Hydrogen Induced Cracking in Titanium Drip Shield of High-Level Waste Repository

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ABSTRACT

Both qualitative and quantitative assessments have been conducted to evaluate the effects of hydrogen induced cracking on the drip shield. The basic premise of the assessments is that failure will occur once the hydrogen content exceeds a certain limit or critical value, H_C. Potential mechanisms for hydrogen absorption in the drip shield have been identified to be general passive corrosion and galvanic couple with steel components. Both qualitative and quantitative evaluations indicated that hydrogen concentration in the drip shield will be below the critical value by a considerable margin. The choice of the mathematical models and associated parameters appears to be reasonable. Continued effort in data collection and development should provide validation and improved level of confidence of the proposed models.

INTRODUCTION

In accordance with Farmer et al. (2000a), the recommended engineering design of the high-level waste repository at the Yucca Mountain site includes a double-wall waste package underneath a protective drip shield. The waste package outer barrier is to be made of Alloy 22 (UNS N06022) while the underlying structural support (or inner barrier) is to be made of 316NG or 316L (UNS S31603). The drip shield is to be made of Titanium Grade 7 (Ti-7) (UNS R52400). For the waste package outer barrier (Alloy 22), Farmer et al. (2000a) concluded that, over the 10,000 years life of the repository, general corrosion of Alloy 22 (being an extremely corrosion resistant material) should not be life limiting and localized breakdown of the passive film is also unlikely. The most likely failure for the waste package outer barrier is the stress corrosion cracking. The modeling and mitigation of this failure mode was addressed by Farmer et al. (2000b). Failure occurs in the drip shield 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 (HIC). The first type of failure mechanism, i.e., wall penetration by crevice and general corrosion, is treated in CRWMS M&O (2000). This paper deals with the failure mechanisms of the drip shield associated with HIC.

CRITICAL HYDROGEN CONCENTRATION, H_C

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. Figure 1 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 following (Shoesmith et al. 1997) has been adopted to predict when HIC might become a potential failure process for the drip shield. The basic premise of the approach is that failure will occur once the hydrogen content exceeds a certain limit or critical value.

Based on observations of the critical hydrogen content, H_C, for Ti-2 and Ti-12 (Shoesmith et al. 1997), a conservative value of H_C = 500 µg/g can be adopted as the critical hydrogen concentration for Ti-2 and Ti-12. H_C data are not available for Ti-7 but more recent data reported by Ikeda and Quinn (1998) indicated that the H_C value for Ti-16 is between 1000 and 2000 µg/g. The H_C value for Ti-7 is assumed to be at least 1000 µg/g. This assumption is based on data reported by Ikeda and Quinn (1998) and the fact that the chemical composition of Ti-7 is almost identical to that of Ti-16 with the only difference that the Pd content is higher in Ti-7 (0.12-0.25%) than in Ti-16 (0.04-0.08%).
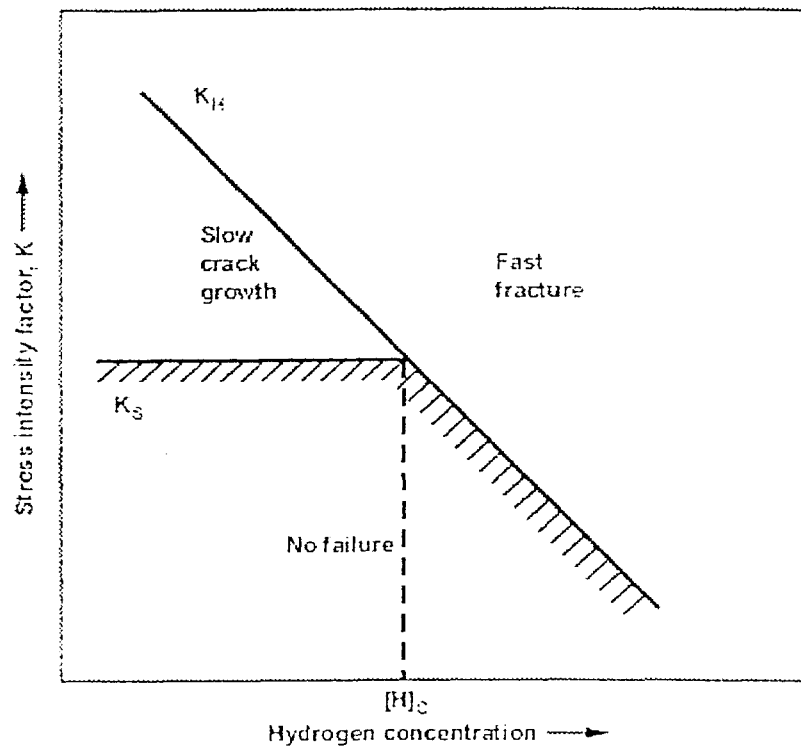
Figure 1. Schematic Showing the Combinations of Stress Intensity Factor and Hydrogen Concentration Leading either to Fast Crack Growth (Brittle Failures) or Slow Crack Growth Due to either Sustained Load Cracking or Ductile Rupture or to No Failure

