



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

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**MEMORANDUM**

To: Participants in International Workshop on Long-Term Extrapolation of Passive Behavior

From: Alberto Sagüés and Carl Di Bella\*

Subject: Questions To Workshop Participants and Background on Corrosion Issues

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**INTRODUCTION**

Each workshop participant is asked to consider the two following questions and formulate answers for brief presentation at the beginning of the workshop and detailed discussion during the rest of the meeting. A written summary of his/her answers is due from each participant after the meeting, as indicated in the *Statement of Work* that was e-mailed earlier.

Each question contains a brief premise statement, which is amplified and supplemented in the *Background on Corrosion Issues* section immediately following the questions. In preparing the answers, the participants should assume the environmental conditions indicated in the *Background Information on Waste Package Environment* memorandum that was e-mailed earlier.

**QUESTIONS**

Question No.1: On the effects of long-term passive dissolution.

*Premise*

Laboratory experiments and industrial experience indicate that, under many of the expected waste package service environments, a recently prepared Alloy 22 surface is likely to spontaneously passivate and remain passive for many years (*that expectation will be challenged in Question 2 but not here*). Fundamental knowledge suggests that the passive layer on such material is thermodynamically stable and self-repairing under many of the expected operating regimes. Present short-term (years) empirical evidence indicates that passive corrosion under such conditions is essentially uniform and proceeds at a rate  $\sim < 0.1$  micrometer/y. Those observations have led to predicting times on the order of  $> \sim 10^5$  years for penetration of the 2 cm thick WP wall when localized corrosion is not expected. Assume now that the passive regime

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\* Drs. Sagüés and Di Bella are Member and Senior Technical Staff, respectively, of the Nuclear Waste Technical Review Board. The content of this document reflects their opinions and not necessarily that of the NWTRB.

thus initiated has continued for several hundreds or even thousands of years, so that the passive corrosion penetration has reached a substantial depth (e.g., > 10 micrometer).

*Question*

- a) Can you propose any plausible mechanism(s) that would cause the long term corrosion rate to increase, once penetration under passive conditions reaches significant values, so that sustained corrosion rates (maybe no longer uniform) exceed ~1 micrometer/y? (Such seemingly small absolute increase in corrosion rate would seriously compromise the present expectations for successful WP performance.) Examples of scenarios that have been proposed for possible consideration are given in the *Background on Corrosion Issues* section.
- b) What experiments and/or theoretical treatment would you propose to assess the validity of the proposed mechanism(s) for Alloy 22 under the proposed repository conditions?

Question No. 2: On the long-term preservation of conditions preventing localized corrosion.

*Premise*

The evidence from present testing, summarized in the *Background on Corrosion Issues* section, suggests that under expected service conditions the open circuit potential at the package surface stays significantly more negative (by a few hundred mV or more) than the critical potential deemed necessary for development of stable localized corrosion. That evidence has led to predicting the absence of significant localized corrosion of Alloy 22, for unstressed portions of the WP, over a performance period stretching to  $10^4$  years and beyond. For simplicity, assume that no significant residual or externally imposed stresses affect the waste packages.

*Question*

- a) Can you propose any plausible mechanism(s) relevant to the waste package that would cause, over long periods of time, shifts in the open circuit and/or the critical potential such that stable localized corrosion could develop? (If you wish, you may consider both potentials as distributed parameters.)
- b) In addition, or as an alternative to (a), can you propose a localized corrosion process that could develop over long times such that initiation and propagation are not amenable to description in terms of a critical potential?
- c) What experiments and/or theoretical treatment would you propose to investigate the issues identified under (a) or (b) for Alloy 22 under the proposed repository conditions?

