Department of Energy
Washington, DC 20585

QA: NA

January 26, 2005

B. John Garrick, Ph.D., P.E.
Chair, Executive Committee
Nuclear Waste Technical Review Board
2300 Clarendon Boulevard
Arlington, VA 22201-3367

Dear Dr. Garrick:

Thank you for the Nuclear Waste Technical Review Board's (Board) letter of July 28, 2004, providing the response to the information presented by the U.S. Department of Energy (Department) at the May 18-19, 2004, meeting of the Board. The Department appreciates the Board's continuing review of our activities as we work to develop and document the technical basis for the License Application for a repository at Yucca Mountain. Our responses to the Board's views and recommendations are summarized in the enclosure to this letter.

The Department continues to benefit from the constructive views of the Board, and we look forward to further dialog on our repository design and related issues.

Sincerely,

Margaret S.Y. Chu, Ph.D.
Director
Office of Civilian Radioactive
Waste Management

Enclosure

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U.S. DEPARTMENT OF ENERGY (DOE) RESPONSES TO THE JULY 28, 2004, LETTER FROM THE NUCLEAR WASTE TECHNICAL REVIEW BOARD (BOARD)

Corrosion Issues

Calcium chloride-rich environment

Based primarily on information presented at the Board's May 2004 meeting, it appears unlikely that dusts that accumulate on waste package surfaces during the preclosure period would contain significant amounts of calcium chloride or that significant amounts of calcium chloride would evolve on waste package surfaces during the thermal pulse. Consequently, the calcium chloride-rich environment selected for corrosion tests does not appear representative of the conditions that can be expected on waste package surfaces in a Yucca Mountain repository. If calcium chloride is not present, calcium chloride-rich brines will not form by deliquescence, and crevice corrosion due to the presence of such brines in the temperature range of roughly 140°C to 160°C will not occur. Thus, the Board concludes that deliquescence-induced localized corrosion during the higher-temperature period of the thermal pulse is unlikely.

Response

We agree with the Board that calcium chloride type deliquescent brines are very unlikely to exist or be stable at Yucca Mountain. In addition, the soluble constituents in the potential dust deposits that could be present on the drip shield and waste package surfaces are rich in beneficial inhibiting ions including nitrate and to a lesser extent sulfate ions. In the presence of these anions, even in the unlikely case where calcium chloride type brines were to form and to remain stable, they would not support localized corrosion. The effect of nitrate on inhibiting localized corrosion in these type brines is quantified and documented in the updated Analysis Model Report on general and localized corrosion of waste package outer barrier. Expected benign response of Alloy 22 exposed to these types of calcium chloride rich deliquescent brines is corroborated by the technical bases discussed in the Electric Power Research Institute's presentation to the Board at the May 2004 meeting (Kessler, J. et al. 2004).

Although we agree that calcium chloride type brines are very unlikely to exist or be stable at Yucca Mountain, other chloride brines with varying amounts of corrosion inhibitors, such as nitrate and sulfate, may be present at elevated temperatures. Understanding the localized corrosion behavior of Alloy 22 given such conditions is important. Thus, the Project is continuing to evaluate the localized corrosion response of Alloy 22 over a broad range of potential salt brine compositions and over the full range of relevant temperature, relative humidity, pH values, etc. For example, the corrosion response in sodium-potassium mixed salts is being evaluated. Current measurements indicate there is a potential for some of these saturated $NaCl\text{-}NaNO_3\text{-}KNO_3\text{-}H_2O$ type deliquescent brines to boil at maximum temperatures on the order of 200°C. To date, DOE has not found that significant corrosion damage will occur under these deliquescent salt conditions. However, the likelihood of formation and consequences of these high-temperature brines are being analyzed further to assess the potential for localized corrosion to occur under high temperature conditions.

Characterization of waste package environment

Ideally, corrosion tests should be carried out both in environments that closely approximate the various conditions to which the waste package alloy will be exposed and in environments that reasonably bound those conditions. The extent to which the DOE has characterized accurately the likely waste package environments (i.e., temperature, relative humidity, and chemical species present) is unclear at this point. Accurate characterization of probable waste package environments and the corrosion response of the waste package alloy to those environments will continue to be a major focus of the Board's technical and scientific review.

