DISCLAIMER

This contractor document was prepared for the U.S. Department of Energy (DOE), but has not undergone programmatic, policy, or publication review, and is provided for information only. The document provides preliminary information that may change based on new information or analysis, and represents a conservative treatment of parameters and assumptions to be used specifically for Total System Performance Assessment analyses. The document is a preliminary lower level contractor document and is not intended for publication or wide distribution.

Although this document has undergone technical reviews at the contractor organization, it has not undergone a DOE policy review. Therefore, the views and opinions of authors expressed may not state or reflect those of the DOE. However, in the interest of the rapid transfer of information, we are providing this document for your information per your request.

12 Nm5507

OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
ANALYSIS/MODEL COVER SHEET

1. QA: QA

Page: 1 of: 21

Complete Only Applicable Items

2. ☒ Analysis — Check all that apply

Type of Analysis:
- ☐ Engineering
- ☐ Performance Assessment
- ☒ Scientific

Intended Use of Analysis:
- ☐ Input to Calculation
- ☒ Input to another Analysis or Model
- ☒ Input to Technical Document

Describe use:

3. ☒ Model — Check all that apply

Type of Model:
- ☐ Conceptual Model
- ☐ Abstraction Model
- ☐ Mathematical Model
- ☐ System Model
- ☒ Process Model

Intended Use of Model:
- ☐ Input to Calculation
- ☒ Input to another Model or Analysis
- ☒ Input to Technical Document

Describe use:

4. Title:
Hydrogen Induced Cracking of Drip Shield

INFORMATION COPY
LAS VEGAS DOCUMENT CONTROL

Document Identifier (including Rev. No. and Change No., if applicable):
ANL-EBS-MD-000006 REV 00

6. Total Attachments:
N/A

7. Attachment Numbers - No. of Pages in Each:
N/A

	Printed Name	Signature	Date
8. Originator	Stephen C. Lu	for Stephen Lu	3/13/00
9. Checker	Denny Jones	David Stahl for Denny Jones	3/13/00
10. Lead/Supervisor	Al Lingenfelter	David Stahl for Al Lingenfelter	3/13/00
11. Responsible Manager	David Stahl	David Stahl	3/13/00

12. Remarks: Editorial corrections were made on pages 15, 16 and 20.

p. 15 . $(g/mm)^3$ changed to (g/mm^3)

p. 16 . Reference to p. 58 changed to p. 59

p. 16 . Reference to Ti-7 changed to Ti-16. David Stahl 3/23/00

p. 20 . Library Tracking No. added.

p. 20 . URN number added to CRWMS M&O 2000 a. 3/23/00

for Stephen Lu 3/21/00

3/21/00 David Stahl for Allen Lingenfelter

OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
ANALYSIS/MODEL REVISION RECORD

Complete Only Applicable Items

1. Page: 2 of: 21

2. Analysis or Model Title:

Hydrogen Induced Cracking of Drip Shield

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

ANL-EBS-MD-000006 REV 00

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

CONTENTS

FIGURES

Page

ACRONYMS AND ABBREVIATIONS

AMR	Analyses and Models Report
CRWMS	Civilian Radioactive Waste Management System
DS	drip shield
HIC	hydrogen induced cracking
M&O	Management and Operating Contractor
MGR	Monitored Geologic Repository
PMR	Process Model Report
QAP	Quality Administrative Procedure
SAW	simulated acidic concentrated water
SCE	saturated calomel electrode
SCW	simulated concentrated water
SDW	simulated dilute water
SSW	simulated saturated water
UNS	Unified Numbering System
WP	waste package
WPD	waste package degradation

1. PURPOSE

One likely failure mechanism for titanium and its alloys under waste disposal conditions is via the absorption of atomic hydrogen in the metal crystal lattice. Decreased ductility and fracture toughness results in brittle mechanical fracture by hydrogen-induced cracking (HIC) also called hydrogen embrittlement.

The purpose of the scientific analysis is to account for the HIC effects on the drip shield (DS). This Analyses and Models Report (AMR) serves as a feed to the Waste Package Degradation (WPD) Process Model Report (PMR) and was developed in accordance with the activity section "Hydrogen Induced Cracking of Drip Shield" of the development plan entitled *Analysis and Model Reports to Support Waste Package PMR* (CRWMS M&O 1999f).

