

Hydrogen-Induced Cracking of Drip Shield

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ANALYSIS/MODEL REVISION RECORD

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ACRONYMS AND ABBREVIATIONS

AMR	Analyses and Models Report
CRWMS	Civilian Radioactive Waste Management System
DS	drip shield
HIC	hydrogen induced cracking
LLNL	Lawrence Livermore National Laboratory
LTCTF	Long Term Corrosion Test Facility
M&O	Management and Operating Contractor
PMR	Process Model Report
QAP	Quality Administrative Procedure
QARD	Quality Assurance Requirements and Description
QP	Quality Procedure
SCC	stress corrosion cracking
SCE	saturated calomel electrode
SCW	simulated concentrated water
SDW	simulated dilute water
SIMS	secondary ion mass spectrometry
SSRT	slow strain rate test
WP	waste package
WPD	waste package degradation
YMP	Yucca Mountain Site Characterization Project

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1. PURPOSE

The most likely failure mechanism for titanium and its alloys under waste disposal conditions is via the process of hydrogen absorption leading to hydrogen-induced cracking (HIC). HIC is also called hydrogen embrittlement, which is a process resulting in a decrease of fracture toughness or ductility of a metal due to the presence of atomic hydrogen. The decrease of fracture toughness can cause the premature brittle fracture of a normally ductile material under sustained load.

The purpose of the process-level model is to account for the HIC effects on the drip shield (DS), which is assumed to be Titanium Grade 7 (Ti-7) [UNS R52400]. This Analyses and Models Report (AMR) serves as a feed to the Waste Package Degradation (WPD) Process Model Report (PMR).

Understanding the degradation of the DS due to HIC is key to one of the most important principal factors in repository performance – the premature failure of the DS. This failure is caused by the decrease in fracture toughness of the DS material due to HIC. 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.

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2. QUALITY ASSURANCE

This document was prepared in accordance with the Civilian Radioactive Waste Management System (CRWMS) Management and Operating Contractor (M&O) Quality Administrative Procedures (QAPs). The information provided in the document is to be indirectly used in the evaluation of the Monitored Geologic Repository waste package and engineered barrier segment. The waste package and engineered barrier segment have been identified as items important to radiological safety and waste isolation in the QAP-2-3 evaluation entitled *Classification of the Preliminary MGDS Repository Design* (CRWMS M&O 1999a p. VI-11). The Waste Package Operations responsible manager has evaluated the document development activity in accordance with QAP-2-0 *Conduct of Activities*. The Activity Evaluation *Neutronics Methodology – SR* (CRWMS M&O 1999b) evaluation has determined the preparation review of the document is subject to *Quality Assurance Requirements and Description* (QARD) (DOE 1999) controls. There is no determination of importance evaluation developed in accordance with Nevada Line Procedure, NLP-2-0, since the document does not involve any field activity. This AMR has been developed in accordance with the Yucca Mountain Site Characterization Project Procedure entitled, *Analyses and Models* (AP-3.10Q, Revision 0, ICN 0).

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3. COMPUTER SOFTWARE AND MODEL USAGE

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

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4. INPUTS

4.1 DATA AND PARAMETERS

Input for this AMR includes data for the critical hydrogen concentration (H_C) and the measured hydrogen concentration of various grades of titanium alloys. H_C values were obtained from a review paper compiled by Shoemith (1999) for the YMP. Data for hydrogen concentration were obtained from results of tests conducted at LLNL for YMP (Roy et al. 1999 and Bedrossian 1999).

4.2 CRITERIA

The criteria applicable to this AMR are stated in Section 1.2, "System Design Criteria," of the *Uncanistered Spent Nuclear Fuel Disposal Container System Description Document* (CRWMS 1999c).

"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 analysis contained in this AMR ensures the integrity of the DS design such that the design criteria for the waste packages will not be compromised.

4.3 CODES AND STANDARDS

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

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5. ASSUMPTIONS

The following assumptions are made to perform the analysis and to develop the model for this AMR:

