UNITED STATES
NUCLEAR WASTE TECHNICAL REVIEW BOARD
2300 Clarendon Boulevard, Suite 1300
Arlington, VA 22201

January 12, 2007

Mr. Edward F. Sproat III
Director, Office of Civilian Radioactive Waste Management
U. S. Department of Energy
1000 Independence Avenue, SW
Washington, DC 20585

Dear Mr. Sproat:

The U. S. Nuclear Waste Technical Review Board's (Board) Panel on the Engineered System conducted a public Workshop on Localized Corrosion of Alloy 22 on September 25-26, 2006, in Las Vegas. Workshop participants included employees and contractors of the Department of Energy, the Nuclear Regulatory Commission, the Center for Nuclear Waste Regulatory Analyses, the Electric Power Research Institute, Nye County, and the State of Nevada. Three Board members, a Board contractor, and I participated in the entire workshop, and three other Board members attended part or all of the workshop.

Following the workshop, Dr. Ronald Latanision and Dr. David Duquette, the two Board members who co-facilitated the workshop, assembled their comments on the issue of screening out deliquescence-induced localized corrosion. Those comments, with which the Board concurs, are attached. As is evident from the attached comments, significant uncertainties in evolution of environments and of corrosion behavior at high temperatures persist, and there are apparent contradictions among some experimental results. Continuing research in deliquescence-induced localized corrosion is clearly warranted.

Unlike deliquescence-induced localized corrosion, which the Project plans to screen out of the total system performance assessment (TSPA), seepage-induced localized corrosion is not screened out of TSPA. Why seepage-induced localized corrosion and deliquescence-induced localized corrosion are not treated consistently in TSPA remains puzzling to us. The important question is, "Does including deliquescence-induced localized corrosion significantly affect the dose received by the reasonably maximally exposed individual?" Even if the effect is not significant, including this phenomenon would add to the completeness, robustness, and credibility of TSPA.

Sincerely,

{Signed By}

B. John Garrick
Chairman

Attachment

SCREENING OUT DELIQUESCENCE-INDUCED LOCALIZED CORROSION
Comments Based on Information Conveyed at the Board's
September 25-26, 2006, Workshop on Localized Corrosion of Alloy 22

Background

Individuals with a wide range of expertise participated in the workshop to help address the issue of localized corrosion of Alloy 22. Unfortunately, a definitive consensus about whether localized corrosion would occur at waste package crevices did not emerge. The majority of the workshop dealt with the possibility of accumulated dust functioning as a crevice and causing localized corrosion. Considerable data were presented but there was no general agreement on a number of the key issues. Those attending the workshop seemed to have a genuine interest in evaluating the feasibility of the Yucca Mountain waste package design.

As we are all aware, DOE has screened out deliquescence-induced localized corrosion of the waste package's Alloy-22 outer barrier in the repository environment at temperatures to ~200°C. DOE's screening-out approach is based on a decision-tree or events-tree analysis consisting of the following questions [BSC 2005]:

1. Can multiple salt deliquescent brines form at elevated temperatures?
2. If deliquescent brines form at an elevated temperature, will they persist?
3. If deliquescent brines persist, will they be corrosive?
4. If deliquescent brines are potentially corrosive, will they initiate localized corrosion?
5. Once initiated, would localized corrosion penetrate the waste package outer barrier?

According to DOE, if the answer to *any* of these questions is NO, then localized corrosion of the waste package's outer barrier due to deliquescence can be screened out, i.e., excluded from consideration in the total system performance assessment for license application (TSPA-LA).

We agree that DOE's approach is reasonable.

The Board has conducted public meetings on deliquescence-induced localized corrosion twice. The first meeting, which was part of a May 2004 meeting of the Board in Washington, D. C., was on the topic of localized corrosion caused by deliquescence of inorganic divalent chloride compounds, e.g., calcium chloride. On the basis in large part of information conveyed at that meeting, the Board concluded that significant amounts of calcium chloride were unlikely to accumulate on waste package surfaces during the preclosure period and therefore, that significant corrosion during the subsequent thermal pulse due to corrosive calcium-chloride-rich brines formed by the deliquescence of calcium chloride would be unlikely [NWTRB 2004]. In that case, then, the answer to the first question was NO, so there was no need to address the next questions.

