

THE U.S. NUCLEAR REGULATORY COMMISSION OFFICE OF NUCLEAR MATERIAL
SAFETY AND SAFEGUARDS REVIEW OF THE U.S. DEPARTMENT OF ENERGY'S
KEY TECHNICAL ISSUE AGREEMENT RESPONSE RELATED TO
THE POTENTIAL GEOLOGIC REPOSITORY AT YUCCA MOUNTAIN, NEVADA:
CONTAINER LIFE AND SOURCE TERM 6.01

1.0 INTRODUCTION

By letters dated December 9, 2003, and June 24, 2004, the U.S. Department of Energy (DOE) submitted a report Technical Basis Document No. 6: Waste Package and Drip Shield Corrosion and Appendix P of Technical Basis Document No. 6 (TBD 6) (Bechtel SAIC Company, LLC, 2004a, 2003a), to satisfy the informational needs of numerous key technical issue agreements pertaining to the environmental degradation of the waste package and drip shield materials and to respond to issues raised by the U.S. Nuclear Regulatory Commission (NRC) related to corrosion processes and design of the waste package and drip shield at the potential repository at Yucca Mountain, Nevada. The information was requested by NRC during technical exchanges in September 2000, February 2001, July 2001, August 2001, and September 2001. This NRC review addresses DOE'S response to agreement Container Life and Source Term (CLST) 6.01 (Schlueter, 2000).

2.0 WORDING OF THE AGREEMENT

CLST.6.01

“Provide the documentation for the path forward items listed on slides 7 & 8: (1) Perform more sensitive measurements of uniform corrosion rates by the same approach as taken for Alloy 22, (2) Confirm no deleterious effects of fluoride ion and trace heavy metal ions in water on corrosion behavior of titanium with a similar approach to that taken in electrochemically based studies on Alloy 22, (3) Establish damaging hydrogen levels in titanium alloys (Grade 2 versus Grades 7 and 16, Grade 5 versus Grade 24) and evaluate hydrogen charged notched tensile specimens and hydrogen pickup of galvanically coupled LTCTF specimens, (4) Conduct SCC testing of titanium, similar to the approach taken for Alloy 22, (5) Confirm intergranular or internal oxidation of titanium is not applicable under Yucca Mountain thermal and environmental conditions. DOE stated that the documentation of the path forward items will be completed and, as results become available, they will be documented in the revision of AMRs (ANL-EBS-MD-000005, Stress Corrosion Cracking of the Drip Shield, the Waste Package Outer Barrier, and the Stainless Structure Materials, and ANL-EBS-MD-000004, General Corrosion and Localized Corrosion of the Drip Shield), to be completed by LA.”

3.0 RELEVANCE TO OVERALL PERFORMANCE

Agreement CLST.6.01 is related to the oxidation, hydrogen embrittlement, stress corrosion cracking, and corrosion of the proposed drip shields that will be emplaced prior to closure of the potential repository. Drip shield performance is an important factor regarding safety because the drip shields are incorporated into the design of the engineered barrier system to limit the amount of water contacting the waste package as a result of dripping and damage to the waste package from rockfall. Initiation of aqueous corrosion of the waste packages depends on the

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deliquescence of dust or the contact with seepage water. The presence of drip shields will delay the contact of seepage water with the waste package surface, resulting in a significantly longer container lifetime. In addition, once the containers are breached, the amount of water available for the dissolution of spent nuclear fuel and high-level waste glass and advective transport of the released radionuclides could be limited, even by the presence of a partially damaged drip shield.

The NRC performed a risk insights analysis that indicates the drip shield integrity has a medium significance to waste isolation (NRC, 2004). The integrity of the drip shield will influence the quantity and chemistry of the water that can develop on the waste package and the potential effects on corrosion modes and rates.

4.0 RESULTS OF THE NRC REVIEW

Agreement CLST.6.01 is included in the integrated subissue for degradation of engineered barriers. This agreement resulted from a staff review of DOE's documentation that is consistent with NRC (2003, Section 2.2.1.3.1.2, Review Method 2). The NRC review of the response for this agreement also was conducted in accordance with the aforementioned review method. This review method includes evaluation of the sufficiency of the experimental data used to support parameters in conceptual models and process-level models.