1. The basic premise in the model is that failure will occur once the hydrogen content exceeds a certain limit or critical value, HC. This model is very conservative because it assumes that, once the environmental and material conditions can support that particular corrosion process, failure will be effectively instantaneous. Clearly, the propagation of a localized corrosion process, whether it be a pit, a crevice, a stress corrosion crack or a hydrogen-induced crack, does not proceed instantaneously to failure. However, if the rate of propagation is fast (per the geologic time scales being considered) then the process can be thought of as instantaneous; e.g., 30 years of “slow” crack growth is irrelevant on a time scale of 10³ to 10⁵ years.
2. Another factor ignored in this analysis is the impact of propagation-limiting processes. For example, with a pit or crevice, repassivation may occur; or with a stress corrosion crack, crack blunting could occur. In this HIC model, no crack initiation or crack blunting processes are considered.
3. The passive oxide is assumed to be permeable to hydrogen. Within a Canadian waste vault, this is a point for discussion. However, under Yucca Mountain conditions, the probability of hydrogen absorption occurring is much lower. For the purpose of this analysis, once this process becomes possible it is conservatively assumed that the oxide is rendered permeable to hydrogen, which then has free access to the alloy; i.e., any hydrogen entering the oxide can be rapidly transported to the metal.
4. Once in the alloy, the hydrogen is transported throughout the entire thickness of the material to yield a uniform distribution of hydrogen. In other words, transport processes within the alloy are rapid compared to the rate of absorption.
5. Data for the critical hydrogen concentration are not available for Ti-7. It is assumed the data available for other grades of titanium are also applicable to Ti-7, and bounding values are used for conservative purpose.

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6. ANALYSIS/MODEL

6.1 DESCRIPTION OF MODEL FOR HYDROGEN INDUCED CRACKING

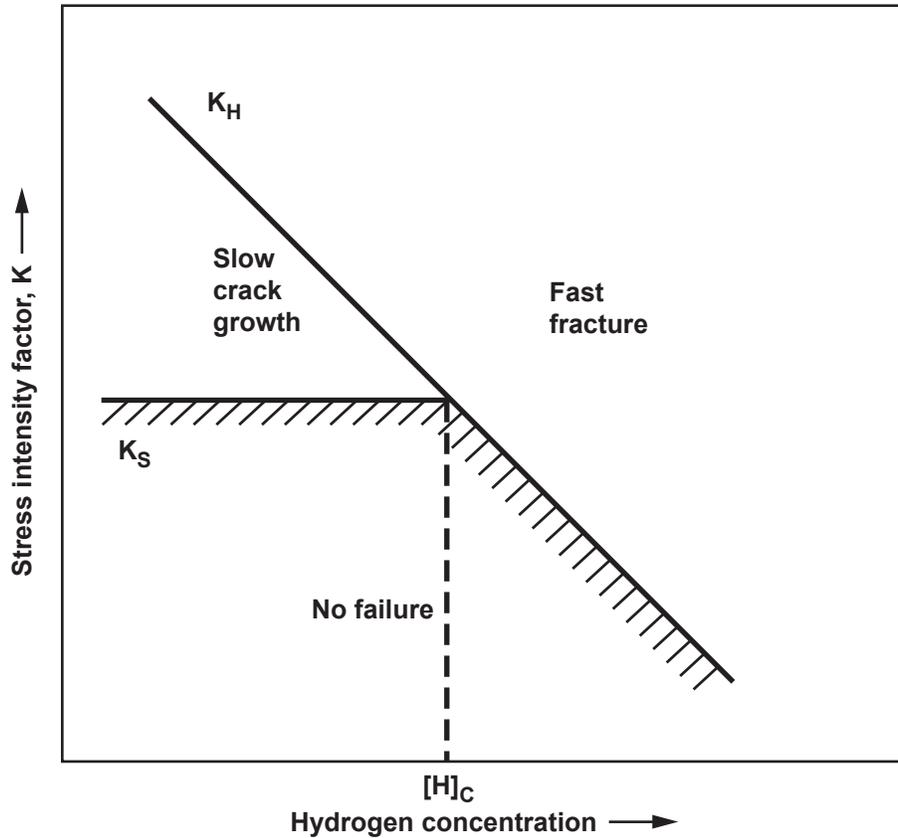
The most likely failure mechanism for titanium and its alloys under waste disposal conditions is via the process of hydrogen absorption leading to hydrogen-induced cracking (HIC). HIC is also called hydrogen embrittlement, which is a process resulting in a decrease of fracture toughness or ductility of a metal due to the presence of atomic hydrogen. The usual failure mode for a ductile material is the ductile tearing observed during slow crack growth. The decrease of fracture toughness can cause the 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 .

Generally, the passive oxide film on titanium (Ti) acts as an excellent barrier to the transport of hydrogen through the oxide, and hydrogen absorption under open-circuit (i.e., natural corrosion) conditions would not be expected and is generally not observed. The concern remains, however, that over normal operating periods (up to tens of years), the process of hydrogen absorption may have been too slow to observe analytically, and that, over the course of many years (10^3 to 10^5), this absorption could lead to a significant accumulation of hydrogen and the danger of HIC.

Modeling HIC could become extremely complicated, involving an attempt to determine the influences of both the corrosion processes and the presence of tensile stresses on such processes. There would be little chance of incorporating such a model into a full-scale performance assessment. The primary drawbacks would be the absence of a meaningful stress analysis, which could be applied to the problem, and a lack of definition on how a crack would start and propagate.