The second public meeting was a day-and-a-half corrosion workshop held on September 25-26, 2006, in Las Vegas, Nevada. The workshop focused on deliquescence-based localized corrosion of Alloy 22 at high temperatures. The issue arose because of the determination made by DOE that salt mixtures containing sodium and potassium nitrates and chlorides would deliquesce at atmospheric pressure at temperatures up to and exceeding 200°C, even in the low-relative-humidity environments likely to be present in a repository in Yucca Mountain during the thermal pulse [DOE 2004]. Unlike calcium chloride, these salts are likely to be present in the dusts deposited on waste package surfaces during the preclosure period. The workshop was held because the Board had expressed its opinion, in December 2005, that the technical information available at that time did not seem sufficiently compelling to support screening out deliquescence-based localized corrosion [NWTRB 2005a]. The Board's opinion was based on the lack of corrosion data above 150°C and the questionable relevance of corrosion-stifling data taken at significantly lower temperatures to corrosion at higher temperatures.

Workshop Observations

Workshop participants seemed to agree that the answer to the first question was YES. There was less consensus on the other questions, particularly the last two.

DOE's and EPRI's positions are that the answers to the final two questions are NO. Their positions appear to rely on the role of nitrates both in the deliquescence process and in mitigating corrosion, based on the following observations/assumptions:

1. The chemical environment that may exist on the package surfaces is a solution of a multisalt assemblage containing $NaCl$, $NaNO_3$, KNO_3 and $Ca(NO_3)_2$ [Bryan 2006]. These salts are found in small amounts in airborne dusts in the Yucca Mountain vicinity.

2. Any stable chloride-containing brines formed by deliquescence at high temperatures must have significant fractions of nitrates [Rebak 2006].

3. Brines formed by deliquescence at high temperatures may change with time, e.g., by degassing HCl or HNO_3 [Bryan 2006; King 2006]. Degassing may result in a decrease in the amount of brine, an increase in pH, and an increase in the nitrate-to-chloride ratio.

4. Only limited amounts of salt and brine are available to initiate corrosion. Calculations indicate that the upper bound of brine volume in the dust deposited on waste package surfaces can be only $1.8\ \mu L/cm^2$, resulting in a brine layer $\sim 18 \mu m$ thick, assuming no geometric isolation due to inert dust

particles. (Note that these calculations are for 120°C; volumes should be less at higher temperatures). DOE claims that much of the brine would be held in the dust by capillary forces and that rapid mass transport in the dust would hinder establishing chemical gradients. DOE believes that these effects, coupled with the small volume of aggressive brine, would prevent initiation of localized corrosion [Brown 2006].

5. If corrosion does initiate, progression of corrosion will be stifled because of (a) obedience to a power law corrosion rate for localized corrosion propagation, with the time exponent in the power law being 0.5 or less; (b) physical retention of brine in the corrosion products; and (c) chemical sequestration of brine components in the corrosion products [Brown 2006].

Several possibly conflicting, or at least confusing, data sets and opinions were presented during the corrosion workshop. Among these were the following:

Localized corrosion of Alloy 22 was reported in Na-K-Cl-NO_3 brines at 160°C and at 220°C. NO_3/Cl ratios of 7.4 and NO_3 concentrations as high as 18.5 molal were not sufficient to inhibit localized-corrosion initiation [Rebak 2006].

Alloy 22 general corrosion rates on the order of 1 µm/yr and as high as 10 µm/yr were reported in Na-K-Cl-NO_3 brines at 150 – 180°C. However no localized corrosion was observed in these studies [Yang 2006].

Contrary to the apparent implicit assumptions of many workshop attendees that conditions on waste package surfaces during the decline of the thermal pulse evolve slowly and are in thermodynamic equilibrium, corrosion environments may be cyclic because of changes in barometric pressure and differential condensation/evaporation due to temperature-difference-driven gas flows along the drift [Walton 2006].

EPRI presented an analysis that raises questions about whether any nitrate-containing salts would be present in airborne dusts in the vicinity of Yucca Mountain [Arthur 2006; King 2006]. (If no nitrate salts are present, deliquescence would not occur at high temperatures, and the answer to the first question would be NO.)