4.1 Titanium Corrosion Rates

Corrosion rates for Titanium Grade 16 were measured using weight loss coupons and crevice corrosion specimens immersed in simulated groundwater for 1 and 5 years at 60 and 90 EC [140 and 194 EF]. The use of corrosion rate data for Titanium Grade 16 instead of Titanium Grade 7 is acceptable because the uniform corrosion rate is not affected by the minor compositional difference between the two titanium-palladium alloys. Also, palladium is a beneficial alloying element for improving the corrosion resistance of titanium. The maximum corrosion rate, determined using weight loss, decreased with exposure time. The DOE indicated that palladium enrichment on the surface, proposed by Nakagawa, et al. (2001), may reduce the uniform corrosion rate. Although definitive evidence for palladium enrichment is lacking, a decrease in the corrosion rate of Titanium Grade 16 with long-term exposure conditions may be a result of improvement in the resistance of the oxide film with time as defects (mostly oxygen vacancies) in the oxide film are eliminated during the annealing process. The corrosion rate data obtained in the 1-year test were conservatively adopted for the model abstraction after eliminating negative values from the distribution (Bechtel SAIC Company, LLC, 2003a). This treatment of the data yields uniform corrosion rates with a median of 18 nm/yr [7.1×10^{-4} mils/yr] and a maximum of 113 nm/yr [4.4×10^{-3} mils/yr] for the coupon specimens and a median of 25 nm/yr [1.0×10^{-3} mils/yr] and a maximum of 319 nm/yr [1.26×10^{-2} mils/yr] for the combined distribution using coupon and crevice specimens.

Compared to data reported by Covington and Schutz (1981), Blackwood, et al. (1988), Brossia, et al. (2001), Brossia and Cragolino (2001), and Cragolino, et al. (1999), the values adopted by DOE, although somewhat low, are consistent with data in the open literature. It does not appear that the life of the drip shield will be limited by uniform corrosion even when the maximum uniform corrosion rate {e.g. 870 nm/yr [3.4×10^{-2} mils/yr]}, is considered.

In the engineering design, the Titanium Grade 7 drip shield will be supported using welded ribs and bulkheads made from Titanium Grade 24, which is the equivalent of Titanium Grade 5 in physical and mechanical properties but with the addition of palladium to impart improved corrosion resistance at high temperatures, low pH levels, or both.

Information provided by DOE on titanium corrosion rates is sufficient to satisfy the intent of the agreements. However, the NRC staff has the following comments which DOE should consider:

- Corrosion rates measured using weight loss methods have several limitations including the lack of corrosion rate data as a function of time. The corrosion rates for container materials were measured using weight loss methods; however, these data were supported by electrochemical methods that confirmed the corrosion rate decreases with time. A similar approach should be considered for the drip shield materials.
- Titanium Grade 24 is an aluminum and vanadium-containing alloy and also is an alpha-beta alloy with the beta phase distributed along the grain boundaries in an alpha matrix. The palladium addition significantly improves its corrosion resistance. With acidic conditions, if the oxide is not stable or continuously removed, it is susceptible to intergranular corrosion. This susceptibility needs to be considered if such conditions are expected to occur within the emplacement drifts.

4.2 Effects of Fluoride, Bromide, and Trace Elements

In the potential repository at Yucca Mountain, the fluoride concentration in seepage water is estimated in the range of $10^{1.5}$ to 1 mol/kg (Bechtel SAIC Company, LLC, 2003b) and the existing Ca^{2+} and other species tend to limit the free available fluoride. The DOE refers to the linear relationship developed by Nakagawa, et al. (2001) for the boundary between passive and active conditions for titanium alloys in fluoride solutions as

$$\text{pH} = 1.49 \log [\text{F}^{\text{I}}] \text{ (in ppm)} + 0.422$$

Based on this relationship, DOE concludes the drip shields will remain passive for the expected range of conditions within the emplacement drifts of the potential repository. The empirical relationship reported by Nakagawa, et al. (2001) was generated for dental applications based on the tests of pure titanium, Ti-6Al-4V, and Titanium Grade 7 at a single temperature of 37 EC [98.6 EF] in 0.012 to 0.47-mol/kg NaF solutions at various pH levels adjusted by H_3PO_4 .

