosion Rates – Assume Weight Loss of 0.001 Grams

Table 1

Parameter	Crevice 6 mo.	Wt. Loss 6 mo.	Crevice 12 mo.	Wt. Loss 12 mo.
w	0.0010	0.0010	0.0010	0.0010
ρ	4.52	4.52	4.52	4.52
t	4296	4296	8760	8760
a	2.0000	2.0000	2.0000	2.0000
b	2.0000	1.0000	2.0000	1.0000
c	0.1200	0.1200	0.1200	0.1200
a	5.0800	5.0800	5.0800	5.0800
b	5.0800	2.5400	5.0800	2.5400
c	0.3048	0.3048	0.3048	0.3048
$\partial y / \partial w$	8.9089E-07	1.6912E-06	4.3690E-07	8.2937E-07
$\partial y / \partial \rho$	1.9710E-10	3.7415E-10	9.6659E-11	1.8349E-10
$\partial y / \partial t$	2.0738E-13	3.9366E-13	4.9874E-14	9.4677E-14
$\partial y / \partial a$	1.6598E-10	3.1598E-10	8.1397E-11	1.5496E-10
$\partial y / \partial b$	1.6598E-10	5.9811E-10	8.1397E-11	2.9332E-10
$\partial y / \partial c$	3.1316E-10	8.4638E-10	1.5358E-10	4.1507E-10
Δw	0.0003	0.0003	0.0003	0.0003
$\Delta \rho$	0.1	0.1	0.1	0.1
Δt	24	24	24	24
Δa	0.00254	0.00254	0.00254	0.00254
Δb	0.00254	0.00254	0.00254	0.00254
Δc	0.00254	0.00254	0.00254	0.00254
$(\partial y / \partial w) \times (\Delta w)$	2.6727E-10	5.0735E-10	1.3107E-10	2.4881E-10
$(\partial y / \partial \rho) \times (\Delta \rho)$	1.9710E-11	3.7415E-11	9.6659E-12	1.8349E-11
$(\partial y / \partial t) \times (\Delta t)$	4.9770E-12	9.4479E-12	1.1970E-12	2.2722E-12
$(\partial y / \partial a) \times (\Delta a)$	4.2158E-13	8.0259E-13	2.0675E-13	3.9360E-13
$(\partial y / \partial b) \times (\Delta b)$	4.2158E-13	1.5192E-12	2.0675E-13	7.4503E-13
$(\partial y / \partial c) \times (\Delta c)$	7.9543E-13	2.1498E-12	3.9009E-13	1.0543E-12
Δy	2.9359E-10	5.5869E-10	1.4274E-10	2.7162E-10
Δy	2.5719E-02	4.8941E-02	1.2504E-02	2.3794E-02
Δy	2.5719E+01	4.8941E+01	1.2504E+01	2.3794E+01

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Table 6 – 14. Error Analysis for LTCTF Corrosion Rates – Assume Weight Loss of 0.01 Grams

Parameter	Crevice 6 mo.	Wt. Loss 6 mo.	Crevice 12 mo.	Wt. Loss 12 mo.
w	0.0100	0.0100	0.0100	0.0100
p	4.52	4.52	4.52	4.52
t	4296	4296	8760	8760
a	2.0000	2.0000	2.0000	2.0000
b	2.0000	1.0000	2.0000	1.0000
c	0.1200	0.1200	0.1200	0.1200
a	5.0800	5.0800	5.0800	5.0800
b	5.0800	2.5400	5.0800	2.5400
c	0.3048	0.3048	0.3048	0.3048
$\partial y / \partial w$	8.9089E-07	1.6912E-06	4.3690E-07	8.2937E-07
$\partial y / \partial p$	1.9710E-09	3.7415E-09	9.6659E-10	1.8349E-09
$\partial y / \partial t$	2.0738E-12	3.9366E-12	4.9874E-13	9.4677E-13
$\partial y / \partial a$	1.6598E-09	3.1598E-09	8.1397E-10	1.5496E-09
$\partial y / \partial b$	1.6598E-09	5.9811E-09	8.1397E-10	2.9332E-09
$\partial y / \partial c$	3.1316E-09	8.4638E-09	1.5358E-09	4.1507E-09
Δw	0.0003	0.0003	0.0003	0.0003
Δp	0.1	0.1	0.1	0.1
Δt	24	24	24	24
Δa	0.00254	0.00254	0.00254	0.00254
Δb	0.00254	0.00254	0.00254	0.00254
Δc	0.00254	0.00254	0.00254	0.00254
$(\partial y / \partial w) \times (\Delta w)$	2.6727E-10	5.0735E-10	1.3107E-10	2.4881E-10
$(\partial y / \partial p) \times (\Delta p)$	1.9710E-10	3.7415E-10	9.6659E-11	1.8349E-10
$(\partial y / \partial t) \times (\Delta t)$	4.9770E-11	9.4479E-11	1.1970E-11	2.2722E-11
$(\partial y / \partial a) \times (\Delta a)$	4.2158E-12	8.0259E-12	2.0675E-12	3.9360E-12
$(\partial y / \partial b) \times (\Delta b)$	4.2158E-12	1.5192E-11	2.0675E-12	7.4503E-12
$(\partial y / \partial c) \times (\Delta c)$	7.9543E-12	2.1498E-11	3.9009E-12	1.0543E-11
Δy	5.3052E-10	1.0207E-09	2.4773E-10	4.7695E-10
Δy	4.6474E-02	8.9413E-02	2.1702E-02	4.1781E-02
Δy	4.6474E+01	8.9413E+01	2.1702E+01	4.1781E+01