Although degassing of Na-K-Cl-NO_3 brines can be made to occur under certain laboratory conditions, the range of temperatures within which degassing would occur *under conditions that would pertain in a Yucca Mountain repository* is unclear. Rates of degassing are highly uncertain, and it is not known whether HCl or HNO_3 preferentially degasses. Degassing was observed in one set of experiments [Yang 2006], but not in another set [Rard 2006].

Initial salt concentrations will not support localized corrosion, because high concentrations of nitrates will effectively displace HCl in crevices [King 2006]. HNO_3 is a passivator and will inhibit localized corrosion.

If localized corrosion is initiated, the deepest penetration that will occur will be only on the order of 5 mm after 200 years, assuming diffusive limitation of mass transfer that result in a power-law growth rate with an idealized exponent of 0.5. Experimental results suggest a power-law exponent closer to 0.1, resulting in wall penetration of less than 1 mm in 2,000 years [King 2006].

Apparent stifling of crevice corrosion propagation was reported in 5M NaCl/2×10^{-4}M $CuCl_2$ solutions, at 95°C [He 2006].

Stifling of localized corrosion will occur because of cathode current capacity, electrolyte resistance, and incompatibility of anode/cathode coupling [Payer/Kelly 2006].

Crevice corrosion was shown to arrest in 4M NaCl solutions at 100°C [Payer/ Kelly 2006].

Discussion

That there are considerable differences of opinion related to the interpretation of experiments conducted to date is obvious. For example, the apparent contradiction in results of localized vs. general corrosion reported by Rebak and Yang was explained by differences in experimental techniques. The experiments presented by Rebak were conducted in autoclaves where acid gases were allowed to reflux, while Yang's experiments were conducted under environmental conditions where gaseous species were allowed to evolve (degas) and were captured in a condenser. The condenser solutions became acidic with time, indicating evolution of acid gases. Few of the experiments that were conducted were performed in environments expected to be found in the repository. For example, the He and Payer/Kelly experiments were conducted in chlorides alone (no nitrates) and at temperatures well below anticipated surface temperatures of the waste packages. Nevertheless, it is possible to address the possibility of screening out localized corrosion during the thermal pulse, based on reasonable interpretations on scientific and engineering results obtained to date, with the *caveat* that experiments and tests currently under way may provide new evidence that will further advance the state of knowledge of the repository environment and its potential effects on the waste packages.

For discussing the possibility of initiating and propagating localized corrosion on waste packages in a repository environment, understanding the current state of the art for the initiation and propagation of localized corrosion in aqueous chloride solutions is important. Passivity on metals and alloys is effected by maintaining an oxidizing potential on the metal or alloy surface. In most engineering situations the oxidizing species is oxygen, dissolved in the aqueous solution from air in contact with the solution. However, in many engineering applications, the oxidizing potential is supplemented by the addition of strong oxidizers, such as nitrates, molybdates, and tungstates. The function of the oxidizing species is to establish a thin, oxygen-rich protective film on the surface and to repair the film if it is chemically or mechanically damaged. When crevices are present on passive metal surfaces, the interior of the crevice becomes depleted in the oxidizer, and the limited diffusion path for admitting more oxidizer establishes a differential oxidation cell. The differential oxidation cell establishes a large surface for reduction of the oxidizer on the passive surface outside of the crevice. The inside of the crevice, depleted of the oxidizer, becomes reducing, resulting in a large cathode (the area outside of the crevice) coupled to a small anode (the area inside of the crevice). Corrosion at the anode accelerates because of the large cathode/anode surface area ratio, which results in the rapid solubilizing of metal ions at the anode.

Initially, the solution in the crevice exhibits approximately the same pH as that outside of the crevice, but metal cations resulting from corrosion in the crevice combine readily with water, and hydrolysis takes place forming hydrated metal hydroxides and hydronium ions, which causes the solution in the crevice to become highly acidic. Thus, a gradient in charge concentration is established between the anode and the cathode. The charge imbalance can be accommodated by the diffusion of negative ions into the crevice. Anions in solution at relatively high concentrations will tend to migrate into the crevice because of conventional concentration gradient considerations. If the anions in the external solution are Cl^-, the solution in the crevice will become a concentrated HCl solution. It is well known that HCl is a strongly reducing acid that will dissolve passive films.