Fluoride concentrations do not appear to alter the crevice corrosion resistance of titanium alloys. Schutz and Grauman (1986) showed that, at low fluoride (F^{I}) concentrations ($5.3 \times 10^{1.3}$ mol/kg) fluoride did not affect the repassivation potentials for Titanium Grades 2, 12, and 7 at 82 EC [180 EF] for pH values as low as 1.5. Crevice corrosion tests reported by Schutz and Grauman suggested that Titanium Grade 7 maintained passivity even at 177 EC [350 EF].

The DOE showed that bromide has no influence on the uniform corrosion rate of Titanium Grade 7 in an acidic (pH = 4) solution (Bechtel SAIC Company, LLC, 2003a). Bromide is known to induce pitting corrosion, possibly by attacking the sensitive defect sites in the oxide film (Casillas, et al., 1994). For waste repository conditions, bromide will concentrate in evaporating seepage waters with concentrations between 1 and 3 molal (median values) according to the Center for Nuclear Waste Regulatory Analyses (CNWRA) staff calculation.

The pitting potential of Titanium Grade 7 is estimated to be in the range 0.5–2 V_{SCE}, from 30 to 180 EC [86 to 356 EF] (Posey and Bohlman 1967; Beck 1973a,b). The pitting potential is higher than corrosion potentials achievable for repository conditions. Thus, it is plausible to claim that pitting of Titanium Grade 7 is unlikely to occur even in the presence of bromide.

Regarding the effects of trace heavy metal ions, DOE has decided not to conduct any tests in waters containing trace heavy metal ions as the concentrations of heavy metal ions in the repository are likely to be very low. Titanium alloys are highly corrosion resistant and there are no reports indicating detrimental effects of trace heavy metal ions on Titanium Grade 7.

Information provided by DOE on the effects of fluoride, bromide and trace elements is sufficient to satisfy the intent of the agreements. However, the NRC staff has the following comments which DOE should consider:

- Although Brossia, et al. (2001) have shown that the corrosion rates of titanium alloys are strongly dependent on fluoride concentration, the effect of fluoride on the drip shield may be limited by the availability of fluoride (Lin, et al., 2003). The assessment of fluoride effects should consider the concentration ranges and temperatures within the emplacement drifts.

4.3 Hydrogen Effects

The critical hydrogen concentrations for Titanium Grades 7 and 24 were estimated to be 1,000 and 400–600 ppm (Bechtel SAIC Company, LLC, 2003a). The selection of these critical hydrogen concentration values is justified based on data for titanium alloys and the effects of palladium additions to titanium alloys. The DOE also addressed this selection in the response to agreements CLST.6.02 AIN–1 and 6.03 AIN–1 (Bechtel SAIC Company, LLC, 2003a). The hydrogen uptake in 10,000 years was estimated to be 124 µg/g based on a passive corrosion rate measured in a long-term corrosion test facility and an uptake efficiency of 0.015. Although galvanic coupling of titanium to active metals such as carbon steels may cause hydrogen absorption by titanium and its alloys, because titanium is likely to act as the cathode, the model proposed by DOE indicates the hydrogen concentration in the drip shield because of a galvanic couple will most likely not exceed the critical value.

Information provided by DOE on the effects of hydrogen is sufficient to satisfy the intent of the agreements. However, the NRC staff has the following comments which DOE should consider:

- According to test results reported by Okada (1983) and recent information reported by Qin and Shoemith (2004), the hydrogen uptake efficiency is dependent on alloy composition, pH, and temperature. The dependence on pH appears to be the most significant, and much higher uptake efficiencies have been measured for titanium alloys in acidic solutions (pH < 3) (Okada, 1983). The increased uptake efficiency in acidic conditions will need to be considered if acidic conditions are expected to occur within the emplacement drifts.

4.4 Stress Corrosion Cracking

The DOE examined stress corrosion cracking of Titanium Grade 7 and showed that, under stressed conditions, stress corrosion cracking of Titanium Grade 7 can occur. In the repository

design, the Titanium Grade 7 drip shield will be fully stress relieved before emplacement. In the absence of disruptive events (e.g., rockfall, drift collapse, or seismicity), there is no source to drive stress corrosion cracking initiation and propagation. For this reason, DOE claims that stress corrosion cracking will not occur in the drip shields in 10,000 years. The effect of rockfall on drip shield performance is considered in Bechtel SAIC Company, LLC (2004b).