PROCESSES BY WHICH HYDROGEN IS ABSORBED

In accordance with Schutz and Thomas (1987), the three general conditions that must exit simultaneously for the hydrogen embrittlement (or HIC) of titanium alloys are:

- A mechanism for generating hydrogen on a titanium surface. The mechanisms may include a galvanic couple, hydrogen produced in atomic form by corrosion processes, and the direct absorption of hydrogen produced by water radiolysis.
- Metal temperature above approximately 80 °C (175 °F), where the diffusion rate of hydrogen into α titanium is significant.
- Solution pH less than 3 or greater than 12, or impressed potentials more negative than -0.7 V(SCE).

Among mechanisms for hydrogen generation, 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 drip shield conditions.

Crevice corrosion, if it initiates, will propagate at a rate much higher than that of general corrosion. Crevice propagation, 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). 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. According to CRWMS M&O (1999), 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. 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 (1999) 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). The localized corrosion model developed by CRWMS M&O (2000a) for Ti-7 drip shield 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) for E_{corr} and $E_{critical}$ show that the threshold $E_{critical}$ is consistently greater than E_{corr}, with indication that the difference, $E_{critical} - E_{corr}$, falls in the range from 500 mV to 1650 mV for the various test environments at temperature from 20-150°C.

It is, therefore, concluded that hydrogen absorption during crevice corrosion may be ignored in the HIC model. Hydrogen generation in titanium alloys will be mostly due general passive corrosion and galvanic couple, which are addressed in the rest of this paper.

HYDROGEN ABSORPTION DURING GENERAL PASSIVE CORROSION

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.

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 drip shield 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) 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 (hence the corrosion rate), 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:

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

where

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

ρ_{Ti} = density of Ti (g/cm^3) = 4.5 (Weast and Astle 1978)

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)

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 mm² 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 mm³ 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 (2000) 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/mm³ of Ti)(1000/($10^{-6}/\rho_{Ti}$), Equation 1 can be rewritten for H_A in µg/g as follows:

$$H_A = 4 \times 10^6 f_h R_{uc}t[M_{Ti}(d_o - R_{uc}t)]^{-1} \qquad \text{(Eq. 2)}$$

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/cm³

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) 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 (2000). 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.

For the drip shield, the time of employment is t = 10,000 years and one half of the minimum wall thickness (15 mm) is assumed for d_o, i.e., d_o = 7.5 mm. Using rate of general passive corrosion R_{uc} = 100x10^{-6} mm/a (90th percentile value) and 25x10^{-6} mm/a (50th percentile value), hydrogen concentration in the drip shield is estimated for the following cases:

Case 1: Conservative Estimate

$$R_{ox} = 100 \times 10^{-6} \, mm/a \, (90^{th} \text{ percentile value})$$

$$f_h = 0.02$$

$$d_o = 7.5 \, mm$$

$$t = 10000 \, a$$

From Equation 2, H_A = 257 μg/g < H_c = 1000 μg/g.

Case 2: Best Estimate

$$R_{ox} = 25 \times 10^{-6} \, mm/a \, (50^{th} \text{ percentile value})$$

$$f_h = 0.02$$

$$d_o = 7.5 \, mm$$

$$t = 10000 \, a$$

From Equation (2), H_A = 58 μg/g < H_c = 1000 μg/g.

HYDROGEN INDUCED CRACKING OF TI-7 DUE TO GALVANIC COUPLE

Given the expected evolution of ground waters potentially contacting the drip shield and the temperature regime within the repository (CRWMS M&O 2000), the required conditions for hydrogen absorption by the titanium drip shield are clearly present when galvanically coupled to sections of the steel components. The efficiency of Fe-Ti galvanic couples to cause hydrogen cracking, however, will be limited for a number of reasons:

(i)   The contact area is likely to be small and the anode to cathode area (area of steel and titanium, respectively) low. Since relatively low volumes of groundwater are likely to contact both metals simultaneously, anode to cathode areas close to one seem likely. If a couple with a small anode to cathode ratio was established (i.e.. a small piece of steel in

contact with a large area of drip shield) then one would expect the couple to be more rapidly exhausted as the steel is consumed. Under these conditions the amount of hydrogen absorbed would be limited.