6.6 DISSOLVED OXYGEN IN THE LONG TERM CORROSION TEST FACILITY

In principle, the corrosion rates observed in the LTCTF should depend upon the concentration of dissolved oxygen. The anodic dissolution of a metal requires a corresponding amount of cathodic reduction. Typically, dissolved oxygen or hydrogen ion is reduced. However, as previously discussed, other reactants such as hydrogen peroxide (due to gamma radiolysis) can also be reduced. Figure 6-24 in the companion AMR on general and localized corrosion of the WPOB (Farmer et al. 1999) shows a comparison of dissolved oxygen measurements in the LTCTF to published data for synthetic geothermal brine (Cramer 1974). The published data spans the range of temperature from 20 to 300°C, and spans the range of oxygen partial pressures from 1 to 30 psi. Note that the partial pressure of oxygen in the atmosphere is about 3 psi. The points representing measurements from the LTCTF tanks are superimposed upon the published data. Clearly, the SDW, SCW, and SAW appear to be saturated (4 to 10 ppm dissolved oxygen).

6.7 LOCALIZED CORROSION

The hydrolysis of dissolved metal in crevices can lead to the accumulation of H^+ and the corresponding suppression of pH. For example, $pH < 2$ has been observed in crevices made of stainless steel, as discussed by Sedriks (1996). Such low pH can exacerbate any problems due to hydrogen induced cracking (HIC). While experimental determinations of the crevice pH have been made in the case of stainless steels, work for titanium-based alloys must still be done.

If the threshold potential for localized attack is exceeded, a corrosion rate representative of localized corrosion (LC) must be assumed. Unfortunately, due to the outstanding corrosion resistance of Ti Gr 7, relatively little data exists for such localized corrosion under plausible conditions. From the reviewed literature (Gdowski 1997 Table 15.1), a crevice corrosion depth of 250 microns was observed in a crevice formed from Ti-0.2%Pd and PTFE after a 582 day exposure in deaerated brine at 90°C (157 microns per year). In a metal-metal crevice, a crevice corrosion depth of 70 microns was observed in a crevice formed from Ti-0.2%Pd after 489 days (52 microns per year). Since these rates are less than the maximum rates represented by Equation 6-19, other more severe values should be considered in the event of passive film breakdown (Gdowski 1997 Appendix A), which are shown in Table 6-15.

Table 6 – 15. Assumed Distribution of Localized Corrosion Rates for Ti Gr 7

Percentile (%)	Localized Corrosion Rate (microns per year)	Conditions
0 th	490	19% HCl + 4% FeCl ₃ + 4% MgCl ₂ at 82°C
100 th	1120	Boiling 3:1 Aqua Regia

6.8 GAMMA RADIOLYSIS

As discussed in the companion AMR on general and localized corrosion of the WPOB, ambient-temperature cyclic polarization studies have been performed with 316L samples in 0.018 M NaCl solution during exposure to 3.5 Mrad h⁻¹ gamma radiation (Glass 1986). This investigator found that the corrosion current shifted in the anodic direction by approximately 200 mV, with

very little increase in the corresponding corrosion current density. However, the separation between the corrosion potential and the threshold for localized attack decreased slightly. This shift in corrosion potential was shown to be due to the formation of hydrogen peroxide. This finding was subsequently confirmed by others (Kim 1999). In this case, ambient-temperature cyclic polarization of 316 stainless steel in acidic (pH~2) 1.5 M NaCl during exposure to 0.15 Mrad h⁻¹ gamma radiation showed a 100 mV anodic shift in the corrosion potential, with very little effect on the corrosion current. While the E_{corr} shift for Ti Gr 7 will probably be somewhat different than that of 316L, it is doubtful that the shift will ever be sufficient for E_{corr} to exceed $E_{critical}$. Thus, even in the presence of gamma radiolysis, general corrosion would be expected.