Under Canadian waste vault conditions a very simple approach was adopted to predict when HIC might become a potential failure process in a waste container (Shoesmith et al. 1995). In essence, this model is a susceptibility model, or the equivalent of an initiation model for localized corrosion processes such as pitting and crevice corrosion. The basic premise of the model is that failure will occur once the hydrogen content exceeds a certain limit or critical value, H_C . Figure 1 represents, schematically, the combinations of stress intensity factor and hydrogen concentration leading to (1) fast crack growth (brittle fracture, K_H), (2) slow crack growth (K_S) due to either sustained load cracking or ductile rupture, or (3) no failure.

This model is very conservative because it assume that, once the environmental and material conditions can support the particular corrosion process, failure will be effectively instantaneous.



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Clearly, the propagation of a localized corrosion process, whether it be a pit, a crevice, a stress corrosion crack or a hydrogen-induced crack, does not proceed instantaneously to failure. However, if the rate of propagation is fast on the geologic time scales being considered then the process can be thought of as instantaneous; e.g., 30 years of “slow” crack growth is irrelevant on a time scale of 10^3 to 10^5 years. Another factor ignored in this analysis is the impact of propagation-limiting processes. For example, with a pit or crevice, repassivation may occur; or with a stress corrosion crack, crack blunting could occur. In the HIC model described below, no crack initiation or crack blunting processes are considered.

The model can best be described as follows:

1. The passive oxide is assumed to be permeable to hydrogen.
2. Hydrogen is generated at the surface of the Ti alloy. This is described by a hydrogen generation rate, which is taken to be equal to the rate of the general passive corrosion rate.

3. A fraction of the hydrogen is absorbed into the oxide and assumed to directly enter the alloy. The remainder combines to yield hydrogen gas, which is lost to the surroundings. The rate of absorption is taken to be directly proportional to the hydrogen generation rate multiplied by an absorption efficiency coefficient.
4. Once in the alloy, the hydrogen is transported throughout the entire thickness of the material to yield a uniform distribution of hydrogen. In other words, transport processes within the alloy are rapid compared to the rate of absorption.
5. The hydrogen content of the alloy is allowed to increase until a critical level is reached. The material then fails immediately.

Below, the rationale and some of the implications of adopting such a model are discussed.

1. The oxide is assumed to be permeable to hydrogen.

Within a Canadian waste vault, this is a point for discussion. However, under Yucca Mountain conditions, the case that the oxide is permeable is much harder to make, and hence the probability of hydrogen absorption occurring is much lower. In this context, the term probability is used loosely and descriptively.

In a Canadian waste vault, the repository is sealed and the only available oxidants are those trapped on sealing, redox conditions will eventually evolve to anoxic conditions. When all available O₂ is effectively consumed, the redox conditions at the Ti waste container surface will be sustained by the reaction with trivial amounts of oxidizing impurities in the vault, or, in their absence, by reaction with water. Under these conditions, the corrosion potential of the container (waste package) surface will decrease.

Providing faults do not exist in the passive oxide on the waste package surface, the package remains impermeable to hydrogen until the electrical potential becomes sufficiently negative that the oxide becomes chemically unstable. Once this occurs, Ti^{IV} within the TiO₂ oxide is reduced to Ti^{III}, and hydrogen can be incorporated as a doping defect. (The chemistry/electrochemistry of this transformation has been discussed in Shoesmith et al. (1997)). Once this process becomes possible it is conservatively assumed that the oxide becomes permeable to hydrogen, which then has free access to the alloy; i.e., any hydrogen entering the oxide can be rapidly transported to the metal.

Several mitigating factors indicate that this is a very conservative scenario. First, experimental evidence (Shoesmith 1999) suggests that total permeability is not established as soon as this oxide transformation begins. Second, it is difficult to imagine that, in the absence of specific reducing reagents, such redox transformations could be induced in the passive film. Experimental observations show this threshold for the introduction of permeability to be as low as -0.6V [vs. saturated calomel electrode (SCE)] in neutral solutions at 30°C (Murai et al. 1977).

Counterbalancing the above factors are the influences of temperature and alloying additions to the Ti. For temperatures above ~70°C, crystallization of the passive oxide could introduce faults and grain boundaries that would facilitate the transport of hydrogen through the oxide. The

alloying elements, such as nickel (Ni) (Ti-12) and palladium (Pd) (Ti-16 and Ti-7), act as catalysts for proton reduction. Their presence as intermetallic particles in the alloy could introduce faults in the oxide (“hydrogen windows”) leading to the possibility of hydrogen absorption at potentials more positive than the threshold value described above. This scenario could lead to the absorption of hydrogen at potentials attainable under open-circuit anoxic corrosion conditions. Evidence exists with Ti-12 and Ti-7 that this “sub-threshold” absorption of hydrogen can occur under electrochemical conditions; i.e., in the presence of an applied polarization. This process does not appear to occur with Ti-16, although the reason for this is unknown. Consequently, under anoxic waste vault/repository conditions, the possibility of hydrogen adsorption by these alloys must be considered.