Titanium Grade 7 (Ti-7) (UNS R52400) is now favored for construction of the drip shield for the waste package due to its excellent corrosion resistance (CRWMS M&O 2000a, p. 10). This alloy consists of 0.3% Fe, 0.25% O, 0.12-0.25% Pd, 0.1% C, 0.03% N, 0.015% H, 0.4% total residuals with the balance being Ti (CRWMS M&O 1999d, p. 45). Other titanium alloys that will be discussed in this report include Ti-2, Ti-12, and Ti-16. Ti-2 is essentially commercially pure titanium. It is believed that the most effective way of reducing hydrogen absorption is to choose a more crevice resistant alloy (Shoesmith et al. 1997, p. 15). This improvement in resistance to crevice corrosion can be attributed to the addition of alloying elements, which reinforce passivity. Therefore, susceptibility to crevice corrosion is eliminated through the alloying series Ti-2→Ti-12→Ti-16 (Shoesmith et al. 1997, p. 15). The major additions are Ni (0.6-0.9%) for Ti-12 and Pd (0.04-0.08%) for Ti-16 (CRWMS M&O 1999d, pp. 49, 51). A decrease in the corrosion rate by the addition of a noble metal such as Pd in Ti-16 is noted in Shoesmith et al. (1997, p. 21). The composition of Ti-7 is almost identical to that of Ti-16, but the Pd content is higher in Ti-7 (0.12-0.25%) than in Ti-16 (0.04-0.08%) (CRWMS M&O 1999d, pp. 45, 51). The similarity between Ti-7 and Ti-16 was also noted by CRWMS M&O (2000a, p. 48).

The DS will experience a wide range of conditions during its service life (CRWMS M&O 2000a, p. 10). Initially, the underlying high-level waste packages will be relatively hot, and DS surfaces will be dry due to the heat generated from radioactive decay. The temperature will eventually drop to levels where both humid air and aqueous phase corrosion will be possible. Crevice corrosion and slow general passive corrosion will produce hydrogen, which can be absorbed into the metal.

HIC of the DS is key to one of the most important principal factors in repository performance–the premature failure of the DS. This AMR proposes a realistic model to account for the degradation of the DS due to the effects of HIC, based upon data generated by the project. The model will follow the approach of Shoesmith et al. (1997).

2. QUALITY ASSURANCE

The Quality Assurance (QA) program applies to this analysis. All types of waste packages (WPs) were classified (per QAP-2-3) as Quality Level-1. CRWMS M&O (1999a, p. 7) in *Classification of the MGR Uncanistered Spent Nuclear Fuel Disposal Container System* is cited as an example of a WP type. The development of this analysis is conducted under activity evaluation *1101213PM7 Waste Package Analysis & Models - PMR* (CRWMS M&O 1999e), 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 2000) requirements.

3. COMPUTER SOFTWARE AND MODEL USAGE

No computer software or models have been used to support the development of the analysis activities described in this AMR.

4. INPUTS

4.1 DATA AND PARAMETERS

The following input data and/or parameters are obtained from Shoesmith et al. (1997, pp. 7-11):

H_C = critical hydrogen concentration.

The following input data and/or parameters are obtained from Shoesmith et al. (1997, p. 19):

R_{uc} = passive general corrosion rate.

The following input data and/or parameters are obtained from Shoesmith et al. (1997, p. 22):

f_h = fraction of absorption efficiency.

The following input data and/or parameters are obtained from Weast and Astle (1978, p. B-177):

ρ_{Ti} = density of titanium

M_{Ti} = Molecular weight of titanium

ρ_{OX} = density of titanium oxides

M_{OX} = Molecular weight of titanium oxides.

The following input data and/or parameters for Ti-7 are obtained from CRWMS M&O (2000a, pp. 38-41):

E_{corr} = the open circuit corrosion potential

$E_{critical}$ = the threshold potential for breakdown of the passive film.

The following input data and/or parameters for Ti-7 are obtained from CRWMS M&O (2000a, p. 58):

> R_{uc} = passive general corrosion rate (50th percentile, 90th percentile and maximum).

All of these input data and parameters will be used to evaluate the HIC effects on the DS.

4.2 CRITERIA

The DS is intended to protect the WP, thereby prolonging WP life. Therefore, the DS must help meet criteria specific to the WP.

In addition to the criteria specifically relevant to the WP, criteria for the DS have now been developed. *Emplacement Drift System Description Document* (SDD-EDS-SE-000001) (CRWMS M&O 2000b), Design Criteria 1.2.1.12 and 1.2.1.18, in the emplacement drift SDD (pp. 10-11), which uses 10 CFR 63 and EDA II as its framework, appear to be the best candidates in supporting this analysis.

The criterion 1.2.1.12 states:

> "The drip shield shall have an operating life of 10,000 years."

The criterion 1.2.1.18 states:

> "The drip shield material shall be Grade 7 Titanium, a minimum of 15-mm thick at the time of emplacement."

These criteria are needed to ensure that the drip shield is designed with an operating life long enough to achieve the functions allocated to it.

4.3 CODES AND STANDARDS

No codes or standards were used to perform the analysis for this AMR.

5. ASSUMPTIONS

The following assumptions are for the HIC model of this AMR:

5.1 Due to the close similarity in chemical composition between Ti-7 and Ti-16, available material properties data for Ti-16 are assumed to be applicable to Ti-7 if the said material properties data are not available for Ti-7. This assumption is used in Sections 6.1 and 6.2.