## BACKGROUND ON CORROSION ISSUES

### Desired Corrosion Performance

In the present repository design approach, the corrosion resistance burden in the waste package (WP) rests on the outer Alloy 22 shell (at this time durability projections take the conservative approach of ignoring the presence of the inner stainless steel shell). Performance analysis calculations indicate that widespread corrosion penetration of the 20 mm Alloy 22 shell during the first 10,000 years of operation could seriously compromise repository performance. Thus, either localized modes of corrosion such as pitting or crevicing, which could lead to rapid wall penetration, or uniform corrosion at greater than very low rates would be very detrimental. Research sponsored by the Department of Energy (DOE) has aimed at ascertaining that for periods amply exceeding 10,000 years under the expected environmental conditions localized corrosion would be very unlikely and, furthermore, that in the absence of localized corrosion the resulting uniform dissolution rate would be small enough that the 20 mm wall would not be penetrated.\*

The uniform dissolution rate requirement is particularly severe, since it implies that the time-averaged rate of corrosion should not exceed a small fraction of 1 micrometer/y over a period of time that is orders of magnitude greater than that covered by engineering experience. Furthermore, corrosion protection of otherwise reactive metal by a passive layer over thousands of years in a moist environment is a phenomenon that does not seem to have any documented natural or man-made analog. This extrapolation uncertainty is the basis for the first and main question examined in this workshop. Because the thermal pulse takes place early, localized corrosion behavior projection may be challenging over a shorter time frame than that for passive corrosion. The absolute time scale is nevertheless still very large, and this issue has been addressed in the second question.

Recent findings of research on both modes of corrosion under conditions relevant to the repository are highlighted in the next sections. Examples of scenarios that may apply to the questions to the participants are also presented. This narrative is for general background information and is not intended as a formal or comprehensive review. Bibliographic references are not provided here but participants are welcome to contact Drs. Di Bella or Sagüés for additional information if desired. Detailed information on much of the work mentioned may be found in the Web site [www.ymp.gov](http://www.ymp.gov).

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\* Other DOE sponsored work examined the opportunities for stress corrosion cracking (SCC) in the WP. That work led to adoption of a conservative WP design with extensive stress relief, which is thought to virtually eliminate the chances of SCC occurring over the performance period of interest. While potentially important, SCC issues will not be discussed in this workshop in the interest of focusing on the other agenda issues.

## Uniform Corrosion

### *Highlights of research findings*

Various research organizations have conducted corrosion rate measurements of Alloy 22 in the passive regime over very short test times (hours-weeks) at temperatures and environments relevant to repository conditions, using electrochemical techniques such as polarization resistance and potentiostatic polarization. The test results suggest that corrosion rates of Alloy 22 in the long term would be below ~0.1 micrometer/y. Gravimetric tests using corrosion test coupons were started by DOE approximately three years ago in a facility that consists of aerated bathtub-size tanks that are maintained at either 60°C or 90°C. The tanks are partially filled with water that contains various amounts of dissolved salts found in the water below the water table at Yucca Mountain. Coupons are placed below the water line, at the interface between the water and the vapor space, and in the vapor space. These tests are scheduled to continue for many more years. Measurements of Alloy 22 coupons removed after two years indicate corrosion rates that are also below ~0.1 micrometer/y (or even much less depending on how the effect of inorganic deposits on the coupon surface is incorporated in the calculations), near the gravimetric detection limit. Within the relatively narrow range of temperatures and solution compositions studied at the test facility, there seem to be no discernible effects of solution composition, vapor space or direct liquid immersion placement, or temperature. There is, however, limited evidence of an increase of passive corrosion rate with temperature in some of the short-term electrochemical experiments, which suggests an activation energy on the order of 30 kJ/mole. No localized corrosion of Alloy 22 has been observed in the test facility, consistent with the expectations from the electrochemical testing findings in the localized corrosion section.

### *Speculative scenarios*

Some speculative scenarios, given below, have been proposed by various investigators for consideration as ways in which passivity might degrade over long time periods, under repository environments that in a shorter time frame would have supported instead very low metal dissolution rates. These items are presented for illustration only. Workshop participants may address any or all of these scenarios if they wish, but are under no obligation to consider them. In the following, it is assumed that either because of dripping or because of condensation and deliquescence a layer of electrolyte is always present on the surface of the WP being considered.