(ii)   Conditions in the repository will be oxidizing, making it less likely that the couple will sustain water reduction, and hence hydrogen absorption. However, at high temperatures in concentrated saline solutions, the amount of O_2 dissolved in the solution forming the couple will probably be too low to displace water reduction as the primary cathodic reaction. However, the ferrous ion product of steel dissolution will be homogeneously oxidized to ferric species by dissolved O_2. If conditions remain neutral this should lead to the formation of insoluble Fe^{III} oxides/hydroxides and little influence would be exerted on the galvanic couple. However, any tendency for acidification or the development of alkaline conditions will increase the ferric ion solubility. Under evaporative conditions this could lead to quite high dissolved ferric ion concentrations and the establishment of a galvanic potential sufficiently positive to avoid hydrogen absorption into the titanium.

(iii)   Titanium has a large tolerance for hydrogen and substantial concentrations must be achieved before any degradation in fracture toughness is observed. This concentration level, as indicated in Section 6.1.3, has been measured to be in the range of 400 to 1000 $\mu g.g^{-1}$ for Ti-2 and Ti-12. Recent measurements suggest that the tolerance for hydrogen of the Ti-16 (a titanium alloy very similar to Ti-7 in chemical composition) may be in the 1000 to 2000 $\mu g.g^{-1}$ range (Ikeda and Quinn 1998). This paper has concluded that the critical hydrogen concentration for Ti-7 is at least 1000 $\mu g.g^{-1}$.

Given the high critical hydrogen concentration, the large volume of available titanium in the drip shield into which absorbed hydrogen can diffuse, and other reasons stated above, hydrogen embrittlement of the Ti DS is highly unlikely.

A mathematical model is proposed to predict the hydrogen concentration in the drip shield due to a galvanic couple between the drip shield and a carbon steel segment. The absorption and diffusion of hydrogen in the drip shield is a complex process. A mathematical model is possible only if a number of necessary assumptions are adopted. These assumptions are:

• The drip shield is treated as an infinite flat plate. The thickness of the plate is denoted as H.

• The contact plane between the drip shield surface and the carbon steel segment is circular in shape. The radius of the circular plane is denoted as r_0.

• Hydrogen is absorbed into the drip shield through the contact plane and immediately reaches the other surface. The initial region of the drip shield with hydrogen absorption has the shape of a circular disk with a radius r_0 and thickness H.

• As hydrogen starts to diffuse in the DS, the radius of the circular region will expand at a constant speed v. As a result, the radius r(t) of the circular disk at a time t is expressed by the following equation:

$$r(t) = r_0 + v t \qquad\qquad (Eq. 4)$$

The amount of hydrogen (in g or mg, for example), $Q(t)$, absorbed in the DS at a time t, therefore, is:

$$Q(t) = \lambda\left(\rho_{Ti}\pi r_0^2\right)Ht + \int_{\tau=0}^{\tau=t}\lambda\rho_{Ti}\left[2\pi r(\tau)\right]H(t-\tau)dr(\tau) \qquad \text{(Eq. 5)}$$

where λ is the hydrogen absorption rate, in ppm (or $\mu g/g$) /day, for example, and ρ_{Ti} is the mass density of the Ti-7 drip shield.

Based on the reaction: $2Fe + 3H_2O \rightarrow Fe_2O_3 + 3H_2$, the maximum amount of hydrogen that can be released from the carbon steel segment is:

$$Q_{max} = f_{Fe}3W/M_{Fe} \qquad \text{(Eq. 6)}$$

where W is the mass of the carbon steel segment, f_{Ti} is the fraction of hydrogen produced by oxidation of the total mass of carbon steel, and M_{Fe} is the atomic mass of Fe.

If t_{max} is the time when $Q(t)$ reaches Q_{max}, t_{max} can be obtained by solving for the following equation:

$$Q_{max} = \lambda\left(\rho_{Ti}\pi r_0^2\right)Ht_{max} + \int_{\tau=0}^{\tau=t_{max}}\lambda\rho_{Ti}\left[2\pi r(\tau)\right]H(t_{max}-\tau)dr(\tau) \qquad \text{(Eq. 7)}$$

Using Eq. 4, Eq. 7 can be written as:

$$Q_{max} = \lambda\rho_{Ti}\pi H\left(r_0^2 t_{max} + r_0 v t_{max}^2 + \frac{v^2 t_{max}^3}{3}\right) \qquad \text{(Eq. 8)}$$

The maximum hydrogen concentration $H_A(r_0)$, in ppm (or $\mu g/g$) for example, will be in the region of the DS beneath the initial contact area and at the time t_{max}, i.e.,

$$H_A(r_0) = \lambda t_{max} \qquad \text{(Eq. 9)}$$

The hydrogen concentration $H_A(r)$ tends to reduce at location with a radius r from the center of the initial contact area, i.e.,

$$H_A(r) = \lambda\left(t_{max} - \frac{r-r_0}{v}\right) \quad \text{for} \quad r_0 \leq r \leq r(t_{max}) \qquad \text{(Eq. 10)}$$

At $t > t_{max}$, $H_A(r)$ will start to decline as the hydrogen diffusion continues and the source of hydrogen exhausts.