Titanium Grade 24 could be more susceptible to stress corrosion cracking than either Titanium Grades 7 or 12 because titanium cracking susceptibility is generally related to the strength of the alloy. No experimental work or literature review has been conducted by DOE to examine the stress corrosion cracking susceptibility of Titanium Grade 24. The stress corrosion cracking susceptibility of Titanium Grade 24 can be assessed by evaluating the stress corrosion cracking behavior of Titanium Grade 5 because they have similar mechanical properties. By comparing it to the single alpha-phase material, which includes ASTM grades 1, 2, 7, 11, and 12, Titanium Grade 5 is more susceptible to stress corrosion cracking (Schutz, 1992), especially in the following environments and with various loading conditions: simulated body environments (Yanishvsky and Hoepfner, 1985), aqueous chloride solutions (Piper, et al., 1968), acidic methanol (Zhang and Vereecken, 1989), and hot salt (Sinigaglia, et al., 1978). The CNWRA staff performed preliminary slow strain rate tests to evaluate the environmentally assisted cracking susceptibility of Titanium Grades 2, 5, and 7 in the presence of fluoride and showed that Titanium Grade 5 is more susceptible to environmentally induced cracking than are the other two materials (Pan, et al., 2002). According to Schutz and Thomas (1987), however, the stress corrosion cracking susceptibility identified in laboratory tests is seldom observed in actual field applications because highly stressed specimens and aggressive solutions often are used in laboratory tests rather than the condition in actual applications. In summary, Titanium Grade 24 may be more susceptible to stress corrosion cracking than is Titanium Grade 7 for some conditions; however, stress corrosion cracking of Titanium Grade 24 is unlikely to occur for the repository conditions in the absence of disruptive events.

Overall, NRC found that the assessment provided by DOE on stress corrosion cracking of titanium is appropriate.

4.5 Intergranular and Internal Oxidation

Titanium Grade 7 is a predominantly alpha-phase material, and titanium forms a compact oxide layer on the surface because of its extremely high affinity for oxygen, which, in turn, makes titanium highly resistant to intergranular and internal oxidations. The temperatures expected in the potential repository at Yucca Mountain are not high enough for oxygen to diffuse into titanium, and cause intergranular and internal oxidations. For such conditions, oxygen is highly unlikely to diffuse into titanium to cause intergranular and internal oxidations. The NRC found that DOE's evaluation of intergranular and internal oxidations is appropriate.

Based on the NRC review of DOE's response to Agreement CLST.6.01 in accordance with methods discussed in the appropriate section of NRC (2003, Section 2.2.1.3.1.2, Review Method 2), NRC found DOE's response to the agreements to be satisfactory.

5.0 SUMMARY

The DOE has provided appropriate information to evaluate the possible corrosion modes of Titanium Grade 7 and Grade 24 for conditions expected in the potential repository at Yucca Mountain with focus on uniform corrosion, effects of fluoride on uniform corrosion and hydrogen uptake, environmentally induced cracking (hydrogen-induced cracking and stress corrosion cracking), and intergranular and internal oxidations. On the basis of this review, NRC agrees with DOE that the information assembled in response to agreement CLST.6.01 is adequate to support the submission of the license application for the potential repository at Yucca Mountain.

6.0 STATUS OF THE AGREEMENT

Based on the preceding review, NRC agrees with DOE that the information provided with respect to agreement CLST.6.01 is adequate to support submission of the license application. Therefore, NRC considers agreement CLST.6.01 to be closed.

7.0 REFERENCES

Bechtel SAIC Company, LLC. "Transmittal of Appendices O, P, U, and V Technical Basis Document No. 6: Waste Package and Drip Shield Corrosion, Revision 01, Addressing Key Technical Issue (KTI) Agreements Related to Container Life and Source Term (CLST) 1.03, 1.10, 1.11, and 6.01 and Preclosure Safety (PRE) 7.05." Las Vegas, Nevada: Bechtel SAIC Company, LLC. 2004a.

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