Response

The projected range of environments that could potentially be present on the waste package surface represents a heterogeneous matrix that will vary with time as the in-drift temperature and relative humidity change. Consequently, the Project has chosen to evaluate the Alloy 22 general and localized corrosion response over a broad range of potentially relevant as well as bounding test environments.

The types of environments expected on the waste package surface over 10,000 years were summarized for the Board at the May 2004 meeting. In addition, the likely concentrated brine environments and their expected frequencies and uncertainties have been calculated based on modeled repository-relevant seepage waters and the modeled behavior of soluble species in dust deposits. Although the frequency of different types of brines was not addressed at the May 2004 meeting, the results were recently documented. Because ranges of geochemical and thermal-hydrologic conditions are possible, there is a range of brine environments that could potentially form on the waste package surface depending on temperature, relative humidity, and the presence of intact drip shields. For the expected case, with the drip shield function intact, expected brines are of the sodium nitrate, potassium nitrate, sodium chloride, or calcium nitrate types. Dust samples collected in the tunnels at Yucca Mountain have been analyzed and grouped to summarize the types of deliquescent brines that could form. Only a few of the dust samples analyzed indicate that a calcium nitrate type brine could form. Deliquescent brines cover a pH range from approximately 6 to 12, depending on brine type and the CO_2 partial pressure. The associated chloride concentration varies from to 1 to 8 molal and decreases with increasing relative humidity. Dissolved fluoride concentrations vary from approximately 10^{-6} molal to 0.3 molal, depending on the individual brines. The nitrate concentrations are greater at lower relative humidity (higher temperature) and decrease at lower temperature (increasing relative humidity). As a result, the nitrate to chloride molal ratio will vary from approximately 0.4 to 26, i.e., well into the beneficial range where nitrate acts as a localized corrosion inhibitor.

Currently work is underway to evaluate the following conditions:

- The amount and composition of dust on waste packages as well as the volume of brine and quantities of dissolved salts, and assess the significance of any acid-gas volatilization.
- Assess the deliquescence-related properties of ammonium salts.
- Study the effects of any chloride-containing silicate minerals or minerals containing hydroxide, which can be replaced by chloride.
- Document the argument(s) for exclusion of localized corrosion of the waste package outer barrier due to the deliquescence of dust constituents.

As mentioned earlier, past and currently ongoing corrosion tests encompass the range of these predicted environments.

Localized corrosion at below boiling temperature

First, the DOE raised the possibility that when temperatures in repository tunnels fall below boiling, localized corrosion could occur in concentrated sodium chloride solutions with low concentrations of inhibitors. The Board believes that further investigation of the possibilities for localized corrosion at below-boiling temperatures is warranted and that such an investigation should focus on (1) possible mechanisms that might create environments that would facilitate localized corrosion and (2) the likelihood that such environments could exist.

Second, the presence of ammonium ion and the implications of its presence for corrosion or other performance aspects need to be explained

Response:

Extensive Alloy 22 localized corrosion test results have been used to develop a localized corrosion predictive model that covers the below boiling temperature range as well as higher temperatures (BSC 2004a). The model quantifies the beneficial effect of soluble nitrate (calculated to be present in all concentrated seepage and deliquescent brines that might form on the waste package surface) and conservatively incorporates a threshold nitrate/chloride molal ratio of 0.5 or greater to rule out localized corrosion at temperatures up to 160°C. Although the model does not take credit for other beneficial anions such as sulfate, carbonate, and bicarbonate, experimental results indicate the presence of these anions (as well as nitrate) contributes to inhibition of localized corrosion (Dunn et al. 2004 and BSC 2004b).

At temperatures near the boiling point (about 96°C at the repository elevation), the projected waste package relative humidity will range from about 35-100 percent and will increase with decreasing temperature (BSC 2004c). With the drip shields intact, any seepage brines will be diverted; and, thus, waste package surface brine environments will result only from deliquescence of soluble salts present in surface deposits. Because the deliquescent dust constituents form brines that have nitrate to chloride molal ratios of at least 0.4 for any exposure condition, localized corrosion will likely be inhibited.

