Department of Energy
Washington, DC 20585

QA: N/A

November 20, 2007

B. John Garrick, Ph.D.
Chairman
Nuclear Waste Technical Review Board
2300 Clarendon Boulevard, Suite 1300
Arlington, VA 22201-3367

Dear Dr. Garrick:

In a letter dated January 12, 2007, the Nuclear Waste Technical Review Board (Board) provided a summary of its observations regarding the Workshop on Localized Corrosion of Alloy 22, held on September 25-26, 2006. The breadth of opinions and supporting data shared at the workshop and in the Board's letter are instrumental in assuring a thorough assessment of the likelihood of localized corrosion under deliquescent conditions. A follow-on letter regarding the effects of organic materials on nitrate/chloride ratios was transmitted on July 10, 2007.

The enclosure to this letter provides discussion of five key areas identified by the Board, in its January letter, as issues associated with the treatment of localized corrosion under deliquescent conditions, and the issue of effects of organic materials as described in the July letter.

We look forward to continuing this dialogue with future technical exchanges. If you have any questions concerning this letter, please contact Claudia M. Newbury at (702) 794-1361.

Sincerely,

Edward F. Sproat, III, Director
Office of Civilian Radioactive
Waste Management

Enclosure

**U.S. DEPARTMENT OF ENERGY RESPONSE TO THE
NUCLEAR WASTE TECHNICAL REVIEW BOARD'S COMMENTS FROM THE
SEPTEMBER 25-26, 2006 WORKSHOP**

The following five topical discussions refer to comments received from the Nuclear Waste
Technical Review Board (Board) on January 12, 2007:

(1) why seepage-induced localized corrosion and deliquescence-induced localized
corrosion are treated differently,

(2) the U.S. Department of Energy (Department) perspectives on the study of the six
circumstances identified by the Board for screening localized corrosion due to
deliquescence,

(3) the impact of cumulative damage of deliquescence-induced and seepage-based
localized corrosion,

(4) inclusion of deliquescence-based general corrosion in the modeling, and

(5) experimental investigation of the effects of surface condition on Alloy 22 corrosion.

The last topic of discussion, the effect of organics on nitrate to chloride ratios, is in response to
additional comments received on July 10, 2007.

**Why Localized Corrosion is Treated Differently under Seepage and Deliquescent
Conditions**

The Board points out that different approaches are used to address the potential for corrosion
under seepage and deliquescent conditions. The Department concurs with this observation, but
has determined that two separate analyses are warranted - and needed - due to the underlying
differences presented by these two types of environments. These differences can be categorized
as (1) differences in physical environment and (2) differences in the composition of the
electrolyte and differences in uncertainty of the composition of the electrolyte.

Although the probability of seepage contacting a waste package is low during the period when
the waste packages are still at elevated temperature, if dripping water does contact the waste
package, the local environment may have characteristics of an inundated system. In such a case,
a local corrosion site will be able to draw cathodic current from the surrounding material defined
by the wetted area and conductivity of the electrolyte. Additionally, if dripping continues in the
same location, a continuous supply of chloride and other ions is available to participate in
electrochemical reactions. In the case of a deliquescent environment, the volume of electrolyte is
predicted to be very small, thus communication between a corrosion site and the surrounding
material will be severely limited in comparison to the seepage condition. The more critical
difference, however, is the limited amount of reactants available in the deliquescent case. The
makeup and quantity of solid components of the dust layer are nominally determined by the
duration of the ventilation period and the composition of the repository air during this time.
Once the waste package reaches a temperature-relative humidity condition where deliquescence
is possible, the total available quantity of reactants (mass per unit area) is fixed and does not
increase. Any corrosion process that results in consumption of aggressive species will be limited

by the initial quantity of reactants and brine volume. The deliquescent environment differs from the seepage environment as limitations on reactants are not as well defined in the seepage case. Consequently, the corrosion model under seepage conditions does not take credit for this damage-limiting mechanism.

A significant difference also exists in the range of possible compositions for seepage environments compared to deliquescent environments. The seepage environment can contain a wide range of dissolved salts; and the final composition will be determined by the initial seepage waters, the effect of salt separation, and the degassing behavior of the system. A high degree of uncertainty dominates the prediction of any particular environment for a specific time and location in the repository. The Department's analysis of the deliquescent environment concludes that this environment is comprised of $NaCl + KCl + NaNO_3 + KNO_3$ (Bryan 2006). The composition of deliquescent environments is bounded because for each temperature-humidity condition there is a minimum NO_3:Cl ratio required for deliquescence (Rebak 2006). Any liquid with a lower NO_3:Cl ratio will evaporate and concentrate to maintain the minimum ratio. In the case of salt degassing, either the Cl salts degas more rapidly resulting in a higher NO_3:Cl ratio or the NO_3 salts degas more rapidly resulting in evaporation and concentration. The implication is that the environments associated with deliquescent salt mixtures are constrained while those associated with seepage are much more uncertain. This difference in level of uncertainty justifies treating the two environmental conditions with different corrosion modeling approaches.

