OFFICE OF NUCLEAR MATERIAL SAFETY AND SAFEGUARDS REVIEW OF THE U.S. DEPARTMENT OF ENERGY KEY TECHNICAL ISSUE AGREEMENT RESPONSE TO CLST.1.08 and 1.09 FOR A POTENTIAL GEOLOGIC REPOSITORY AT YUCCA MOUNTAIN, NEVADA

1.0 INTRODUCTION

By letter dated December 9, 2003, and July 22, 2004, the U.S. Department of Energy (DOE) submitted a report, Technical Basis Document No. 6 (TBD 6): Waste Package and Drip Shield Corrosion and Appendix N of the technical basis document (Bechtel SAIC Company, LLC, 2004, 2003), to satisfy the informational needs of numerous key technical issue agreement items 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, and September 2001. Specific agreements addressed in this NRC review of the information provided by DOE in the technical basis document include CLST.1.08 and 1.09 (Schlueter, 2000).

2.0 AGREEMENTS

Wordings of the two agreements are provided next.

CLST.1.08

"Provide the documentation for Alloy 22 and titanium for the path forward items listed on slides 16 and 17: (1) calculate potential pH diagrams for multicomponent Alloy 22; (2) grow oxide films at higher temperatures in autoclaves, in air and/or electrochemically to accelerate film growth for compositional and structural studies; (3) resolve kinetics of film growth, including parabolic or higher order, whether film growth becomes linear, and if, as film grows, it becomes mechanically brittle and spalls off; (4) determine chemical, structural, and mechanical properties of films, including thickened films; (5) correlate changes in E_{corr} measured in the Long-Term Corrosion Test Facility (LTCTF) with compositional changes in passive film over time; (6) perform analyses on cold-worked materials to determine changes in film structural properties; (7) perform examination of films formed on naturally occurring Josephinite; and (8) compare films formed on Alloy 22 with other similar passive film alloys with longer industrial experience. DOE will provide the documentation in a revision to AMRs (ANL–EBS–MD–000003 and ANL–EBS–MD–000004) prior to LA."

CLST.1.09

"Provide the data that characterizes the passive film stability, including the welded and thermally aged specimens: (1) characterize film stability on base metal, (2) characterize film stability on welds, (3) characterize film stability on thermally aged materials, and (4) titanium. DOE will provide the documentation in a revision to AMRs (ANL–EBS–MD–000003 and ANL–EBS–MD–000004) prior to LA."

Enclosure

3.0 RELEVANCE TO OVERALL PERFORMANCE

Agreements CLST.1.08 and 1.09 are related to the long-term persistence of a passive film on the proposed waste package outer containers. The waste package, composed of the containers and the waste forms, is the primary engineered barrier controlling the release of radionuclides from spent nuclear fuel and high-level waste glass. Because corrosion processes, promoted by the presence of an aqueous environment contacting the surface of the containers, will be the primary cause of container failure under undisturbed conditions, the mode and rate of corrosion needs to be evaluated to determine container lifetimes. Corrosion processes potentially important in the degradation of the engineered barriers include humid-air and uniform aqueous corrosion, localized (pitting, crevice, and intergranular) corrosion, microbially influenced corrosion, stress corrosion cracking, and hydrogen embrittlement. Fabrication processes, such as cold working, welding, and postweld heat treatments, may alter the corrosion resistance of the waste package materials.

Drip shield performance is important because the drip shields are incorporated into the design of the engineered barrier system to limit both 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 deliquescence of dust or direct 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 the advective transport of the released radionuclides could be limited, even by the presence of a partially damaged drip shield.

The high corrosion resistance of the waste package and drip shield materials is a result of the formation of a protective film on the surface of the materials. Under environmental conditions where a stable oxide film is maintained, corrosion is uniform and occurs at an extremely slow rate. Typical values for the passive corrosion rate of Titanium Grade 7 and Alloy 22 are in the range 10^{-5}–10^{-3} mm/yr [3.9×10^{-4}–3.9×10^{-2} mpy] (Bechtel SAIC Company, LLC, 2003; Brossia, et al., 2001; Pensado, et al., 2002). Passive corrosion rates are generally independent of pH, redox potential, and solution composition but exhibit an Arrhenius dependence on temperature with higher corrosion rates at higher temperatures. Data exist to show that passive oxide film is formed in the expected repository condition (Gordon, 2002). Long-term testing in simulated Yucca Mountain-relevant waters is ongoing. Long-term thermal aging studies to determine the passive film behavior at longer time scales also are ongoing.

NRC performed a risk insights analysis that indicates persistence of a passive film has a high significance to waste isolation (NRC, 2004). The stability of oxide film on passive alloys is dependent on the materials and the exposure conditions. Loss of passivity can lead to corrosion rates that are orders of magnitude greater than those measured under passive conditions. Fabrication processes, including welding and postweld high temperature heat treatment, as well as aggressive water chemistry conditions have a potentially detrimental effect on the stability of the passive film and may accelerate the corrosion rate over extended surface areas (Bechtel SAIC Company, LLC, 2001; Dunn, et al., 2004a,b).