The drip shield is expected to perform its design function of seepage diversion for the next 10,000 years. Even if the drip shields were to fail, it is estimated that only a small fraction (1 percent) of the seepage brines could evaporatively concentrate into concentrated chloride brines (BSC 2004c). In general, the nitrate to chloride ion ratio in seepage brines tends to be lower than for the dust deliquescent brines. The localized corrosion model implemented in the total system performance assessment-license application initiates localized corrosion if the nitrate to chloride ion ratio is less than 0.5. The value of 0.5 was conservatively selected, and no localized corrosion has been observed in expected lower temperature Na, K, Cl, NO_3 brines and sulfate brines under open circuit potential conditions for nitrate to chloride ratios between 0.05 and 0.5 (Payer 2004). Under accelerated cyclic potentiostatic polarization conditions, inhibition of localized corrosion, i.e., $E_{corr} < E_{crit}$. was observed at chloride to nitrate ratios above 0.15 at $80^{o}C$ (Payer 2004).

It is evident that a minimum nitrate concentration is needed to counteract the aggressive nature of the chloride ion at the surface of the passive film. The mechanisms for nitrate inhibition of localized corrosion are likely to involve:

1. Electro-reduction of the nitrate ion to the ammonium ion leading to a beneficial increase in local pH in the creviced regions.

2. Electro-reduction of the nitrate ion to atomic nitrogen, followed by adsorption of nitrogen on the depassivated metal in the crevice or at the base of an incipient pit. In this case, nitrogen may act as an anodic site blocker. Once adsorbed, nitrogen might then undergo further reduction to the ammonium ion.

The ongoing ammonium studies are addressing the importance of ammonium salts as they may affect the volatilization of nitrate, and solution conditions that result from the behavior of ammonia. Our current understanding based on handbook data and published literature is that ammonium nitrate and ammonium chloride, two common constitutents of atmospheric dust, will volatilize completely on the waste package surface either during preclosure ventilation or within a few years afterward. Ammonium sulfate and bisulfate salts are less deliquescent and relatively nonvolatile.

The currently available data on the ammonium content in dust comes from reanalysis of tunnel dust samples, and from the National Airfall Deposition Program monitoring data (collection station at Red Rock). These data indicate that ammonium and nitrate have generally comparable molalities, so there is the potential for volatilization of nitrate (e.g., as HNO3 or N2O). Understanding the extent to which nitrate in the dust analyses is incorporated in nonvolatile compounds (NaNO3 and KNO3) depends on the partitioning of ammonium among the various common atmospheric compounds. We are investigating the literature for atmospheric chemistry to establish this partitioning and its uncertainty.

Volatilization of ammonia from deliquescent brine could lower brine pH, but there is ample buffering capacity associated with the silicate mineral constituents of the dust, to maintain brine pH in the neutral range.

Third, the State of Nevada suggested that nitrates could be aggressive corrodents in some circumstances. The Board believes that it would be worthwhile to review existing corrosion data *to determine whether they bound nitrate-containing environments that reasonably could be anticipated at Yucca Mountain.*

Response:

The State of Nevada studies used an unrealistic experimental design involving the collection and condensation of acidic gas volatiles (e.g., HNO_3 and HCl) from evaporation of groundwaters (Pulvirenti, et al. 2004). It is more likely that in the open repository system these volatiles will disperse to the drift wall and become neutralized by reaction with the surrounding rock. In this way, acid-gas volatility will limit, rather than increase, the development of low pH (acidic conditions) on the waste package surface. Exposure environments such as the one created *in vitro* by Pulvirenti et al. (2004) are not realistic or expected repository environments.