5.2 The H_C value for Ti-7 is assumed to be at least 400 μg/g. The rationale for this assumption is that 400 μg/g is the lower bound value observed for other similar titanium alloys (e.g., Ti-2 and Ti-12) by Shoesmith et al. (1997, pp. 7-11). H_C data are not available for Ti-7. This assumption is used in Subsections 6.1.3 and 6.2.2.

5.3 Corrosion is the only feasible source of hydrogen for absorption (Shoesmith et al. 1997, p. 15). The rationale for this assumption is that the direct absorption of radiolytically produced hydrogen is insignificant except at high dose rate (> 10^2 Gy/h) and high temperature (> 150°C), clearly unattainable under Yucca Mountain DS conditions. This assumption is used in Subsections 6.1.4 and 6.1.5.

5.4 The film growth rate and, hence, the corrosion rate are assumed to be constant in time for the formula used to calculate the concentration of hydrogen in the metal (Shoesmith et al. 1997, p. 22). The rationale for this assumption is that the assumption of constant corrosion rate is conservative and less conservative corrosion models assume that the rate decays with time (CRWMS M&O 2000a, p. 48). This assumption is used in Subsections 6.1.5 and 6.2.3.

6. ANALYSIS/MODEL

6.1 DESCRIPTION OF MODEL FOR HYDROGEN INDUCED CRACKING

6.1.1 Introduction

The DS will experience a wide range of conditions during its service life (CRWMS M&O 2000a, p. 10). Initially, the underlying high-level waste packages will be relatively hot, and DS surfaces will be dry due to the heat generated from radioactive decay. The temperature will eventually drop to levels where both humid air and aqueous phase corrosion will be possible. Crevice corrosion and slow general passive corrosion may be initiated and propagate in the metal. Both types of corrosion will produce hydrogen, which can be absorbed into the metal (Shoesmith et al. 1997, p. 2).

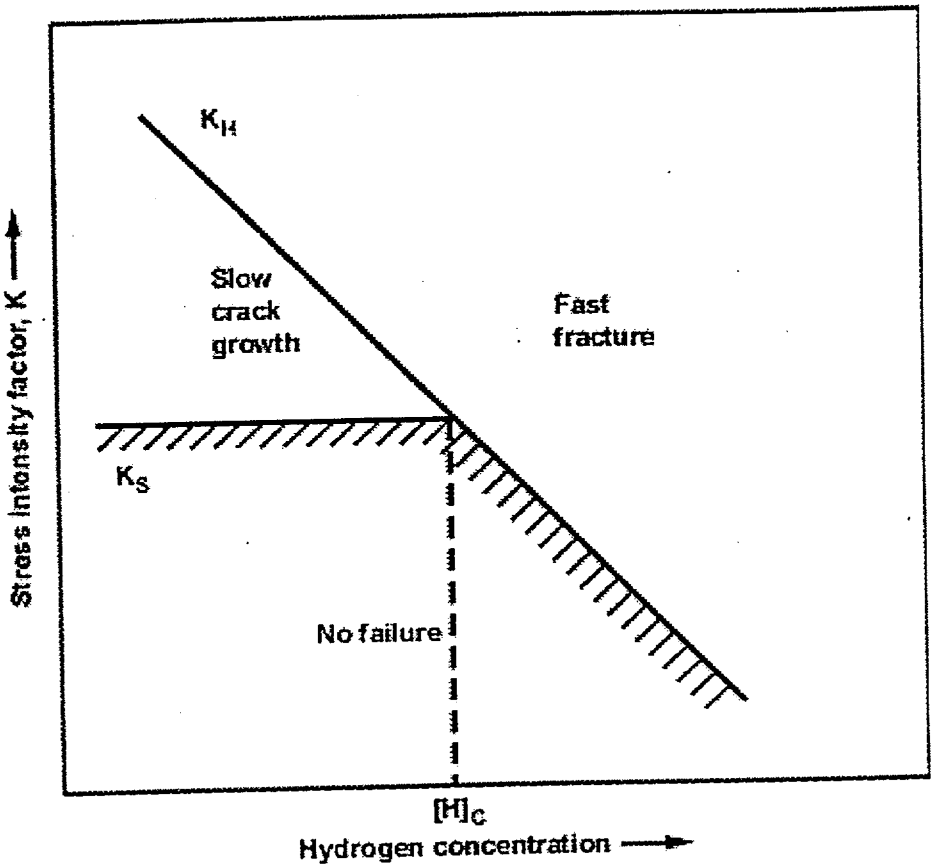
Failure occurs if (1) the wall penetration by corrosion exceeds the corrosion allowance or (2) the amount of hydrogen absorbed exceeds the critical hydrogen concentration, H_C, for failure due to hydrogen induced cracking. The first type of failure mechanism, i.e., wall penetration by crevice and general corrosion, is treated in another AMR (CRWMS M&O 2000a). This AMR deals with the failure mechanism associated with HIC.