4.0 RESULTS OF THE NRC REVIEW

Agreements CLST.1.08, and 1.09 are included in the degradation of engineered barriers integrated subissue. These agreements resulted from a staff review of the DOE documentation that is consistent with NRC (2003, Section 2.2.1.3.1.2, Review Method 2). The NRC review of the response for these agreements 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 CLST.1.08

The focus of CLST.1.08 was to address the nature and stability of the oxide film. The DOE response (Bechtel SAIC Company, LLC, 2004) identifies that for an oxide film to be protective in a given environment, it must be chemically stable, and it must act as a barrier to block or slow electronic and ionic transport across the film. If the film is not chemically stable, it will break down and expose fresh metal to electrochemical dissolution or oxidation. All of the requested information for waste package material is provided in Appendix N (Bechtel SAIC Company, LLC, 2004) as raw data. The outer layer of passive film dissolves continuously, whereas the inner layer of the passive film forms continuously, therefore, the passive film thickness remains constant.

Important conclusions regarding the formation of a protective oxide film that acts as a barrier to block or slow the electronic and ionic transport across the film for Alloy 22 are supported by the data (Bechtel SAIC Company, LLC, 2004). The film growth kinetics study indicates a logarithmic increase in film stability and thickness in acidic, neutral, and basic solutions. The general corrosion rate is low for the kinetically formed film in Alloy 22. This low rate is supported by data presented in Appendix N (Bechtel SAIC Company, LLC, 2004).

Although the staff considers this agreement closed, DOE should consider the following comment:

- Data beyond five years exposure in the long-term corrosion test facility may further confirm that the steady-state chemical characteristics of passive film represent long-term behavior of passive film in DOE’s model abstraction. Alloy 22 forms a thin, conformal chromium oxide scale as do other industrial nickel-iron-chromium alloys. Alloy 22 exhibits particularly good corrosion resistance for a wide range of solution compositions and environments, partly as a result of its chromium content and molybdenum content. The thickness of the passive film is maintained in the range 1–5 nm [3.9×10^{-5}–2.0×10^{-4} mils] by continuous formation at the metal/oxide interface and dissolution at the oxide/solution interface for an exposure of 5 years (Bechtel SAIC Company, LLC, 2004). Data from long-term exposures would support the conclusion that the passive film could be maintained for the geological time period. This conclusion also may indicate that thermodynamic stability of passive oxides may not be necessary for long-term durability.

Based on the NRC review of the DOE response to Agreement CLST.1.08 in accordance with methods discussed in the appropriate section of NRC (2003, Section 2.2.1.3.1.2, Review Method 2), NRC found the DOE response to the agreements satisfactory.

4.2 CLST.1.09

The focus of CLST.1.09 is related to the characterization of passive film stability, including the welded and thermally aged specimens. DOE characterized the oxide film stability on the base metal and the welded specimens using two electrochemical metrics: the corrosion rate derived from the polarization resistance and the corrosion rate derived from the final current after holding samples at a fixed potential (Bechtel SAIC Company, LLC, 2004). The oxide film that formed on Alloy 22 following a solution-annealing step also was characterized. The approximately 1-μm [3.9×10^{-5} in-] oxide that formed on the surface of the solution-annealed Alloy 22 is composed of chromium oxide, iron oxide, and nickel oxide. Oxides that form at the lower temperatures of 400 to 750 °C [752 to 1,382 °F] but with longer timeframes also form a thick, predominantly chromium oxide scale similar to that formed on solution-annealed specimens. Passive film studies about the titanium drip shield material were not planned based on a low uniform corrosion rate and resistance to passive film breakdown evident during electrochemical testing.

Characterization of passive films and surface analyses of the Alloy 22 and Titanium Grade 7 have been reported (Kim, et al. 2002; Szmodis, et al., 2003; Wong, et al., 2004). The passive oxide films on Alloy 22 and Titanium Grade 7 appear to reach a steady state thickness of 5 to 6 nm [2.0×10^{-4} to 2.4×10^{-4} mil] after an exposure of two months however, exposure times greater than two months were not reported (Kim, et al., 2002). The composition of the passive film was dependent on potential. At anodic potentials above $-200 mV_{SCE}$ the concentration of molybdenum, tungsten, and chromium increased in the outermost oxide layer (Kim, et al. 2002). Szmodis, et al. (2003) reported that the oxide film on Alloy 22 has an inner layer rich in nickel, chromium, molybdenum and iron and a porous outer oxide rich in nickel and iron. The composition of the oxides on both Titanium Grade 7 and Alloy 22 does not appear to change with time with the exception that there were artificial silica deposits (Kim, et al., 2002). The concentration of silica, which is likely to be present in groundwater, can be observed after an exposure of 1 month. After 5 years, the silica deposits are readily apparent but do not appear to accelerate the corrosion rate of Alloy 22 (Wong, et al. 2004)

Although the staff considers this agreement closed, DOE should consider the following comment:

- The uniform corrosion rates for Alloy 22 and the titanium alloys used for the drip shield are low under conditions where the passive films on the alloys are stable. Models for long-term passivity should be consistent with the data that characterizes the properties of the passive film and the evolution of the thickness, composition and structure of the passive films considering the range of metallurgical conditions and alloy composition used to construct the waste packages and the drip shield.