As mentioned earlier, DOE has focused on evaluating corrosion behavior over a broad range of potentially relevant and accelerated test environments. Based on the results of the Physical and Chemical Environment model (BSC 2004c), the calculated maximum chloride concentration in the range of relevant seepage and deliquescent concentrated brines is about 13 molal, and the calculated maximum nitrate concentration is about 28 molal. In comparison, existing cyclic polarization data for creviced specimens include a broad range of chloride and nitrate concentrations up to 36 molal chloride plus 18 molal nitrate tested at 160°C. This essentially bounds the expected maximum nitrate levels for the full range of seepage and deliquescent dust brines. There appears to be no deleterious effect of nitrate concentration on the general corrosion rate. For example, test results for Alloy 22 covering a range of nitrate levels up to and above the calculated maximum nitrate level of 13 molal were reported at the May 2004 Board Meeting (Payer 2004). Also, specimens exposed in 2.7 molal NaCl + 15.1 molal KNO_3 for 158 days at temperatures up to 160°C exhibited very low corrosion rates of <0.2 µm/year. In addition, a limited amount of cyclic polarization data have been collected in concentrated nitrate solutions at high temperatures (e.g., 22.5 m $Ca(NO_3)_2$ + 0.225 m $MgCl_2$ at 145°C and 15 m $Ca(NO_3)_2$ + 1.5 m $CaCl_2$ at 125°C). No hysteresis was observed and no evidence of localized corrosion was found indicating that nitrate ions are beneficial to localized corrosion resistance even at high concentrations and at higher exposure temperatures.

Integration

DOE contractors have been performing corrosion tests at high-temperatures in high-chloride brines for several years, presumably because it was thought that the test conditions might occur at Yucca Mountain or might reasonably bound actual conditions. However, as became clear as a result of presentations at the May 2004 meeting, geochemical considerations preclude high-temperature, high-chloride brine conditions at Yucca Mountain, rendering the corrosion tests of limited relevance. This situation underscores the need for thorough integration and close cooperation among diverse technical disciplines, particularly when "coupled" processes are involved. For example, excellent integration among geochemists and corrosion scientists/engineers was evident at the meeting and helped bring clarity to an extremely important corrosion issue. Continuing integration will be necessary for resolving other issues associated with the DOE's current repository design.

Response

We agree that integration among diverse technical disciplines is an important element of assuring that there are no unintended gaps or inconsistencies between the models, data, and parameters developed and implemented by analysts in these different disciplines. The example cited by the Board of the calcium chloride, high-temperature corrosion test conditions not being representative of potential geochemical conditions at Yucca Mountain is a good example of the need for assuring such integration takes place. However, we disagree that these tests were of little relevance. Defining the corrosion potential and critical potential of Alloy 22 over a range of possible environmental conditions, including but not limited to high-chloride conditions and high-temperature conditions, was (and continues to be) an important element of the corrosion testing program. Although we agree that calcium chloride type brines are very unlikely to exist or be stable at Yucca Mountain, other chloride brines with varying amounts of corrosion inhibitors, such as nitrate and sulfate, may be present at elevated temperatures. Given such conditions, understanding the localized corrosion behavior of Alloy 22 is important. The tests cited by the Board give additional lines of evidence to support the confidence in the model when extrapolated to such conditions. Because a range of geochemical and thermal-hydrologic conditions are possible on the waste package surface, DOE intends to test Alloy 22 over this range and to extend the range to bound the possible behavior of the Alloy in extreme environments. This notwithstanding, the need for continued integration among diverse scientific and engineering disciplines remains an ongoing area of focus for the Department, particularly in the area of coupled processes.

Hydrology and Thermohydrology Issues

After reviewing the information presented at the May 2004 meeting, the Board continues to question the pervasiveness of vaporization and capillary barriers because of persistent uncertainties related to the expected repository tunnel environments. Examples of uncertainties include (1) the conceptual basis for the drift-scale thermohydrologic seepage analysis, including the axial convective transport of water vapor, air, and thermal energy in drifts; (2) the source of liquid water observed in the bulkheaded part of the cross drift; (3) the effects of drift degradation on the waste package environment; and (4) potentially unrealistic combinations of parameters used in the performance-assessment calculations of seepage.

The Board understands that significant scientific challenges are associated with analyzing the complex hydrology at Yucca Mountain, especially when the repository is subject to a large thermal perturbation. However, the Board believes that addressing uncertainties such as those noted above could create a more solid technical basis for determining whether the DOE's high confidence in the effectiveness of capillary and vaporization barriers is warranted.