In nickel-based alloys, such as the Ni-Cr alloys, there is a further complication that the solutions in the crevice eventually become saturated in metal chlorides. At room temperature, the pH of a saturated $NiCl_2$ solution is 2.7 and that of a saturated $CrCl_3$ solution is -1.4. The crevice-corrosion process then is considered to be autocatalytic in that, while the large cathode-to-small anode couple may be maintained, the solution inside the crevice is sufficiently aggressive that it need not be maintained to support corrosion. The only limiting factor to crevice-corrosion crack growth becomes the continuous supply of Cl^- to maintain the reducing acid inside the crevice. Under laboratory conditions where the crevices are purposefully tightly clamped and times are relatively short, diffusion of chloride into the crevice may be curtailed as the crevice propagates, precipitation of solid corrosion products may occur near the mouth of the crevice where the solution attempts to return to neutrality, and the crevice may effectively be "stifled." In practice, however, the crevice-corrosion propagation rate may slow down until the interior of the crevice can be replenished in chloride, to form HCl and allow the reaction to continue. Crevice corrosion seldom is observed to be stifled under industrial conditions. If it were, crevice corrosion would not be a particular problem for practical applications.

Under repository conditions, where the times will be exceptionally long, it is doubtful that any crevice corrosion that might occur because of chlorides would be stifled because of diffusion considerations. Laboratory studies such as those conducted by He and by Scully [Scully/Bocher 2007][1] do not appropriately model a chloride-induced crevice condition since they are performed with concentrated chloride solutions, often with low pHs. Thus, no appreciable concentration gradients are established.

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[1] See page 34 of Joe Payer and Rob Kelly's workshop presentation [Payer/Kelly 2006].

In general, crevice corrosion tests performed in a laboratory are highly useful in determining if crevice corrosion is likely to occur for an environment-alloy couple, assuming that the service environment can be reasonably simulated. Laboratory tests to determine propagation morphology or rates are less useful because of variabilities in crevice geometries, crevice-forming devices, and time constraints. For example, in tests performed specifically for the Yucca Mountain project, just changing the crevice former from a ceramic to PTFE had major consequences in the crevice-corrosion attack observed in simulated repository environments [Payer/Kelly 2006]. Accordingly, the use of laboratory experiments, or exposure tests, to screen out localized corrosion propagation — or even localized corrosion initiation — due to deliquescent salts is highly questionable.

On the other hand, a consideration of the environments likely to be present in the repository suggests that crevice corrosion due to deliquescent salts during the thermal pulse may allow the phenomenon to be screened out under the following circumstances :

1. Concentrated chloride/nitrate brines have been postulated to degas both HCl and HNO_3 in the open repository environment, and at least one laboratory test confirmed volatility of some acid species [Yang 2006].[2] Assuming degassing and subsequent volatilization, the questions become (a) the rates of degassing and volatilization and (b) which of the two acids degasses/volatilizes more rapidly. If EPRI is correct in that both acids are highly volatile, the salts in the repository may very well be dominated by sulfates and carbonates, and brines either would not form during the thermal pulse or would be essentially benign. If HNO_3 is more volatile, the result would be a concentration of acid chlorides on the waste package surfaces, which would be detrimental. However, if HCl is more volatile, waste package surfaces will become more concentrated in nitrates, and initiation and propagation of localized corrosion due to deliquescence at high temperatures likely would be mitigated.

2. Aqueous nitrates apparently have a higher transfer rate than chlorides [King 2006]. This is an important observation because the charge imbalance in the crevice must be neutralized by the migration of some ion into the crevice. If nitrate exists in concentrations in excess of 1:1, and if it in fact has a higher transference number, the charge neutrality will be achieved by nitrate migration, resulting in a passivating environment in the crevice. Proof of this concept must await an analysis of the crevice chemistry from corrosion tests performed in appropriate environments at appropriate temperatures.

3. It has been postulated that nitrates are effective inhibitors at $[NO_3^-]:[Cl^-]$ ratios as low as 0.5 at temperatures as high as 200°C [King 2006].

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[2] The experiments presented at the workshop by Yang were not at Yucca Mountain conditions. For example, it appeared that the activity of water was higher than would be expected in deliquescent brines. Higher water activity could lead to increased degassing.