Based on the NRC review of the DOE response to Agreement CLST.1.09 in accordance with methods discussed in the appropriate section of NRC (2003, Section 2.2.1.3.1.2, Review Method 2), NRC found the DOE response to the agreements to be satisfactory.

5.0 SUMMARY

NRC reviewed the DOE key technical issue agreement responses within TBD 6 and Appendix N to determine whether any important aspect of Agreements CLST.1.08 and 1.09 was excluded from the response. In addition, NRC performed an independent assessment to determine whether the information provided would support submission of a potential license application for a geologic repository. Notwithstanding new information that could raise new questions or comments concerning these agreements, the information provided satisfies the intent of the agreements. On the basis of this review, NRC agrees with DOE that the information assembled in response to agreements CLST.1.08 and 1.09 is adequate to support the submission of a license application for the potential repository at Yucca Mountain.

6.0 STATUS OF THE AGREEMENTS

Based on the preceding review, NRC agrees with DOE that the information provided with respect to agreements CLST.1.08 and 1.09 is adequate to support submission of the license application. Therefore, NRC considers agreements CLST.1.08 and 1.09 to be closed.

7.0 REFERENCES

Bechtel SAIC Company, LLC. "Transmittal of Appendices N and S of the Technical Basis Document No. 6: Waste Package and Drip Shield Corrosion, Revision 1, Addressing Key Technical Issue (KTI) Agreement Related to Container Life and Source Term (CLST) 1.08, 1.09, and 2.03 Additional Information Need (AIN)–1." Las Vegas, Nevada: Bechtel SAIC Company, LLC. 2004.

———. "Technical Basis Document No. 6: Waste Package and Drip Shield Corrosion." Rev. 1. Las Vegas, Nevada: Bechtel SAIC Company, LLC. 2003.

———. "Waste Package Operations Fabrication Process Report." TDR–EBS–ND–000003. Rev. 02. Las Vegas, Nevada: Bechtel SAIC Company, LLC. 2001.

Brossia, C.S., L. Browning, D.S. Dunn, O.C. Moghissi, O. Pensado, and L. Yang. "Effect of Environment on the Corrosion of Waste Package and Drip Shield Materials." CNWRA 2001-003. San Antonio, Texas: CNWRA. 2001.

Dunn, D.S., D. Daruwalla, and Y.-M. Pan. "Effect of Fabrication Processes on Material Stability–Characterization and Corrosion." CNWRA 2004-01. San Antonio, Texas: CNWRA. 2004a.

Dunn, D.S., Y.-M. Pan, D. Daruwalla, and A. Csontos. "The Effects of Fabrication Processes on the Mechanical Properties of Waste Packages—Progress Report." CNWRA 2004-03. San Antonio, Texas: CNWRA. 2004b.

Gordon, G.M. "Corrosion Considerations Related to Permanent Disposal of High-Level Radioactive Waste." *Corrosion*. Vol. 58, No. 10. pp. 811–825. 2002.

Kim, Y.-J., P.L. Andresen, P.J. Martiniano, J. Chera, M. Larsen, and G.M. Gordon. “Passivity of Nuclear Waste Canister Candidate Materials in Mixed-Salt Environments.” Proceedings of the CORROSION 2002 Conference. Paper No. 544. Houston, Texas: NACE International. 2002.

NRC. “Risk Insights Baseline Report.” Washington, DC: NRC. April 2004. <http://www.nrc.gov/waste/hlw-disposal/reg-initiatives/resolve-key-tech-issues.html>

———. NUREG–1804, “Yucca Mountain Review Plan—Final Report.” Rev. 2. Washington, DC: NRC. July 2003.

Pensado, O., D.S. Dunn, G.A. Cragnolino, and V. Jain. “Passive Dissolution of Container Materials—Modeling and Experiments.” CNWRA 2003-01. San Antonio, Texas: CNWRA. 2002.

Schlueter, J. “U.S. Nuclear Regulatory Commission/U.S. Department of Energy Technical Exchange and Management Meeting on Container Life and Source Term (September 12–13, 2000).” Letter (October 4) to S. Brocoum, DOE. Washington, DC: NRC. 2000. <www.nrc.gov/waste/hlw-disposal/public-involvement/mtg-archive.html#KTI>

Szmodis, A.W., K.L. Anderson, J.C. Farmer, T. Lian, and C.A. Orme. “Environmental Influence on Passive Films Formed on Alloy 22 (UNS N06022).” Proceedings of the CORROSION 2003 Conference. Paper No. 692. Houston, Texas: NACE International. 2003.

Wong, L.L., T. Lian, D.V. Fix, M. Sutton and R.B. Rebak. “Surface analysis of Alloy 22 Coupons Exposed for Five Years to Concentrated Groundwaters.” Proceedings of the CORROSION 2004 Conference. Paper No. 701. Houston, Texas: NACE International. 2004.