- 1) *Defect sweeping.* As passive corrosion proceeds, the barrier layer dissolves on the electrolyte side and builds up on the alloy bulk side, effectively sweeping into the metal. In this sweeping action the layer encounters a growing number of precipitates or other microstructural features. If those features leave an adverse cumulative effect on the layer (for example, increasing crystal defect density), after enough time there could be a significant increase in the rate of passive corrosion because of enhanced ionic transport across the layer.
- 2) *Vacancy buildup.* Passive corrosion may proceed at different rates for various alloy components. This imbalance could lead to accumulation of vacancies at the barrier layer-metal

interface, which after a long enough time would cause oxide spalling and consequent increase of the average rate of corrosion compared with that at earlier times.

3) *Debris accumulation.* As time progresses the corrosion products from passive dissolution accumulate on the WP surface creating a macroscopically thick layer of likely hydrated metal ions. If this layer acts as an anion-selective membrane it may promote localized corrosion.

4) *Incipient transpassive behavior.* Because of the high Mo content of Alloy 22, transpassive dissolution may already develop at modestly noble potentials at a rate that would be negligible in an industrial application, but unacceptable in the repository. The neutral-to-high solution pH projected by some performance analysis calculations could be a factor in promoting this mode of degradation. Slow, long term excursion of the open circuit potential in the noble direction could result from, for example, deposition over long times of passive corrosion debris on the WP surface with consequent increase in cathodic efficiency.

### Localized Corrosion

DOE's localized corrosion model for Alloy 22 is based on the assumption that localized attack would occur only if the open circuit corrosion potential (OCP) exceeds a critical potential for a given environmental condition. DOE has sponsored research to determine the range of OCP that may develop, and the proposed repository regimes where localized corrosion would or would not occur. Much of the information used for those determinations was obtained from conventional cyclic polarization experiments on Alloy 22 at temperatures ranging from 30°C to 120°C, in environments representing concentrated water (both from below the water table and from rock pores). In these experiments, the critical potentials were found to be always at least several hundred mV higher than the OCP estimated from the same experiments. Other work sponsored by DOE showed by means of cyclic polarization and potential step experiments that crevice corrosion could be sustained on Alloy 22 at ~90°C at potentials closer to the anticipated OCP when the Cl<sup>-</sup> concentration in the bulk solution was greatly in excess of that of beneficial anions (e.g., NO<sub>3</sub><sup>-</sup>). However, environments with high ratios of Cl<sup>-</sup> to beneficial anions have been deemed by DOE, for performance modeling purposes, to be unrepresentative of WP service conditions.

Work conducted by the Center for Nuclear Waste Regulatory Analyses (CNWRA, located at Southwest Research Institute and funded by the U.S. Nuclear Regulatory Commission) has used potential step methods that also indicate highly noble threshold (repassivation) potentials for Alloy 22 at high temperatures (e.g., 95°C), except at Cl<sup>-</sup> concentrations that were very high (e.g., ~4M) and much in excess of beneficial anions. CNWRA tests of Ni-Cr-Mo alloys with potential hold times in the month-years range have shown that localized corrosion was sustained at potentials just above the repassivation potential determined in shorter term (hours) tests, supporting their approximate validity as threshold potentials. Recently, concern has also been expressed about possible localized corrosion of Alloy 22 from elements such as As, Hg, or Pb, which are present in ppb or ppt levels in the rock pore water. Investigations are in progress at various laboratories to determine if these elements could become sufficiently enriched to be detrimental under repository conditions.

The estimates of what the OCP of Alloy 22 may be under expected repository conditions are based on experiments of very short duration (hours in the case of cyclic polarization experiments — months in other cases) compared to the repository time frame. At present OCP values on the order of ~ -50 to -200 mV (Ag/AgCl/KCl sat.) are considered to be likely. Attempts are in progress to measure OCP of samples exposed for a few years in the DOE coupon test facility described in the Uniform Corrosion section. As a result of this and other ongoing investigations, the anticipated range of OCP values is likely to be revised in the future.

The validity of the approach presently used to evaluate whether localized corrosion will occur in the repository depends on how applicable a critical potential criterion may be for the material, surface area (>10,000 packages), environment, and time frame considered. Assuming that the criterion were appropriate, its successful application would require reliable bounding of the range of both critical and OCP potentials anticipated. Those issues are the theme of the second question presented to the workshop participants.