As a numerical example, the following input data are considered:

H = Ti-7 plate thickness = 15 mm

r_o = radius of the initial contact area = 50.8 mm (2 in.)

ρ_{Ti} = density of Ti-7 = 4.5×10^6 $\mu g/cm^3$

f_{Fe} = fraction of hydrogen available for absorption by Ti-7 DS = 0.01

W = mass of carbon steel = 22.727×10^6 μg (50 lb.)

M_{Fe} = atomic mass of Fe = 55.847 (Weast and Astle 1978)

The corrosion potential of carbon steel is estimated to be about -0.6 V (SCE), and a galvanic couple would polarize Ti down to that level. Based on Shoesmith (2000), Figure 11, the hydrogen absorption rate, λ, for Ti-7 would be about 0.5 $\mu g/g/day$. No data are available for the hydrogen diffusion rate, v, in Ti-7. For the base case of the numerical example, the values used for λ and v are, respectively, 0.5 $\mu g/g/day$ and 1mm/day. For the parametric study, λ = 0.5, 0.7 $\mu g/g/day$ and v = 1, 2, 3 mm/day are considered, and plots of hydrogen concentration versus distance from the original contact area are shown in Figure 2. It can be seen that, in all cases of the parametric study, the hydrogen concentration does not exceed the critical hydrogen concentration of 1000 $\mu g/g$ for Ti-7 by a rather comfortable margin.

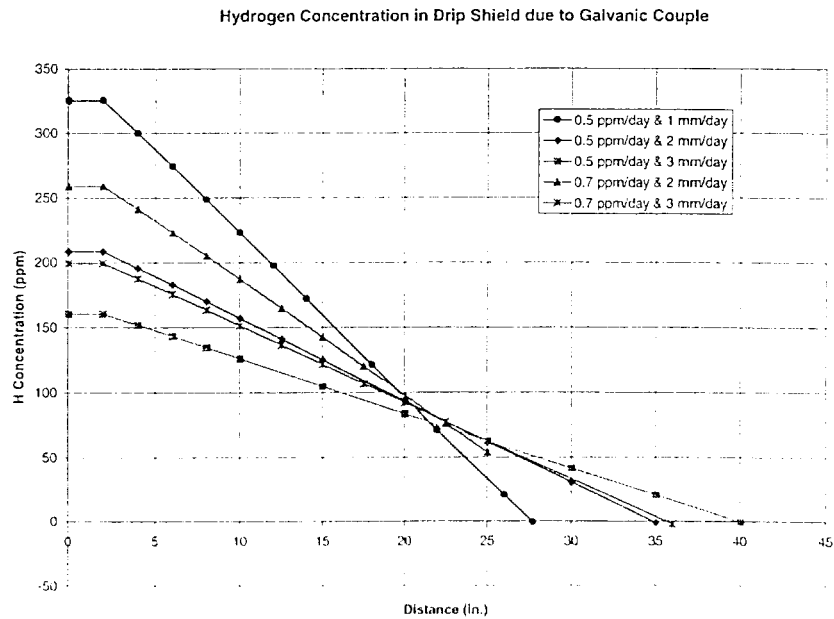**Hydrogen Concentration in Drip Shield due to Galvanic Couple**

Figure 2. Hydrogen Concentration in Drip Shield Versus Distance from Contact Area

CONCLUSION

Both qualitative and quantitative assessments have been conducted to evaluate the effects of hydrogen induced cracking on the drip shield. The basic premise of the assessments is that failure will occur once the hydrogen content exceeds a certain limit or critical value, H_c. Potential mechanisms for hydrogen absorption in the drip shield have been identified to be general passive corrosion and galvanic couple with steel components. Both qualitative and quantitative evaluations indicated that hydrogen concentration in the drip shield will be below the critical value by a considerable margin. The choice of the mathematical models and associated parameters appears to be reasonable. Continued effort in data collection and development should provide validation and improved level of confidence of the proposed models.

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