However, Yucca Mountain will not achieve anoxic conditions. In the early stages of vault lifetime, when temperatures are high, the oxygen content of the vault will be low, but so will the water content, which is the only significant potential source of hydrogen (due to reaction with the Ti). Eventually, oxidizing conditions will be established and an open-circuit corrosion potential, too positive to allow the redox transformations in the oxide, will be established. Also, for oxidizing conditions, any exposed noble metal intermetallic particles (e.g., Ti_2Ni in Ti-12, Ti_xPd in Ti-16/Ti-7) will be passivated by a surface oxide film, and their catalytic properties for hydrogen production and absorption will be lost.

The possibility exists that between the states of a hot, dry, low-oxygen condition and a cooler, wet, oxygenated condition, a warm, extremely saline solution of unpredictable pH could exist on the Ti surface. This pH could conceivably rise as high as 14. There is a concern that hydrogen absorption could occur in this environment, and, indeed, the prospect cannot definitely be ruled out. However, available industrial experience indicates this is a remote possibility.

Assuming that the maximum temperature at which an aqueous condition can be sustained on the Ti is 125°C, a pH > 13 would be required for significant hydrogen absorption (see Figure 31, Schutz and Thomas, 1987). It would be judicious to assume, therefore, that hydrogen absorption is possible within the temperature range of ~100°C to 125°C. This range effectively defines a “window of susceptibility” for hydrogen absorption.

The probability of hydrogen absorption by Ti alloys at Yucca Mountain is low, but cannot be ruled out within the window of susceptibility defined by the temperature range of 100°C to 125°C.

2. Hydrogen is generated at the surface of the titanium alloy.

The only feasible source of absorbable hydrogen appears to be the reaction of Ti with water. The direct absorption of radiolytically produced hydrogen requires a combination of high dose rate (> 10^4 R/h) and high temperature (> 200°C) (Shoosmith and King 1999) and a steam or aqueous environment. This combination of conditions seems extremely unlikely at Yucca Mountain. Under open-circuit conditions, the rate of hydrogen production will be directly related to the general corrosion rate. In the presence of dissolved oxygen this rate has been shown to be extremely low, and effectively immeasurable by standard procedures such as weight change measurements. Consequently, the rate of hydrogen production (the essential model boundary

condition) will also be extremely low. Swedish workers reached similar conclusions (Mattsson and Olefjord 1990, Mattsson et al. 1990).

However, noble metal/alloy intermetallics could be catalysts for water reduction, leading to enhanced corrosion of the Ti and production of hydrogen. Under anoxic vault conditions, this is a significant consideration. However, under oxic conditions it will not lead to a significant enhancement of general corrosion; the process will be blocked by the excellent protective properties of the passive TiO₂ film. Also, under oxic conditions, the intermetallics should be covered by a passive oxide film and their catalytic properties severely degraded.

As discussed above, for the temperature range 100°C to 125°C, some enhanced absorption of hydrogen may be possible. However, it is not sufficient that the Ti surface, or the intermetallics within it, possess catalytic cathodic properties. No cathodic process can occur without a simultaneous anodic process. Therefore, the passive oxide formed along with the hydrogen must be of sufficiently poor quality that anodic oxide growth can continue. This process seems extremely unlikely on the Pd-containing alloys, because continued oxide growth (as TiO₂) would lead to the eventual ennoblement of the alloy as Pd concentrated in the alloy surface (Shoesmith 1999). On Ti-12, evidence suggests that, in extremely saline solutions, enhanced film growth accompanied by hydrogen absorption is sustainable, at least for a few years (see papers by Oriani in Shoesmith and King, 1999).

Under Yucca Mountain conditions the corrosion rate of Ti alloys (with the possible exception of Ti-12), and, hence, the rate of hydrogen production, will most likely be slow and transitory. Evidence suggests that even when corrosion, in the form of film growth, is initially accelerated under oxic conditions, the accumulation of mineral precipitates leads to the eventual blocking of the corrosion process (Pan et al. 1996).

