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

International Workshop on Long-Term Extrapolation of Passive Behavior (Draft Agenda)

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July 19-20, 2001

Workshop purpose: to obtain a broad range of views from experts here and abroad regarding potential issues for extrapolating corrosion resistance for many thousands of years

Thursday, July 19

8:30 a.m. **Call to order/welcome**
Daniel Bullen, Member, Nuclear Waste Technical Review Board (NWTRB) and Chair of the NWTRB's Panel on the Repository

8:35 a.m. **Introduction of panelists (Panelists are listed on page 2.)/Background and scope of workshop**
Alberto Sagüés, Member NWTRB

8:50 a.m. **Overview of proposed waste package designs and waste package environments**
Carl Di Bella, NWTRB Professional Staff
9:05 a.m. Questions/discussion

9:15 a.m. **Overview of research on Alloy-22 corrosion/Questions 1 and 2**
Alberto Sagüés
9:35 a.m. Questions/discussion

9:55 a.m. **Initial responses to questions 1 and 2** (Questions are attached.)
Panelists
Each panelist has 5-10 minutes to outline his/her *initial* response to the questions, followed by 1-2 minutes for clarifying queries.

10:30 a.m. **Break (15 minutes)**

10:45 a.m. **Initial responses to questions 1 and 2 (concluded)**
Panelists

12:30 p.m. **Lunch (1 hour 15 minutes)**

1:45 p.m. **Roundtable discussion of question 1**
Panelists

3:00 p.m. **Break (15 minutes)**

3:15 p.m. **Roundtable discussion of question 1 (concluded)**
Panelists

5:00 p.m. **Comments from the public**

5:30 p.m. **Recess until 8:30 a.m., Friday, July 20**

Friday, July 20

8:30 a.m. **Reconvene**
Dan Bullen

8:40 p.m. **Roundtable discussion of question 2**
Panelists

10:00 a.m. **Break (15 minutes)**

10:15 a.m. **Roundtable discussion of question 2 (concluded)**
Panelists

11:30 a.m. **Comments from the public**

12:00 p.m. **Closing remarks and adjournment**
Alberto Sagüés

List of workshop panelists

Ugo Bertocci		USA
Hans Boehni	Swiss Federal Institute of Technology	Switzerland
Gustavo A. Cragnolino	Center for Nuclear Waste Regulatory Analyses (Southwest Research Institute)	USA
Alison J. Davenport	University of Birmingham	UK
Jerome Kruger	Johns Hopkins University, Emeritus	USA
Digby D. Macdonald	The Pennsylvania State University	USA
Barry R. MacDougall	National Research Council Canada	Canada
Philippe Marcus	L'Ecole Nationale Superieure de Chimie de Paris	France
Roger C. Newman	University of Manchester Institute of Science and Technology	UK
Howard W. Pickering	The Pennsylvania State University	USA
Robert A. Rapp	Ohio State University, Emeritus	USA
Norio Sato	Hokkaido University, Emeritus	Japan
Toshio Shibata	Osaka University, Emeritus	Japan
Susan Smialowska	Ohio State University, Emeritus	USA
Hans-Henning Strehblow	Heinrich-Heine University Duesseldorf	Germany

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 ~< 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 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 a seemingly small absolute increase in corrosion rate would seriously compromise the present expectations for WP performance.) Examples of scenarios that have been proposed for possible consideration are given in the *Speculative Scenarios* section below.

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?

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.

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

Premise

The evidence from present testing 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?