HIC (also called hydrogen embrittlement) is characterized by decreased fracture toughness or ductility of the metal due to absorbed atomic hydrogen. The usual mechanical failure mode for a ductile material is the ductile tearing observed during slow crack growth. Decreased fracture toughness causes fast crack growth (brittle fracture) of a normally ductile material under sustained load. During slow crack growth, material will fail as the stress intensity factor K reaches a value K_S. During fast crack growth, the same material will fail as the stress intensity factor K reaches a value K_H, which is less than K_S (Shoesmith et al. 1997). Figure 1 (from Shoesmith et al. 1997, page 9, Figure 7) represents, schematically, the combinations of stress intensity factor and hydrogen concentration leading to (1) fast crack growth (brittle fracture) controlled by K_H, (2) slow crack growth controlled by K_S due to either sustained load cracking or ductile rupture, or (3) no failure.

An approach has been adopted to predict when HIC might become a potential failure process for the DS, following a Canadian precedent (Shoesmith et al. 1997). The basic premise of the model is that failure will occur once the hydrogen content exceeds a certain limit or critical value.

This report will address:

- Processes by which Ti-7 can absorb hydrogen and, hence, eventually become susceptible to HIC
- Analysis procedures for predicting the consequences of hydrogen absorption
- Acquisition of input data for the analysis parameters
- Results.



SL_AMR1_fig6-1

NOTE: Shoesmith et al. (1997)

Figure 1. Schematic Showing the Combinations of Stress Intensity Factor and Hydrogen Concentration Leading either to Fast Crack Growth (Brittle Failures) or Slow Crack Growth Due to either Sustained Load Cracking or Ductile Rupture or to No Failure

6.1.2 Processes by which Hydrogen is Absorbed

Both crevice corrosion and general passive corrosion will be accompanied by hydrogen production and, hence, possibly by the absorption of hydrogen into the metal.

For crevice corrosion the hydrolysis of dissolved metal cations leads to acidification within the occluded area and the development of active conditions in which the metal is unprotected by an oxide film. Once initiated, crevice corrosion is supported by both the reduction of oxygen on passive surfaces external to the crevice and the reduction of protons ($Ti + 4H^+ \rightarrow Ti^{++} + 2H_2$) on exposed metal surfaces inside the crevice. The latter process can lead to the absorption of atomic hydrogen into the metal in sufficient quantities to produce extensive hydride formation (Shoesmith et al. 1997, Figure 3, p. 4).

For the passive non-creviced or the repassivated crevice conditions expected to prevail, the corrosion of the titanium alloy will be sustained by reaction with water under neutral conditions ($Ti + 2H_2O \rightarrow TiO_2 + 2H_2$) and will proceed at an extremely slow rate. This process will generate hydrogen, which must pass through the TiO_2 film before absorption in the underlying Ti alloy can produce HIC. .Redox transformations (Ti^{IV}-> Ti^{III}) in the film are required before the oxide becomes significantly transparent to hydrogen. Significant cathodic polarization of the metal (generally only achievable by galvanic coupling to carbon steel or the application of a cathodic protection potential) is required for these transformations to occur. Measurements of absorbed hydrogen suggest a threshold potential of –0.6 V versus saturated calomel electrode (SCE) above which no absorption occurs (Shoesmith et al. 1997, p. 4). Only impressed current cathodic protection or galvanic coupling to active alloys of Fe, Zn, or Mg could readily produce such active potential. Thus, hydrogen generation rates are expected to be very low on Ti alloy surfaces.

6.1.3 Critical Hydrogen Concentration, H_C

Provided that wall penetration by corrosion does not exceed the corrosion allowance, HIC failure is assumed to occur when the material has absorbed enough hydrogen to exceed the critical hydrogen content, H_C. Observations regarding the critical hydrogen content, H_C, for Ti-2 and Ti-12 (Shoesmith et al. 1997, pp. 7-11) are summarized as follows:

Using the slow strain rate technique on precracked compact tension specimens precharged with known amounts of hydrogen, it has been shown that the fracture toughness of Ti-2 and Ti-12 is not significantly affected until hydrogen content exceeds H_C. Once above H_C, there is no slow crack growth, and only fast crack growth is observed.

H_C is sensitive to the microstructure and texture of the material with respect to the orientation of the crack and the applied stress. Preferential pathways for cracking are formed along β-phase stringers introduced through the manufacturing process. An H_C of 500 μg/g has been measured in Ti-12 containing cracks propagating in the directions defined by these stringers. Crack propagation perpendicular to these features in not observed up to H_C = 2000 μg/g. Heat treatment to remove this laminar structure by randomly reorienting the residual β-phase can lead to a decrease in H_C to ~400 μg/g.