3. A fraction of the hydrogen is absorbed into the metal.

Even if the oxide film present on the Ti surface provides just a semipermeable barrier to hydrogen absorption into the metal, only a fraction of the hydrogen produced will actually be absorbed into the metal, and hence contribute to the eventual embrittlement of the alloy. The question is, what is the value of this fraction? A consistent single value may not represent the real absorption efficiency of the alloy because this efficiency would be expected to change as the condition of the surface changed. The initial surface could be relatively free of absorbed hydrogen and the initial absorption efficiency could be high.* Subsequently, it would be expected to decrease as the number of available surface sites for absorption become saturated. These absorption sites could be the usual defects and dislocations known to trap hydrogen and, in addition, noble metal intermetallic particles, which would have a high solubility for hydrogen. Alternatively, the formation of surface hydrides could lead to a change in the mechanism of proton reduction and a decrease in the rate of hydrogen absorption into the alloy. Evidence supports these views, but consistent, usable values of the efficiency remain to be measured.

* All Ti alloys contain a certain amount of hydrogen in the absorbed state. This hydrogen is widely distributed and present in the form of precipitated hydrides.

Two extreme values of the efficiency of absorption are available (Shoesmith 1999). Okada (1983) measured the efficiency electrochemically as a function of pH for Ti, Ni-plated Ti, and Pd-plated Ti. For pH > 3.5, the efficiency for all these systems was $\leq 5\%$ ($\sim 5\%$ for Ni-plated, $\sim 2\%$ for Ti). These values seem appropriate for passive neutral conditions and could be considered conservative, since the Ti-alloy structure used at Yucca Mountain would not be noble-metal-coated.

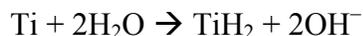
However, the concern remains that, in the temperature range 100°C to 125°C, in the presence of an aggressive saline solution, the passive oxide will be degraded and the hydrogen absorption efficiency increased. There are two sources for an absorption efficiency value. Oriani (1989a and 1989b) measured both the film growth rate (i.e., the rate of hydrogen production) and the hydrogen absorption rate for Ti-12 in extremely saline solutions at 25°C and at $T > 100^\circ\text{C}$. These values would be appropriate for degraded passive conditions, because they closely resemble those anticipated at Yucca Mountain. Noel et al. (1996) measured absorption efficiencies in simulated crevice solutions and obtained values between 5% and 15%. The latter value could be taken as an upper value for the efficiency because it was measured in actively propagating crevices at temperatures in excess of 100°C. Consequently, Noel et al. (1996) values are very conservative when used for passive conditions.

4. Once in the metal the hydrogen is transported throughout the entire thickness of the material to yield a uniform distribution.

Once hydrogen is in the metal its fate becomes dependent on the diffusion rate, and how that rate is affected by the microstructure of the material and the strength and distribution of stresses within the material. Developing a model incorporating all these variables would be complex, and it would be difficult to test. A major drawback would be a complete lack of knowledge of the strength and distribution of stresses. Consequently, no attempt was made to deal with these features within a model.

It was assumed that, because the rate of absorption of hydrogen into the metal would be very slow, its transport throughout the bulk of the material would be comparatively rapid. Hence, the hydrogen would be uniformly distributed throughout the alloy. At the very much higher absorption rates generally found during the electrochemical experiments, absorbed hydrogen lead to the formation of a surface hydride layer (Noel et al. 1996). Such a layer is commonly observed industrially at potentials in the region of -1.0V (vs. SCE) (applied for cathodic protection or achieved due to galvanic coupling to carbon steel) and is innocuous, not leading to failure by cracking. The presence of such a layer appears to impede the absorption of further hydrogen; i.e., its presence reduces the absorption efficiency of the alloy.

If the absorption rate is slow relative to the transport rate, then calculating the uniform distribution of hydrogen is assumed to be simple. This approach was used in the Canadian model (Shoesmith et al. 1995). If the absorption rate is sufficiently high to cause the formation of a surface hydride layer, then it can be treated as a layer growth in the same manner one would consider an oxide film growth; i.e., as a general passive corrosion process. The rate of formation of this layer could be calculated from the hydrogen generation rate multiplied by the absorption efficiency according to the following reaction:



According to Phillips et al. (1972) The composition of this hydride is in the range $\text{TiH}_{1.21}$ to $\text{TiH}_{1.48}$. The amount of hydrogen absorbed could be expressed as a surface layer thickness, and considered as “lost” wall thickness as one would do for a general corrosion process. This may be the best way to view hydrogen absorption in the susceptible range between 100°C and 125°C .

However, this hydrogen accumulates at the Ti surface. A conservative assumption is that it remains available for transport into the alloy. Consequently, once the temperature is low enough that the transport rate can be assumed to exceed the absorption rate ($< 100^\circ\text{C}$), then this layer will lose thickness as the hydride is redissolved in the alloy at the hydride/alloy interface; i.e., the “stored” surface hydrogen now acts as an input boundary condition for transport and accumulation of hydrogen in the bulk of the material. From this point on the hydride redissolves until it is gone and the transport rate then becomes equal to the absorption rate.