Response

The pervasiveness of a capillary barrier has been tested and verified in both the middle nonlithophysal and lower lithophysal repository units. The testing ranges from several-meter scale in the niches to tens-of meters scale in Alcove 1 and Alcove 8-Niche 3. That a seepage threshold (orders of magnitude larger than predicted infiltration) exists has been shown by the field tests and their analysis, although the performance calculation employs a more conservative approach in selecting the seepage relevant parameters. All of the field tests are incorporated into relevant seepage models.

As for the effectiveness of a vaporization barrier, modeling addressing explicitly model uncertainties and parameters uncertainties, including effects of drift degradation, has been performed. However, at the present time, field data that directly address the issue of seepage under thermal conditions and hence the pervasiveness of the vaporization barrier do not exist. If appropriate and consistent with the Department's safety case, experimental investigations along these lines may be considered in the future to add confidence in the effectiveness of a vaporization barrier.

Seismic Update

We were very pleased to learn from the update at the May 2004 meeting that the DOE has initiated a program aimed at deriving more realistic estimates of seismic hazard at the Yucca Mountain site. In its June 27, 2003, letter to you, the Board indicated its concern about what may be physically unrealizable estimates of very low-probability (annual probabilities of exceedance of 10^{-6} *or less) seismic ground motion being calculated for Yucca Mountain by the DOE and its contractors. The new program appears to be a thoughtful first step. It is based on using the extent of fracturing observed in the tunnels at Yucca Mountain to limit the ground motions that could have taken place at the site during the last 10 million years. As discussed in our June 2003 letter, deriving limits to low-probability ground motions will be challenging. We therefore urge the DOE to implement an external peer review of these efforts.*

Response

The Department is pursuing both mid- to long-term and short-term activities to establish limits on low-probability earthquake ground motions. An external peer review of these efforts would be premature as they have just begun. However, the Department is actively soliciting input from the cognizant technical community in formulating its plans.

The longer term activities are being conducted under the Science and Technology (S&T) program, which has as a goal the achievement of a fundamental advancement in the approach to probabilistic seismic hazard analysis. The timeframe for this effort is 5-10 years. This advancement is envisioned to involve numerical modeling of ground motion from specific faults and nonlinear propagation of seismic waves from the source to the locations of engineered facilities. Limits on low-probability ground motions will be incorporated through empirical and theoretical limits on seismic source parameters and nonlinear material properties along the propagation path. The S&T program has established a review panel with the charter of recommending research activities to further the program's objectives. The panel is focusing, first, on research to establish limits on extreme ground motions. The panel conducted a workshop on this subject on August 23-25, 2004, in Menlo Park, California, and is preparing its recommendations at this time.

The Office of Repository Development also is pursuing activities to develop a technical basis for limiting low-probability ground motions, but in a timeframe (12-18 months) that will allow the results to be used to support the licensing hearings and the final design of the repository. This shorter term effort likely will focus on (1) the observation that the rocks at Yucca Mountain, which are over 10 million years old, do not appear to have been fractured by extreme earthquake ground shaking and (2) numerical modeling of the propagation of seismic waves through the mountain, accounting for the finite strength of the rock. To obtain input from the cognizant technical community on the specific activities to be conducted, the Office of Repository Development conducted a workshop in Las Vegas, Nevada, on September 28-29, 2004.

Transportation Planning

Information presented at the May 2004 meeting indicates that real progress is being made in planning a transportation system for a Yucca Mountain repository. The timelines that the DOE presented at the meeting identify several important milestones that your Office of National Transportation plans to develop further into detailed project plans with cost, schedule, and technical baselines. The Board's Panel on the Waste Management System has tentatively scheduled a meeting for October 13-14, 2004, in Salt Lake City, Utah. We look forward to a more detailed review of progress in transportation planning at that time. We also would like to discuss aircraft hazard and public perceptions of transportation risk at the panel meeting.

Response:

DOE appreciates the Board's recognition of the progress being made in planning a transportation system for the Yucca Mountain repository. In the meeting of the Panel on Waste Management System held last month in Salt Lake City, DOE gave an update on more recent activities in the transportation area. DOE is committed to working with the States and local entities, and the Tribes in a cooperative manner to address transportation issues relative to the Yucca Mountain repository, such as routing and emergency response training similar to the Foreign Research Reactor and Waste Isolation Pilot Plant programs.

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