Even for manufactured plate materials that do not have high β-phase content, e.g., Ti-2, the laminar structure introduced by rolling appears to dominate the cracking behavior. As a consequence, depending on crack orientation, H_C varies between ~400 and 1000 μg/g. Since Ti-2 does not contain as much β-phase as Ti-12, heat treatment does not exert a significant influence on H_C. Welding produces a larger change in the microstructure than does heat treatment. The high weld temperature results in significant microstructural changes in the weldment. This results in a small decrease in strength. The heat affected zone does not appear to be sufficiently large to influence the cracking behavior because, for both Ti-2 and Ti-12, H_C is slightly decreased near the weld metal compared to the base metal. It did not decrease below 500 μg/g.

It can also be assumed that failure is less likely at elevated temperature. The assumption is justified, in part, by recognizing that the hydrogen solubility would be higher at elevated temperature. Experimental results indicated that the value of H_C increases with increasing temperature. A conservative value of $H_C = 500$ µg/g can be adopted as the critical hydrogen concentration in rolled plate material for predicting container lifetime.

H_C data are not available for Ti-7. The H_C value for Ti-7 is assumed to be at least 400 µg/g, which is the lower bound value observed for Ti-2 and Ti-12 as indicated previously. This assumption appears to be extremely conservative based on data reported by Ikeda and Quinn (1998, p. 7), which indicated that the H_C value for Ti-16 is between 1000 and 2000 µg/g. As noted in Section 1, Ti-7 and Ti-16 are similar alloys because of their similar chemical compositions.

6.1.4 Hydrogen Absorption During Crevice Corrosion

Crevice corrosion, if it initiates, will propagate at a rate much higher than that of general corrosion. Crevice propagation, as mentioned in Section 6.1.1, can lead to failure by wall penetration as well as failure due to HIC because of hydrogen transported into the metal.

The most effective way to reduce hydrogen absorption is to choose a more crevice corrosion resistant alloy (Shoesmith et al. 1997, p. 15). Improvements in resistance to crevice corrosion have been attributed to alloying elements, which reinforce passivity. Susceptibility to crevice corrosion is eliminated through the alloying series Ti-2→Ti-12→Ti-16 (Shoesmith et al. 1997, p. 15). In accordance with CRWMS M&O (1999d, pp. 49, 51), the major additions are Mo (0.2-0.4%) and Ni (0.6-0.9%) for Ti-12 and Pd (0.04-0.08%) for Ti-16. Decreased crevice corrosion rate by adding alloying elements such as Mo and Ni in Ti-12 and Pd in Ti-16 is noted in Shoesmith et al. (1997, Figure 12, p. 16). The effect of deliberate alloying of Ti-12 with Ni and Mo, which segregate at grain boundaries and intermetallics, is to improve the susceptibility to crevice corrosion from repassivation after some crevice corrosion in Ti-2 to repassivation after minor crevice corrosion damage in Ti-12. The effect of adding Pd to ennoble titanium while avoiding segregation in Ti-16 is to further improve the susceptibility to crevice corrosion from repassivation after minor crevice corrosion in Ti-12 to no crevice corrosion damage in Ti-16. It can be seen from CRWMS M&O (1999d, pp. 45, 51) that the composition of Ti-7 is almost identical to that of Ti-16, but the Pd content is even higher in Ti-7 (0.12-0.25%) than in Ti-16 (0.04-0.08%). Therefore, Ti-7, like Ti-16, is not expected to suffer any crevice damage.

Crevice corrosion is one form of localized corrosion of a metal surface (ASM 1987, p. 4). The localized corrosion model developed by CRWMS M&O (2000a, p. 34) for Ti-7 DS assumes that localized attack occurs only if the open circuit corrosion potential, E_{corr}, exceeds the threshold potential for breakdown of the passive film, $E_{critical}$. Experimental measurements reported by CRWMS M&O (2000a, pp. 38-41) for E_{corr} and $E_{critical}$ were obtained from various test environments expected in the repository. These test environments 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. SCW is about one thousand times more concentrated than J-13 well water and is slightly alkaline (pH~8). SAW is about one thousand times more concentrated than J-13 well water and is acidic (pH~2.7). J-13 well water (Harrar et al. 1990) is the groundwater at some distance from Yucca Mountain. The experimental measurements show that the threshold $E_{critical}$ is consistently greater than E_{corr}. CRWMS M&O (2000a, Table 5, p. 41) indicated that the difference, $E_{critical} - E_{corr}$, falls in the range from 500 mV to 1650 mV for the various test environments of SDW, SCW, SAW, and SSW at temperature from 20˜150°C.

It is, therefore, concluded that hydrogen absorption during crevice corrosion may be ignored in the HIC model.