Study of Six Circumstances for Screening Localized Corrosion Due to Deliquescence

The Department appreciates the Board's suggestions for potential areas of discovery and analysis that can improve the confidence in the decision to screen out localized corrosion under deliquescent conditions. The Department recognizes that there are a number of approaches to reaching this goal and that an open discussion of the available alternatives will aid in building consensus within the scientific community. Although the Department may or may not pursue a particular line of investigation, the discussion of these strategies helps to identify and clarify the important issues.

1. Degassing of HCl and HNO_3 - The Board suggested two possible paths for the evolution of the deliquescent brine environment based on the relative rates of acid degassing. If HCl can be shown to degas more rapidly than HNO_3 then the brine composition will evolve to a high-pH, nitrate rich composition, and localized corrosion will be mitigated. The Board postulates that if HNO_3 degasses more rapidly then the resulting environment will contain a high concentration of acid chlorides, an aggressive condition.

The EQ3/6 calculations in the dust deliquescence feature, event, or process (FEP) screening report (BSC 2006) suggest that HCl degasses more readily than HNO_3. These calculations are based on thermodynamic data in the Yucca Mountain Project Pitzer database, from Barin and Platzki (Barin 1995), a widely used compilation of thermodynamic data. An examination of the log(K)-temperature grids shows that HCl is predicted to degas more readily than HNO_3 over the entire temperature range from 25°C-300°C. Experimental results have been observed that both agree and disagree with this analysis. The formation constants of HCl(g) and HNO_3(g) were measured at Oak Ridge National Laboratory (ORNL) with the results agreeing with the analysis

in the dust deliquescence FEP screening report (BSC 2006). This work yielded a relative ranking of volatility (decreasing) (Cole 2006):

$$HF \gg HCL > HNO_3 \gg H_2SO_4$$

However, other work at ORNL, which was conducted under the Office of Science and Technology and International Program, indicated that HNO_3 degassed more rapidly than HCl. This result was based on monitoring the gas composition that formed from heating a 0.4-mol/kg ionic strength solution of approximately equimolal nitrate, chloride, and sulfate.

Regardless of whether HCl or HNO_3 degasses more rapidly, the effect of degassing will be a beneficial rise in pH resulting in less corrosive brines. Additionally, it has been shown (Rebak 2006) that deliquescent brines have a minimum NO_3 to Cl ratio that is temperature-dependent. Brines that would have a more aggressive composition will evaporate and concentrate, leaving smaller volumes of brine that maintain the minimum NO_3 to Cl ratio. In the limiting case of complete loss of HNO_3 or HCl, the remaining brine is likely to dry out, leading to an environment on the waste package surface that cannot support electrochemical reactions.

While the Department agrees with the Board that an increased understanding of the absolute and relative degassing rates of HCl and HNO_3 would aid in improving confidence in screening out localized corrosion due to dust deliquescence, the current understanding is adequate for the analysis.

2. Transference Rate of Nitrate and Chloride - The Board references the Electric Power Research Institute (EPRI) presentation (King 2006) with respect to the relative transference rates within a brine of nitrates compared to chlorides. The postulate is that a higher transference rate for nitrate will result in an increase in nitrate to chloride ratio in a crevice. Such a process would result in maintenance of a passive environment. If it can be conclusively demonstrated, such a process could add confidence to the screening justification. However, the Department is not in possession of data that unequivocally support this mechanism. The mobility of Cl^- is slightly higher than that of NO_3^- at room temperature in dilute solutions, but they are close enough to be considered equivalent for a qualitative discussion. Taking the mobilities as equal, the transference numbers will be a function of the concentrations in solution. If the nitrate to chloride ratio is high in solution, it follows that the charge carried will be greater for nitrate than chloride and a high ratio will be maintained in the crevice chemistry. However, no data were presented at the September 2006 workshop that allows quantification of mobilities in concentrated, high temperature brines. In the absence of these data, the prediction of relative concentrations of species in the crevice remains speculative. For this reason, the Department does not rely on a relative transference number justification for supporting the decision to screen out localized corrosion due to dust deliquescence.

3. Inhibition by Nitrates at Elevated Temperature - The presentation from EPRI (King 2006) includes a plot of critical temperature versus nitrate to chloride ratio which shows the critical temperature to be in excess of 200°C for a nitrate to chloride ratio of 0.5. The Department's data from cyclic polarization experiments (Rebak 2006) show a beneficial effect from NO_3^- at temperatures up to 150°C. The Department concurs that validating the beneficial impact of NO_3^- at elevated temperatures could strengthen the screening justification.