6.9 MICROBIAL INFLUENCED CORROSION

It has been observed that titanium based alloys are very resistant to Microbial Influenced Corrosion (MIC). Furthermore, it is believed that microbial growth in the repository will be limited by the availability of nutrients. Ultimately, the impact of MIC will be accounted by adjusting E_{corr} , $E_{critical}$, pH, and the sulfide concentration. The possible acceleration of abiotic corrosion processes by microbial growth has also been a concern. Bacteria and fungi alter local environment in biofilm. For example, H⁺ is known to be generated by bacterial isolates from Yucca Mountain. Any lowering of pH could tend to exacerbate hydrogen induced cracking. Furthermore, thiobacillus ferrooxidans oxidize Fe²⁺, while geobacter metallireducens reduce Fe³⁺. Other microbes can reduce SO₄²⁻ and produce S²⁻. In the future, we hope to calculate concentration transients in biofilms with a relatively simple bioreactor model.

6.10 SUMMARY OF MODEL

The model for the general and localized corrosion of Ti Gr 7 is summarized in Figure 6-17. The threshold RH is first used to determine whether or not dry oxidation (DOX) will take place. If dry oxidation is determined to occur, the parabolic growth law represented by Equations 6-5 and 6-7 is then used to calculate the corrosion rate as a function of temperature. If the threshold RH is exceeded, HAC will occur in the absence of dripping water, and aqueous phase corrosion will occur in the presence of dripping water. If aqueous phase corrosion is assumed to occur, the corrosion and critical potentials are used to determine whether the mode of attack is general or localized. The correlation of data represented by Equation 6-11 and Table 6-1 are used as the basis for estimating these potentials at the 50th percentile. Since the material specifications will be based partly on the measured corrosion and critical potentials, it will be assumed that these potentials will be uniformly distributed about the 50th percentile values determined from the correlation. For example, the 0th and 100th percentile values of E_{corr} will be assumed to be at E_{corr} (50th percentile) $\pm$ 325 mV. This acceptable margin was determined by splitting the differences shown in Table 6-2. Similarly, the 0th and 100th percentile values of $E_{critical}$ will be assumed to be at $E_{critical}$ (50th percentile) $\pm$ 325 mV. Material falling outside of these specified ranges will not be accepted. If the comparison of E_{corr} to $E_{critical}$ indicates general corrosion, the distribution of rates determined from the LTCTF will be used as the basis of the general corrosion rate.

Figure 6 - 16. Schematic Representation of Corrosion Model for Drip Shield.

7. CONCLUSIONS

Ti Gr 7 is an extremely corrosion resistant material, with a very stable passive film. Based upon exposures in the LTCTF, it has been determined that the general corrosion and oxidation rates of Ti Gr 7 are essentially below the level of detection. In any event, over the 10,000 year life of the repository, general corrosion and oxidation should not be life limiting. The large separation between measured corrosion and threshold potentials indicate that localized breakdown of the passive film is unlikely under plausible conditions, even in SSW at 120°C. In the future, the pH and current in crevices formed from Ti Gr 7 should be determined experimentally.

With exposures of two years, no significant evidence of crevice corrosion has been observed with Ti Gr 16 in SDW, SCW, and SAW at temperatures up to 90°C, though many of the samples have a beautiful green patina. An abstracted model has been presented, with parameters determined experimentally, that should enable performance assessment to account for the general and localized corrosion of this material. A feature of this model is the use of the materials specification to limit the range of corrosion and threshold potentials, thereby making sure that substandard materials prone to localized attack are avoided.

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9. ATTACHMENTS

Attachments to this document are listed in Table 26 below. The 100 MB ZIP Disk includes a data inventory in the form of an Excel spreadsheet.

Table 9 - 1. List of Attachments

Attachment Number	Description	Size
I	100 MB ZIP Disk for IBM with Supporting Data	
II		
III		
IV		
V		
VI		
VII		
VIII		
IX		
X		