6.1.5 Hydrogen Absorption During General Passive Corrosion

According to Shoesmith et al. (1997, p. 15), there are two processes by which hydrogen could be produced, and possibly absorbed, under passive conditions: (1) direct absorption of hydrogen produced by water radiolysis and (2) absorption of atomic hydrogen produced by the corrosion process to produce oxide. The direct absorption of radiolytically produced hydrogen does not appear to be significant except at high dose rate (> 10^2 Gy/h) and high temperature (> 150°C) (Shoesmith et al. 1997, p. 16). This condition is clearly unattainable under Yucca Mountain DS conditions and will not be considered, leaving the corrosion process as the only feasible source of hydrogen for absorption.

Under anoxic conditions, when passive corrosion should prevail, the corrosion potential for passive titanium must reside at a value at which water reduction can couple to titanium oxidation,

$$\mathrm{Ti} + 2\mathrm{H_2O} \rightarrow \mathrm{TiO_2} + 2\mathrm{H_2}$$

and, hence, must be at, or more negative than, the thermodynamic stability line for water. At such potentials, titanium hydrides are thermodynamically stable with respect to the metal. Consequently the passive film can be considered only as a transport barrier and not as an absolute barrier. The rate of hydrogen absorption at the corrosion potential will be controlled by the rate of the corrosion reaction, which dictates the rate of production of absorbable hydrogen. Since titanium oxide, TiO, is extremely stable and protective in the DS environment, the corrosion reaction will be effectively limited to an oxide film growth reaction.

While the rate of hydrogen production and, hence, absorption may be assumed directly proportional to the rate of film growth, the fraction of hydrogen absorption needs to be determined. Based on available test data, Shoesmith et al. (1997, p. 22), suggests the use of 0.1 and 0.02 for fractional efficiency for absorption values, f_h, to represent high and low hydrogen absorption efficiencies for titanium alloys. The low value would appear most appropriate for Ti-2 since the passive film is a good transport barrier to hydrogen absorption. For Ti-12, since Ni, in either Ti_2Ni intermetallics or in β phase, is present, the higher value would be more conservative. For Ti-16 in which intermetallic formation is avoided, the lower value is appropriate. The lower value should also be used for Ti-7 because of the similarity in chemical composition between Ti-7 and Ti-16.

Based on a constant film growth rate and, hence, the corrosion rate, Shoesmith et al. (1997, p. 22) indicated that the concentration of hydrogen in the metal, H_A, in g/mm^3 can be calculated as a function of time of emplacement (t in years) from the expression:

$$H_A = 4(\rho_{Ti}/10^3)f_h R_{uc} t[M_{Ti}(d_o - R_{uc}t)]^{-1} \qquad \text{(Eq. 1)}$$

where

H_A = *hydrogen* content (g/mm^3)

ρ_{Ti} = density of Ti (g/cm^3) = 4.5 (Weast and Astle 1978, p. B-177)

f_h = fractional efficiency for absorption

R_{uc} = rate of general passive corrosion (mm/a)

t = time of emplacement in years (a)

M_{Ti} = atomic mass of Ti = 47.9 (Weast and Astle 1978, p. B-177)

d_o = original corrosion allowance (mm) = container wall thickness

The fractional efficiency for absorption, based on previous discussion, is $f_h = 0.02$ for Ti-7.

Considering a Ti-7 plate with 1 mm^2 surface area, it is noted in Equation 1 that: (1) hydrogen in grams produced by the general corrosion after t years of emplacement is $4(\rho_{Ti}/10^3)R_{uc}t/M_{Ti}$ based on the reaction $Ti + 2H_2O \rightarrow TiO_2 + 2H_2$; (2) multiplication by the factor f_h converts the produced hydrogen into absorbed hydrogen; and (3) the remaining volume of Ti-7 alloy in mm^3 is presented by $(d_o - R_{uc}t)$. The derivation of Equation 1 is based on a constant general corrosion rate. It was noted by CRWMS M&O (2000a, p. 48) that the assumption of constant corrosion rate is conservative and less conservative corrosion cases assume that the rate decays with time.

Using the relationship H (μg of H/g of Ti) = H (g of H/mm^3 of Ti)(1000/(10^{-6}/ρ_{Ti}), Equation 1 can be rewritten for H_A in μg/g as follows:

$$H_A = 4x10^6 f_h R_{uc} t[M_{Ti}(d_o - R_{uc}t)]^{-1} \qquad \text{(Eq. 2)}$$

where

H_A = hydrogen content (μg/g)

The rate of general passive corrosion, R_{uc}, can be calculated from the rate of oxide film thickness, R_{ox} by the following formula:

$$R_{uc} = R_{ox}(\rho_{ox}/M_{ox})(\rho_{Ti}/M_{Ti})^{-1} \qquad \text{(Eq. 3)}$$

where

ρ_{ox} = density of the oxide in g/cm^3

M_{ox} = molecular mass of the oxide

since the value of $(\rho_{ox}/M_{ox})(\rho_{Ti}/M_{Ti})^{-1}$ is always greater than unity, it is conservative to assume that $R_{uc} = R_{ox}$.