4. Properties of the Dust Layer that Impede the Formation of Localized Corrosion Cells - The Board makes an important distinction that crevices due to dust accumulation will differ significantly from those from manufacturing defects or design features. The size of dust particles that will be transported into the drifts is analyzed in the dust deliquescence FEP screening report (BSC 2006), and the case is made that annular droplets of brine beneath such small particles cannot support the diffusive chemical gradients necessary to initiate or sustain localized corrosion. The porosity of the dust is very high (50% or higher), which is an indicator that the permeability will be very high as well. There is insufficient salt in the dust for deliquescent brines to cause saturation so the dust environment is unsaturated and the gas phase should exchange readily.

5. Insufficient Liquid Water to Form a Continuous Water Film Under the Dust Particles – The Department concurs with the Board's assessment that it is likely there will be insufficient water to form a continuous water film under the dust particles. As was noted in the September 2006 workshop, the Department conservatively estimates the quantity of deliquescent brine at 120°C and applies this volume to higher temperatures where the quantity will be even less than the bounding estimate of an 1.8 $\mu L/cm^2$ (an 18 μm thick layer). Furthermore, much of this solution will be bound within the dust layer itself and within the resulting corrosion products (if any).

6. Limited Temperature Range for Deliquescent Environments Due to Acid Degassing – The Department concurs with the Board's assessment that should degassing result in dry-out of brines at higher temperature; deliquescence leading to localized corrosion would only be an operative mechanism at lower temperatures. However, the data presented at the September 2006 workshop and discussed in this letter do not provide conclusive evidence that the rates or extent of brine degassing is known for the environments relevant to the repository. Should conclusive data become accessible, the Department will use this information to strengthen the justification for screening out localized corrosion under deliquescent conditions.

Impact of Cumulative Damage of Deliquescence-Induced and Seepage-Based Localized Corrosion

The Board raises the issue of the impact of coupling corrosion under deliquescent conditions with corrosion under seepage conditions. This is an important issue to consider irrespective of the result of the analysis. The three main concerns are (1) the possibility that deliquescence-induced corrosion lowers the barrier for localized corrosion under seepage conditions, (2) that a residual chemical effect results from the deliquescent environment, and (3) that the barrier capability for corrosion resistance has been reduced resulting in overestimation for the time until penetration under seepage conditions. The Department's position is that none of these concerns will impact the performance of the engineered barrier for the following reasons:

The most probable mechanism for corrosion under deliquescent conditions to lower the barrier for initiation of localized corrosion is by forming a repassivated oxide that has less resistant properties than the native oxide. However, although a repassivated oxide might be less resistant than an air-formed oxide, the model for localized corrosion initiation used in the Total System Performance Assessment (TSPA) is not linked to the oxide properties or to oxide breakdown. The parameter used for prediction of localized corrosion under seepage conditions is the crevice

repassivation potential -- a parameter which is evaluated under experimental conditions (active crevice) where there is no metal oxide present.

The environment on the surface of the waste package in the post-deliquescent period will be determined by the composition of the seepage water that contacts the package. The mass per unit area of salt available from dust decorating the package surface is insignificant in comparison to the quantity of salts in the seepage waters. As the corrosion models assume an excess of available aqueous environment (data for the model are collected under fully immersed conditions), any increase in reactants available from the dust layer will be insignificant compared to the experimental conditions used.

In order to determine how degradation under deliquescent conditions contributes to decrease in barrier capability it is necessary to review how failure occurs for both localized corrosion and general corrosion in the modeling. In the case of localized corrosion, the TSPA assumes that after initiation, localized corrosion continues at an extremely rapid rate until failure of the waste package occurs. Thus, any additional change in the thickness of the material, due to generalized corrosion, will have an unnoticeable impact on when a package fails. Additionally, the available quantity of reactants is extremely limited such that the extent of any localized corrosion damage during the deliquescence period would be very small in magnitude compared to the dimensions of the barrier.

Inclusion of Deliquescence-Based General Corrosion in the Modeling

The Board makes the observation that general corrosion processes may be relevant under conditions of dust deliquescence. The same reasoning for limiting localized corrosion can be used to propose limits on the total extent of general corrosion possible under dust deliquescence environments. In the absence of a source of reactants, the corrosion processes (localized and uniform) will be bounded by the initial surface concentration of contaminants. Although by this reasoning, uniform corrosion will not significantly degrade the waste package under deliquescent conditions, the model for general corrosion is invoked during the entire repository lifetime.

The only data presented at the September 2006 workshop that suggests high corrosion rates are those from the Center for Nuclear Waste Regulatory Analyses (CNWRA) (Yang 2006). The Department does not have confidence that those experiments accurately reflect the environment expected in the repository during the thermal pulse. The difference in quantity of available reactants – extremely low in the case of the dust layer vs. essentially infinite in the case of the CNWRA test – calls into question the applicability of CNWRA's results in predicting degradation under deliquescent conditions.

