Proceedings From An International Workshop On Long-Term Extrapolation Of Passive Behavior
July 19-20, 2001
Arlington, Virginia

Alberto A. Sagüés and Carlos A. W. Di Bella, eds.

United States Nuclear Waste Technical Review Board

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Dr. Paul Craig, for formulating and posing philosophical questions during the Workshop.

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Collectively, the members of the U.S. Nuclear Waste Technical Review Board for permission and wherewithal to conduct the Workshop and publish these Proceedings.

And last, but very important, the fourteen participants: Drs. Bertocci, Cragnolino, Davenport, Kruger, Macdonald, MacDougall, Marcus, Newman, Pickering, Rapp, Sato, Shibata, Smialowska, and Strehblow. They agreed to participate on relatively short notice, prepared themselves for the Workshop, participated with vigor and enthusiasm, and contributed the expanded abstracts and reports that constitute this publication.

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PREFACE

The main corrosion barrier of the conceptual package for containing high-level nuclear waste and spent fuel at the proposed repository at Yucca Mountain, in Nevada, is a 2-centimeter-thick shell of Alloy 22. This alloy is a very corrosion resistant material that depends on a passive layer only nanometers-thick for its corrosion resistance.

Technical experience with Alloy 22 is only a few decades long. Experience with passive Cr-rich alloys like Alloy 22 has lasted only a few more decades. And experience with any metal or alloy that owes its corrosion resistance to a passive layer spans little more than a century.

Thus, if our experience is limited to a century or so, what are the theories and the assumptions that form the basis for extrapolating corrosion resistance for thousands and thousands of years? As reflected in recent Board reports and letters (available on the Board's web site, www.nwtrb.gov), the Board has considered this question of paramount importance for several years.

To address the question, the Board decided to conduct a workshop on issues related to predicting corrosion behavior for periods of unprecedented duration. Because the Secretary of Energy was expected to make a Site Recommendation decision — a key, legally required decision on the suitability of the Yucca Mountain site (including the relationships between repository engineering features and the geologic medium) — very soon, conducting the workshop as soon as possible was imperative.

So that broad, diverse, and independent views could be obtained, individuals from around the world were selected for invitation from a spectrum of corrosion disciplines, and — for the most part — among those with little or no direct recent involvement in the Yucca Mountain Project. Participants are listed beginning on the next page.

The workshop was held on July 19 and 20, 2001. A transcript and other information about the workshop are on the Board's web site. Initial plans called for each participant to submit after the workshop a two-page report containing afterthoughts on issues discussed at the workshop. As the considerable success of the workshop became clear during its course, participants were asked whether they would be interested in submitting somewhat longer postworkshop reports. Virtually all participants responded positively. These Proceedings are a compilation of those reports.

WORKSHOP PARTICIPANTS

Ugo Bertocci: doctorate in chemistry from University of Milan; research interests in the field of electrochemistry; retired about nine years ago from the National Institute of Standards and Technology (NIST, formerly the National Bureau of Standards); continues to conduct research extensively in electrochemistry in the United States and abroad.

Gustavo A. Cragnolino: licenciado degree and doctorate in chemical sciences from University of Buenos Aires; research interests include experimental research and modeling of corrosion and thermal stability of metallic container materials for high-level radioactive waste disposal; staff scientist in Center for Nuclear Waste Regulatory Analyses at Southwest Research Institute in San Antonio, Texas; former posts include Argentina Atomic Energy Commission, Fontana Corrosion Center at Ohio State, and Brookhaven National Laboratory.

Alison J. Davenport: doctorate in materials science and metallurgy from University of Cambridge; research interests include the structure, chemistry, and stability of passive oxide films and the effect of microstructure and alloying additions on corrosion and surface treatment of metals; lecturer at University of Birmingham (UK) in the School of Metallurgy and Materials; former posts include Brookhaven National Laboratory.

Jerome Kruger: doctorate in physical chemistry from University of Virginia; professor emeritus of John Hopkins University in Materials Science and Engineering Department; former posts include National Bureau of Standards (now NIST) and Naval Research Laboratory; fellow of National Association of Corrosion Engineers, Electrochemical Society, and Institute of Corrosion in the UK.

Digby D. Macdonald: BS and MS degrees in chemistry from University of Auckland and doctorate in chemistry from University of Calgary; research interests include passivity, nuclear reactor technology, and high-temperature aqueous electrochemistry; professor of Materials Science and Engineering and director of Center for Electrochemical Science and Technology at Pennsylvania State University; fellow of NACE and Electrochemical Society.

Barry R. MacDougall: doctorate in electrochemistry from University of Ottawa; research interests include the formation and breakdown of passive oxide films on metals and alloys, with emphasis on the mechanism of film breakdown leading to localized pit initiation, and improving understanding of fundamentals of corrosion processes of metals and alloys through the use of surface electron spectroscopies to study the composition and structure of surface layers; leader, Electrochemical Technology Group at National Research Council of Canada; fellow of NACE and Chemical Institute of Canada.

Philippe Marcus: doctorate in chemistry from University of Pierre et Marie Curie in Paris; research interests include the effect of atomic layers of absorbed sulfur on dissolution and passivation of metallic surfaces, the study of passivity of metals and alloys, and the use of photoelectron spectroscopy toward the standard relationships between the chemical nature of passive films and their corrosion resistance; directs the laboratory of physical chemistry of surfaces, part of National Center for Scientific Research at University of Pierre et Marie Curie.