5. The hydrogen content of the material is allowed to increase until a critical level is reached and failure occurs.

The slow strain rate tests (Shoesmith et al. 1997 and references therein) show that titanium can tolerate substantial amounts of hydrogen before it becomes susceptible to cracking. This critical hydrogen concentration is not related to the solubility of hydrogen in the alpha matrix of the alloy, but to the number density of precipitates, which must be capable of supporting a crack propagation process through the material. Values for this critical hydrogen concentration are given in Shoesmith (1999) for Ti-2, Ti-12 and Ti-16 (preliminary value). The high value for Ti-16 ($> 1,000 \mu\text{g/g}$) appears to be due to the ability of the intermetallics to soak up hydrogen, thereby preventing them from forming hydride precipitates in the alloy.

Whichever model is assumed for the dispersion of hydrogen throughout the Ti alloy, failure is assumed to occur once this critical value is achieved. However, this remains a very conservative approach because slow strain rate tests have determined the point at which the necessary stress level will inevitably be achieved. Also, the critical value is a threshold value, representing the lowest concentration at which any influence of hydrogen is observed. It is quite feasible that much higher concentrations of hydrogen could be tolerated before failure actually occurs.

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 drip shield for the waste package. Based on Pasupathi (1999), 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.

6.2.2 Determination of the Critical Hydrogen Concentration, H_C

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 their hydrogen content exceeds a critical value, H_C . The

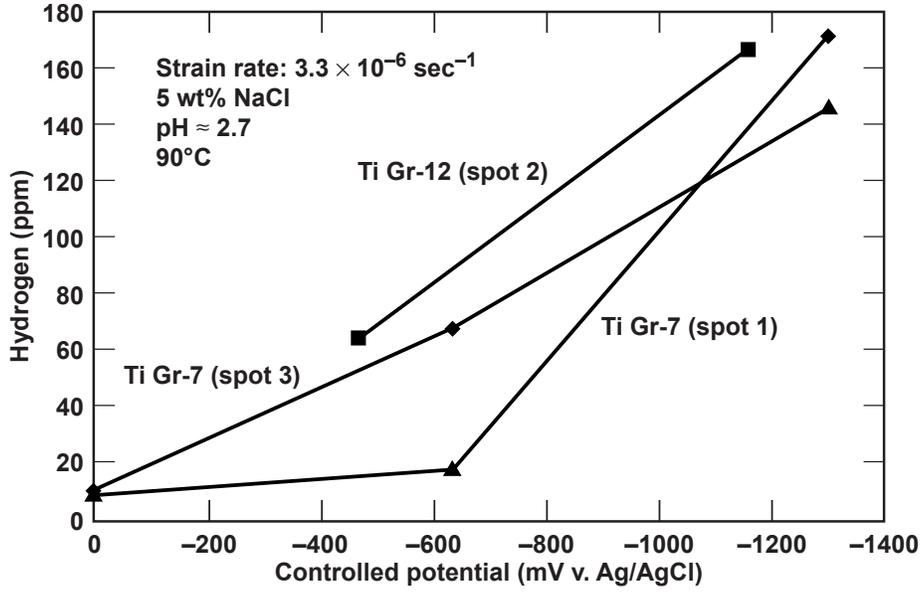
as-received materials, containing 20 to 50 $\mu\text{g/g}$ of hydrogen, are very tough, and fail by ductile overload under high stress. This ductile tearing is also observed during slow-crack growth for both materials. The H_C is the hydrogen concentration above which slow-crack growth is no longer observed and only fast-crack growth occurs. This behavior is schematically presented in Figure 1.

In accordance with Shoesmith (1999), Sorensen (1990) and coworkers have demonstrated that the alloy Ti-12 requires a hydrogen content of $> 500 \mu\text{g/g}$ before any measurable loss of ductility occurs. Shoesmith (1999) also reported that, based on test results reported in Shoesmith et al. (1997), values of H_C of 500 to 800 $\mu\text{g/g}$ for Ti-2 and 400 to 600 $\mu\text{g/g}$ for Ti-12 have been determined. More recent measurements (Ikeda, unpublished data) show that hydrogen for Ti-16 is at least 1,000 $\mu\text{g/g}$, 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 $\mu\text{g/g}$, which is the lower bound value observed for Ti-2, Ti-12, and Ti-16, as indicated above.