The Department's model for general corrosion accumulates damage throughout the repository lifetime based on the general corrosion model which is applied for all repository conditions, including the thermal pulse where the maximum modeled corrosion rate at 200°C is on the order of 10 μm/year. In order for the barrier capacity to be reduced by deliquescence-induced corrosion beyond the extent already captured in the TSPA, the uniform corrosion rate under deliquescent conditions would need to be higher than that predicted from inundated experiments. As the quantity of reactants is severely limited under deliquescent conditions and essentially

infinite under inundated experimental conditions, the Department maintains that the current model implementation adequately accounts for this damage process.

Investigation of the Effects of Surface Condition on Alloy 22 Corrosion

With regards to surface condition, the Department considers its current models to be conservative and appropriate. Most of the samples used for model development include welds, while only a small portion of the waste package is welded. Furthermore, by using the Alloy 22 crevice data for weight loss, the model overestimates the expected corrosion rates because these samples were not polished on the backside resulting in an overestimate of the corrosion rates as compared to samples that were polished on both sides. However, the Department agrees that the effects of surface condition should be further studied and plans are under development for future testing of surface condition effects.

Effect of Organics on Nitrate To Chloride Ratios

Dust samples from the Drift Scale Test (DST) heated drift have been analyzed by the U.S. Geological Survey (USGS) both for bulk dust compositions and for leachate compositions for soluble components. These compositions show some differences from the dust samples collected within the Exploratory Studies Facility (ESF) outside of the DST heated drift. The DST dust sample leachate compositions show higher chloride to nitrate ratios than the ESF samples (and than samples of ambient surface dust). The DST dust appears to have accumulated in an environment heavily influenced by the local materials and relatively isolated from ambient dust, which is introduced into the ESF via active ventilation. There are a number of possible sources of chloride in the materials, for example, the concrete liner cement, but no currently identified sources of nitrate. Both the DST bulk dust compositions and the leachate compositions show variations related directly to whether they were in the concrete lined section or not. Given this, and the discussion below, it does not appear that the DST dusts ever had higher nitrate content than measured currently, and it does not appear that the thermal evolution caused a change to that content.

It does not appear at this time that the observed variation in chloride/nitrate ratio for these DST dusts was due to evolution of the salts during heating. Rather the variation is more likely due to the relatively isolated nature of the heated drift from the ventilation system for the ESF. That is, there does not appear to be a large, if any, contribution of the outside natural ambient dust within the DST dust samples. What is clear, as indicated in the Marshall and Peterman (2007 USGS) Goldschmidt meeting abstract, is that the DST dust samples contain constituents derived from the concrete liner (occupying the last 10 meters of the heated drift), as well as from the steels within the heated drift. Preliminary evaluation of the DST liner concrete (and the cement in it) indicates that the DST dust compositions lie on a mixing trend between the rocks of the Topopah Spring Welded hydrogeologic unit, the ESF tunnel dust, and the concrete liner. The DST dust contains a larger fraction, based on calcium and silica content, of cement/concrete compared to the ESF dust. Even within the DST dust, the variation in the concrete liner contributions can be seen by comparing the bulk composition of the dust sample in the unlined section and the composition of the two samples that were within the concrete lined section. Although this does not directly account for the chloride and nitrate contents in the soluble fractions of the DST dust,

it does establish that this environment was sufficiently isolated from the ESF itself to develop a locally derived composition. This is not surprising given that the ESF tunnel dust itself shows location dependent compositional variation.

A number of other specific materials may have contributed to the chloride, bromide, and fluoride contents that appear to be enriched in the soluble fraction of the DST dust relative to the mean ESF dust leachate composition. These include (a) the LiBr traced construction water used in the excavation of the heated drift and emplacement of ground support and (b) volatiles released from packer/gasket materials in the rock close to wing heater boreholes that achieved higher temperatures than the drift heaters. Given the additional materials in the DST, it is not a direct representation of the expected material environment within the emplacement drifts at post-closure. Because much of the nitrate within the dust expected to be in the post-closure emplacement environment would come from atmospheric dust pulled into the active ventilation stream and deposited on the waste packages over the 50-year ventilation period, the starting dust composition is expected to be different from that collected in the DST.

The Department appreciates the thought that has gone into the Board's suggestions for potential areas of discovery and analysis that can improve the confidence in the decision to screen out localized corrosion under deliquescent conditions. The Department recognizes that there are a number of approaches to reaching this goal and that an open discussion of the available alternatives will aid in building consensus within the scientific community. Although the Department may or may not pursue a particular line of investigation, the discussion of these strategies helps to identify and clarify the important issues.

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