Three values are given by Shoesmith et al. (1997, p. 19) for the oxide film growth rate (and, hence, the general corrosion rate), i.e., 0.44 nm/a, 3.3 nm/a, and 1.1 nm/a. The rate given by 0.44 nm/a is considered the most likely value for both Ti-12 and Ti-16; the rate 3.3 nm/a represents a conservative maximum for Ti-12; and the rate 1.1 nm/a is the maximum for Ti-16.

Higher general corrosion rates for Ti-7, however, have been reported by CRWMS M&O (2000a, p. 58). The rate at the 50th percentile is approximately 25nm/a; the rate at the 90th percentile is approximately 100 nm/a; and the maximum rate is less than 350 nm/a.

6.2 APPLICATION OF HIC MODEL TO DRIP SHIELD

6.2.1 Material

Titanium Grade 7 (Ti-7) (UNS R52400) is now being considered for construction of the DS for the WP. As indicated in Section 1, this alloy consists of 0.3% Fe, 0.25% O, 0.12-0.25% Pd, 0.1% C, 0.03% N, 0.015% H, and 0.4% total residuals with the balance being Ti.

Both crevice corrosion and general passive corrosion will be accompanied by hydrogen production and, hence, possibly by the absorption of hydrogen into the metal. It has been concluded in Section 6.1.4 that hydrogen absorption during crevice corrosion will not be considered in the HIC model since crevice corrosion is essentially eliminated for Ti-7.

General corrosion rates for Ti-16 reported by CRWMS M&O (2000a, p. 59) indicated that the rate at the 50th percentile is approximately 25nm/a (or 25×10^{-6} mm/a); the rate at the 90th percentile is approximately 100 nm/a (or 100×10^{-6} mm/a); and the maximum rate is less than 350 nm/a.

6.2.2 Determination of the Critical Hydrogen Concentration, H_C

As discussed in Section 6.1.3, Shoesmith et al. (1997, p. 11), concluded that a conservative value of H_C = 500 μg/g can be adopted as the critical hydrogen concentration in rolled plate material and Ti-12 is ~400 μg/g. Ikeda and Quinn (1998) indicated that H_C for Ti-16 is at least 1000 μg/g and may be much greater.

H_C data are not available for Ti-7. The H_C value for Ti-7 is assumed to be at least 400 μg/g, which is the lower bound value observed for Ti-2 and Ti-12 as indicated previously. This assumption appears to be extremely conservative based on data reported by Ikeda and Quinn (1998) for Ti-16. As noted in Section 1, Ti-7 and Ti-16 are similar alloys because of their similar chemical compositions.

6.2.3 Determination of Hydrogen Concentration

Based on Equation 2, the hydrogen concentration in the metal can be rewritten as follows:

$$H_A = 4x10^6 f_h R_{uc} t[M_{Ti}(d_o - R_{uc}t)]^{-1}$$

where

H_A = hydrogen content (μg/g)

ρ_{Ti} = density of Ti in g/cm^3 = 4.5 (Weast and Astle 1978, p. B-177)

f_h = fractional efficiency for absorption

R_{uc} = rate of general passive corrosion (mm/a)

t = time of emplacement in years (a)

M_{Ti} = atomic mass of Ti = 47.9 (Weast and Astle 1978, p. B-177)

d_o = original corrosion allowance (mm) = container wall thickness

The fractional efficiency for absorption, based on previous discussion, is $f_h = 0.02$ for Ti-7. The rate of general passive corrosion is $R_{uc} = 100x10^{-6}$ mm/a (90th percentile value) or $25x10^{-6}$ mm/a (50th percentile value) based on Section 6.2.1. The time of employment is t = 10,000 years. A minimum wall thickness of 15 mm is assumed for d_o.

Case 1: Conservative Estimate

$R_{ox} = 100x10^{-6}$ mm/a (90th percentile value)

$f_h = 0.02$

$d_o = 15$ mm

$t = 10000\ \text{a}$

From Equation 2, $H_A = 119\ \mu g/g < H_c = 400\ \mu g/g$.

Case 2: Best Estimate

$R_{ox} = 25\ x10^{-6} \text{mm/a}$ (50th percentile value)

$f_h = 0.02$

$d_o = 15\ \text{mm}$

$t = 10000\ \text{a}$

From Equation (2), $H_A = 28\ \mu g/g < H_c = 400\ \mu g/g$.

6.2.4 Results

The analytical estimate presented in Section 6.2.3 based on Equation 2 indicated that there exists a big margin of safety for the drip shield against the effects of HIC. The hydrogen concentration in the DS at 10,000 years after emplacement is 119 μg/g resulting from a conservative estimate and 28 μg/g from a best estimate. The estimated hydrogen concentration in either case is less than the critical hydrogen concentration of 400 μg/g for Ti-7.