6.2.3 Determination of Hydrogen Concentration

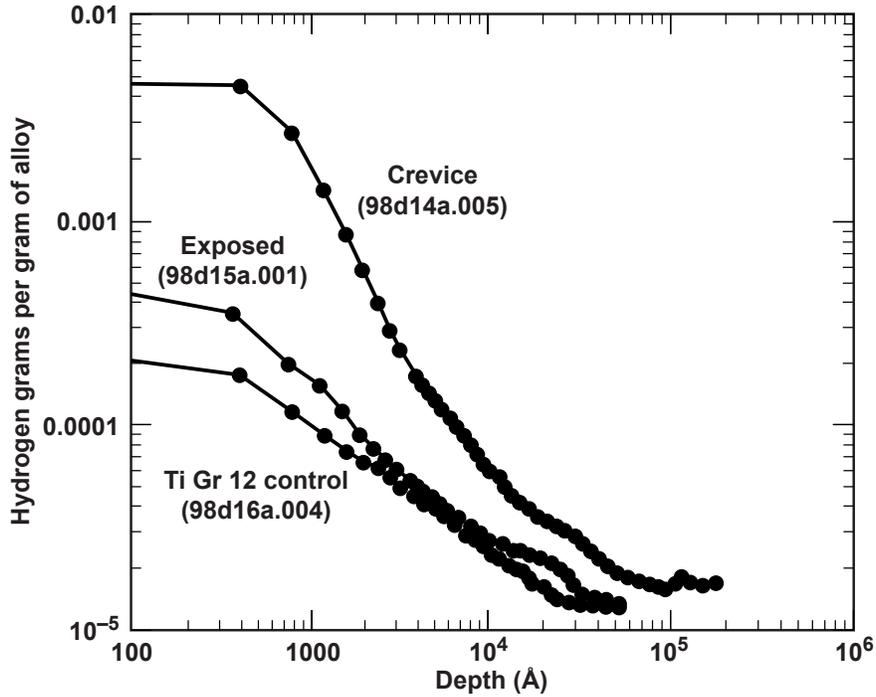
The effect of controlled electrochemical potential on the absorbed hydrogen concentration analyzed by secondary ion mass spectrometry (SIMS) for Ti-7 and Ti-12 was observed by Roy et al. (1999). The slow strain rate test (SSRT) technique was used, and the tests were performed in a deaerated 90°C acidic brine ($\text{pH} \cong 2.7$) containing 5 weight percent sodium chloride (NaCl) using a strain rate of $3.3 \times 10^{-6} \text{ sec}^{-1}$. Figure 6 of Roy et al. (1999), which summarizes the test results, is reproduced as Figure 2 below. The test data in Figure 2 indicate that the concentration of hydrogen in both Ti-7 and Ti-12 was increased with more cathodic applied potential. These results may also suggest that the amount of hydrogen generated in these alloys as a result of potentiostatic polarization at comparable cathodic potentials was not significantly influenced by their chemical compositions. The basic difference in composition between these two alloys is that Ti-7 contains palladium (Pd) while Ti-12 is alloyed with molybdenum (Mo) and nickel (Ni). Figure 2 also indicates that the hydrogen concentration does not exceed 180 ppm (or $\mu\text{g/g}$) in the controlled potential range.

Data reported by Bedrossian (1999) for SIMS analyses of crevice coupons tested at the Long Term Corrosion Test Facility (LTCTF) of LLNL show hydrogen content inside the crevices, relative to measurements taken outside the crevices and to an uncorroded control. Test coupons of Ti-12 and Ti-16 were tested under various combinations of different conditions of temperature (90°C and 60°C), environment (simulated concentrated water (SCW) and simulated dilute water (SDW)), and phases (vapor and aqueous). A typical result is illustrated by Figure 3, which shows the SIMS depth profiles for hydrogen in Ti-16 specimen tested under 90°C, SDW, and aqueous phase after one year. This figure shows that the hydrogen content is below the critical hydrogen concentration (1,000 $\mu\text{g/g}$), except in the crevices near the surface, and the hydrogen content drops very quickly to the tens $\mu\text{g/g}$ level at about 10^4 \AA from the surface. Although the data reported by Bedrossian (1999) are not qualified, they present a better than qualitative indication of low hydrogen pick-up by titanium materials.



*****1*****6*2

F*****2*****1999



*****1*****6*3

F*****3*****16*60*****1999

6.2.4 Results

In the description of the HIC model presented in Section 6.1, extensive evidence has been provided to support a qualitative assessment of Ti-7 as an excellent choice of material for the drip shield with regard to degradation caused by hydrogen-induced cracking. LTCTF test data observed at LLNL, although unqualified, provided additional indication beyond a qualitative level that hydrogen concentration appears to be low in titanium materials.

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 hydrogen-induced cracking. Available test data show that the hydrogen concentration is below 180 $\mu\text{g/g}$, which is less than the critical hydrogen concentration of 400 $\mu\text{g/g}$ for Ti-7.

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 . This model is very conservative because it assumes that, once the environmental and material conditions can support that particular corrosion process, failure will be effectively instantaneous. In the description of the HIC model presented in Section 6.1, extensive evidence has been provided to support a qualitative assessment of Ti-7 as an excellent choice of material for the drip shield with regard to degradation caused by hydrogen-induced cracking. LTCTF test data observed at LLNL, although unqualified, provides additional indication beyond a qualitative level that hydrogen concentration appears to be low in titanium materials.