4. Individual dust particles may be too small to support crevices, or the dust layer may be permeable to oxygen [King 2006]. Crevices at manufacturing defects and mechanical design features are likely to function very differently than a layer of accumulated dust. At this time, however, no quantitative data have been presented to the Board on the size or shape of the dust particles or on the permeability of dust layers that would deposit on waste-package surfaces.

5. Insufficient liquid water may be present to provide a continuous water film under dust particles, because much of the water will reside in interstices between the dust particles [Bryan 2006].

6. For the environments postulated for the repository, with acid degassing, the evolution of the relative humidity in the repository is such that the package will not be wet until temperatures have declined to the vicinity of 100–120°C — when deliquescence-induced crevice corrosion may be unlikely [King 2006].

Conclusions

If any of the conditions cited in 1–6 are met, crevice corrosion due to deliquescence during the thermal pulse period could be screened out. Of each of these six scenarios, preferential charge neutralization by nitrate in the crevice is perhaps the most important, because the nitrate will be an effective inhibitor inside any crevices that are formed, at least for temperatures up to ~160°C.

The Board understands that the chemistry of the crevice environment is currently under study. Demonstrating an adequate technical basis for screening out deliquescence-based localized corrosion during the thermal pulse requires (a) determining the nitrate-to-chloride ratios that are inhibitive for the entire range of temperatures that deliquescent brines may occur on waste package surfaces and (b) confirming the hypothesis that the preferential migration of nitrate ions into the crevice is sufficient to maintain nitrate-to-chloride ratios that are inhibitive.

Although deliquescence can occur at any temperature below about 200ºC, our concern about deliquescence-induced localized corrosion is principally in the higher part of the temperature range, i.e., 150-200ºC. On the other hand, seepage-based corrosion may not occur above approximately 100ºC. Conceivably, deliquescence-based localized corrosion could occur on a waste package and then be followed by seepage-based localized corrosion at the same place on the package later during the thermal decline. Any damage caused by deliquescence-induced localized corrosion could result in earlier penetration by subsequent seepage-based corrosion than would occur in the absence of deliquescence-induced localized corrosion. Cumulative damage due to the combined effects of deliquescence-induced and seepage-based localized corrosion was not discussed at the workshop. However, the topic merits some analysis to determine its possible significance.

As things stand now, seepage-based localized corrosion is included in TSPA and deliquescence-induced localized corrosion is excluded. This always has struck us as incongruous because the processes are the same and particularly because the temperature range of concern about deliquescence-based localized corrosion is higher. We wonder whether the same degree of conservatism that is being applied to "screen out" deliquescence-induced localized corrosion is being applied to "screen in" seepage-based corrosion.

Additional Observations

The topic of general corrosion arose during the workshop in conjunction with experiments to obtain information about localized corrosion. Localized corrosion was observed in the LLNL autoclave experiments [Rebak 2006], so general corrosion would be expected to occur, also. However, no useful data on general corrosion could be obtained from those experiments. In contrast, localized corrosion seemed not to occur in CNWRA experimental results obtained under somewhat similar conditions [Yang 2006], but general corrosion was observed. The rates of general corrosion rates derived from that data were unexpectedly high and showed a maximum with respect to temperature, which also is unexpected. These anomalies require explanation. In any case, particularly since the proposed regulations for Yucca Mountain [70FR173, pp 53313-53320] require general corrosion to be modeled in TSPA, deliquescence-based general corrosion should be included in such modeling.

Mill-annealed and welded specimens prepared for the experiments discussed at the workshop generally were polished to a uniform surface finish before being placed in the experimental apparatus. The polishing step is useful for helping compare results within a laboratory or among laboratories. However, the actual waste packages emplaced in a repository will have been treated to remove the scale caused by heat treating by, e.g., blasting with abrasive particles or electropolishing, and will have scratches, dents, etc. from handling. Although some experimental investigation of the effects of surface condition on Alloy 22 corrosion has been undertaken, we are not sure that the effects have been investigated adequately. The discussion of the effect of surface condition on corrosion in the Alloy 22 corrosion AMR [BSC 2004], for example, is brief and is limited to the effect of surface condition on crevice corrosion.

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