6.2.5 Model Validation

Model validation has been accomplished following guidelines cited in ASTM procedure C 1174, 1997 (sections 19.3 and 20.4). According to ASTM C 1174 (section 20.4.3.1) validation of model means the model can account for all available data. In this AMR, data obtained in the laboratory for the Yucca Mountain Site Characterization Project along with published data available from the open scientific literature have been used to fit into well-known mathematical models to predict hydrogen induced corrosion behavior (e.g., corrosion rates, hydrogen concentration, etc.) of the proposed DS material (i.e., Ti-7). The model predicted values showed excellent agreement with the experimental data obtained by short-term laboratory tests. Additional data that are being collected will help improve the level of confidence in the model.

7. CONCLUSIONS

A simple and conservative model has been developed to evaluate the effects of hydrogen induced cracking on the drip shield. The basic premise of the model is that failure will occur once the hydrogen content exceeds a certain limit or critical value, H_C. Quantitative evaluation based on the HIC model described in Section 6.1 indicates that the drip shield material (Ti-7) is able to sustain the effects of HIC.

The quantitative evaluation includes analytical estimates presented in Section 6.2.3 based on Equation 2, indicating that there exists a big margin of safety for the drip shield against the effects of HIC. The hydrogen concentration in the DS at 10,000 years after emplacement is 119 μg/g resulting from a conservative estimate and 28 μg/g from a best estimate. The estimated hydrogen concentration in either case is less than the critical hydrogen concentration of 400 μg/g for Ti-7, a conservative value based on Section 6.1.3.

Model validation in this AMR was accomplished using short term data available to date. Additional data that are being collected will help improve the level of confidence in the model.

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.

8. INPUTS AND REFERENCES

8.1 DOCUMENTS CITED

ASM International 1987. *Corrosion.* Volume 13 of *Metals Handbook.* 9th Edition. Metals Park, Ohio: ASM International. TIC: 209807.

CRWMS M&O 1999a. *Classification of the MGR Uncanistered Spent Nuclear Fuel Disposal Container System.* ANL-UDC-SE-000001 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19990928.0216.

CRWMS M&O 1999b. Not used.

CRWMS M&O 1999c. Not used.

CRWMS M&O 1999d. *Waste Package Material Properties.* BBA000000-01717-0210-00017 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19990407.0172.

CRWMS M&O 1999e. *1101213PM7 Waste Package Analysis & Models - PMR.* Activity Evaluation. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19991012.0219.

CRWMS M&O 1999f. *Analysis and Model Reports to Support Waste Package PMR.* TDP-EBS-MD-000003 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19990809.0401.

CRWMS M&O 2000a. *General Corrosion and Localized Corrosion of the Drip Shield.* ANL-EBS-MD-000004 REV 00. Las Vegas, Nevada: CRWMS M&O URN-0135.

CRWMS M&O 2000b. *Emplacement Drift System Description Document.* SDD-EDS-SE-000001 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000121.0119.

DOE (U.S. Department of Energy) 2000. *Quality Assurance Requirements and Description.* DOE/RW-0333P, Rev. 9. Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: MOL.19991028.0012.

Harrar, J.E.; Carley, J.F.; Isherwood, W.F.; and Raber, E. 1990. *Report of the Committee to Review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations.* UCID-21867. Livermore, California: Lawrence Livermore National Laboratory. ACC: NNA.19910131.0274.

Ikeda, B. M. and Quinn, M. J. 1998. *Hydrogen Assisted Cracking of Grade-16 Titanium: A Preliminary Examination of Behavior at Room Temperature.* 06819-REP-01200-0039 R00. 1. 13. Toronto, Ontario: Atomic Energy of Canada Ltd. Library Tracking Number 1388.

Shoesmith, D.W.; Hardie, D.; Ikeda, B.M.; and Noel, J.J. 1997. *Hydrogen Absorption and the Lifetime Performance of Titanium Waste Containers.* AECL-11770. Pinawa, Manitoba, Canada: Atomic Energy of Canada Limited. TIC: 236220.

Weast, R.C. and Astle, M.J., eds. 1978. *CRC Handbook of Chemistry and Physics.* 59th Edition. pp. D-265, D-299, D-300, -304 , F-61 and F-62. Boca Raton, Florida: CRC Press. TIC: 246395.

8.2 CODES, STANDARDS, REGULATIONS, AND PROCEDURES

AP-3.10Q, Rev. 02, ICN 0. *Analyses and Models.* Washington D.C., Washington D.C.: Office of Civilian Radioactive Waste Management. ACC: MOL.20000217.0246.

ASTM C 1174-97. 1997. *Standard Practice for Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste.* West Conshohocken, Pennsylvania: American Society for Testing and Materials. TIC: 246015.

QAP-2-3, Rev. 10. *Classification of Permanent Items.* Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19990316.0006.

QAP-2-0, Rev. 5. *Conduct of Activities.* Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19980826.0209.