Quantitative evaluation based on the HIC model described in Section 6.1 indicates that the hydrogen concentration does not exceed the critical value. It is concluded that drip shield material (Ti-7) is able to sustain the effects of hydrogen-induced cracking.

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9. ATTACHMENTS

Attachment	Title
I	Document Input Reference Sheet

**OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
DOCUMENT INPUT REFERENCE SHEET**

1. Document Identifier No./Rev.: ANL-EBS-MD-000006 REV 00A		Change: N/A	Title: Hydrogen Induced Cracking of Drip Shield						
Input Document		3. Section	4. Input Status	5. Section Used In	6. Input Description	7. TBV/TBD Priority	8. TBV Due To		
2. Technical Product Input Source Title and Identifier(s) with Version	Unqual.						From Uncontrolled Source	Un-confirmed	
2a 1	Kim, Y.J. and R.A. Oriani, 1987. "Corrosion Properties of the Oxide Film Formed on Grade 12 Titanium in Brine Under Gamma Radiation". Corrosion 43, (1987).	p. 90	Journal paper	6.1, p 15-16	Hydrogen absorption rate and oxide film growth rate (Corroborating data)				
2	Okada, T. 1983. "Factor Influencing the Cathodic Charging Efficiency of Hydrogen by Modified Titanium Electrodes". Electrochimica Acta, 28(8), (1983).	p. 1117, Figure 5	Journal paper	6.1, p 15	Hydrogen absorption efficiency (Corroborating data)				
3	Pasupathi, V. 1999. Waste Package Material Properties. CRWMS Report BBA000000-01717-0210-00017. Rev 00, February 23, 1999.	5.12, p. 45	YMP report	6.2.1, p. 17	Ti-7 material data (Corroborating data)				

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2. Technical Product Input Source Title and Identifier(s) with Version							Unqual.	From Uncontrolled Source	Un-confirmed
2a 4	Phillips, I. I., P. Poole and L. L. Shrier. 1972. "Hydride Formation During Cathodic Polarization of Ti — Effect of Current Density on Kinetics of Growth and Composition of Hydride." Corrosion Science (12).	p. 855	Journal paper	6.1, p. 16	Range of hydride composition (Corroborating data)				
5	Roy, A. K., M. K. Spragge, D. L. Flaming and B. Y. Lum. 1999. Cracking of Titanium Alloys under Cathodic Applied Electrochemical Potential. Lawrence Livermore National Laboratory. UCRL Report. (to be published).	Figure 6	TBV (LLNL UCRL report to be published)	4.1, p. 9 and 6.2.3, p. 18	Measured hydrogen concentration for Ti-7 (Direct data)				
6	Schutz, R. W. and D. E. Thomas. "Corrosion of Titanium and Titanium Alloys." Metals Handbook. Ninth Edition. Vol. 13.	p. 686	Handbook	6.1, p. 14	Temperature and pH window of susceptibility for HIC (Corroborating data)				

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**OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
DOCUMENT INPUT REFERENCE SHEET**

1. Document Identifier No./Rev.: ANL-EBS-MD-000006 REV 00A		Change: N/A	Title: Hydrogen Induced Cracking of Drip Shield						
Input Document			4. Input Status	5. Section Used In	6. Input Description	7. TBV/TBD Priority	8. TBV Due To		
2. Technical Product Input Source Title and Identifier(s) with Version		3. Section					Unqual.	From Uncontrolled Source	Un-confirmed
2a									
7	Shoesmith, D. W. 1999. Review of the Expected Behaviour of Alpha Titanium Alloys under Yucca Mountain Conditions. Report to US DOE.	p. 17 p. 59 p. 78	TBV (YMP report)	4.1, p. 9 6.1, p. 17 6.2.2, p. 17 6.1, p. 13 6.1, p. 15	Critical hydrogen concentration (Direct data) Hydrogen absorption rate (Corroborating data) Hydrogen absorption efficiency (Corroborating data)				
8	Shoesmith, D. W., D. Hardie, B. M. Ikeda and J. J. Noel. 1997. Hydrogen Absorption and the Lifetime Performance of Titanium Waste Containers. Atomic Energy of Canada Ltd. Report AECL-11770, COG-97-035-I.	p. 9 p. 3 2.1, p. 7 p. 22	Technical report	6.1, p. 11 6.1, p. 13 6.1, p. 17 6.2.3, p. 18	HIC model description (Corroborating data) Chemistry/electrochemistry transformation (Corroborating data) Slow strain rate tests (Corroborating data) Hydrogen concentration determination (Corroborating data)				

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