WORKSHOP PARTICIPANTS (CONTINUED)

Roger C. Newman: doctorate in metallurgy and materials science from University of Cambridge; research interests include passivity, localized corrosion, and stress corrosion cracking, especially the formation of oxide films on alloys, mechanisms of growth of pits and cracks, and prediction of pitting or cracking thresholds; professor of Corrosion and Protection at University of Manchester Institute of Science and Technology; former posts include Brookhaven National Laboratory; fellow of UK Institute of Materials and of NACE.

Howard W. Pickering: doctorate from Ohio State University; research interests include selective element dissolution from alloys, localized electrochemical degradation processes, such as crevice, pitting and grain boundary corrosion, hydrogen evolution and its absorption and diffusion into metals, and surface reconstruction in metal electrodissolution and electrodeposition in aqueous solutions using scanning tunneling microscopy and atomic force microscopy; distinguished professor of Materials Science and Engineering at Pennsylvania State University

Robert A. Rapp: doctorate in metallurgical engineering from Carnegie Institute of Technology in Pittsburgh, a predecessor to Carnegie-Mellon University; research interests include corrosion mechanisms, coating and protection, extractive metallurgy, and high-temperature materials; distinguished university professor emeritus in Department of Materials Science and Engineering at Ohio State University; member of National Academy for Engineering and fellow of ASM, TMS, Electrochemical Society, and NACE, as well as two foreign societies.

Norio Sato: doctorate in engineering from Hokkaido University in electrochemistry; research interests include electrochemical science, with specialization in corrosion and fundamental understanding of metallic passivity and its breakdown; emeritus professor at Hokkaido University; fellow of NACE, Japan Society of Corrosion Engineering, Institute of Corrosion in the UK, and Electrochemical Society.

Toshio Shibata: doctorate from Hokkaido University; research interests include the passivity of stainless steel and its breakdown, including pitting, and stress corrosion cracking; professor emeritus in the Department of Materials Science and Processing of Osaka University.

Susan Smialowska: doctorate in chemical engineering at Silesian Technical Institute and University (Poland); research interests include investigation of the kinetics of the mechanism of electroprocesses, pitting corrosion, stress corrosion cracking, corrosion inhibitors, hydrogen embrittlement, aqueous corrosion at high temperatures and passivity; professor emeritus at Ohio State University.

Hans-Henning Strehblow: doctorate in physical chemistry from Free University of Berlin; research interests include electrochemistry, corrosion, surface analyses, and the physical chemistry of surfaces; professor of physical chemistry at Institute for Physikalische Chemie and Elektrochemie at Heinrich-Heine University in Duesseldorf.

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BACKGROUND AND STATEMENTS OF THE TWO QUESTIONS POSED TO PARTICIPANTS IN THE WORKSHOP ON LONG-TERM EXTRAPOLATION OF PASSIVE BEHAVIOR
July 19-20, 2001
Arlington, Virginia

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INTRODUCTION

The extraordinarily long time frame (e.g., 10,000 years) involved in disposing of high-level nuclear waste leads to many questions about the ability of present knowledge in materials science and corrosion to anticipate waste package (WP) behavior in the distant future. The NWTRB formulated two seminal questions as they apply to the proposed repository at Yucca Mountain for discussion by a panel of 14 internationally recognized corrosion scientists.

In the first question, each panelist was asked to propose (if deemed plausible) mechanisms that would cause the corrosion rate under passive conditions to increase as a result of that passive regime having been in place for long time periods. The second question asked for mechanisms that may cause alloy potential or a critical potential, or both, to evolve adversely over long times and result in localized WP corrosion (and, more broadly, whether a potential threshold criterion was adequate at all for long exposure times). Suggestions for experiments to examine the validity of proposed mechanisms were asked for both questions.

The detailed questions and their context — as given to each participant before the Workshop — are presented in this introductory paper. (The context appears first, and the two questions are on pages 8 and 9.) Names and affiliations of the 14 participants are listed on page iv of these "Proceedings." The questions were discussed at a Workshop held in Arlington, Virginia, on July 19-20, 2001. Each participant first presented brief answers to the two questions, after which a general discussion followed. The discussions were recorded and transcribed, and are available in their entirety at the NWTRB web site, www.nwtrb.gov. Following the Workshop, the participants were invited to prepare statements on their views in the form of extended abstracts or brief papers. Most participants replied with submissions, which are collected in these "Proceedings."

Each question contained a brief premise statement, which is amplified and supplemented in the "Background on Corrosion Issues" section. In preparing the answers, the participants were

[1] Dr. Sagüés is a member of the NWTRB. Dr. Di Bella is a member of the NWTRB's technical staff. Statements and opinions indicated in this paper are those of Dr. Sagüés and Dr. Di Bella and do not necessarily represent any position of the NWTRB.

asked to assume the WP configuration and environmental conditions summarized in the "Background on WP Configuration and Environment" section. A complete version of the latter is available at the NWTRB web site, and extensive supplemental material produced by the Yucca Mountain Project (YMP) is available through the YMP web site, www.ymp.gov [1, 2, 3]. Because of the often rapid evolution of knowledge and priorities in this complex endeavor, it is important to emphasize that both background statements reflect the status of the issues concerned only up to the time of the Workshop.

BACKGROUND ON WP CONFIGURATION AND ENVIRONMENT

WP Placement and Configuration

As currently conceptualized by the U.S. Department of Energy (DOE), the repository would consist of an underground area of approximately 500 hectares containing approximately 60 km of 5.5m-diameter, near-horizontal tunnels. All the tunnels would be essentially on the same plane, approximately 1,100 m above sea level. The distance from the tunnels to the surface would be at least 200 m.

The waste would be emplaced horizontally in the tunnels in more than 10,000 sealed cylindrical waste packages approximately 1½-2 m in diameter and 3½-6 m long. The outer shell of each waste package would be 20-mm-thick Alloy 22 (UNS No. N06022; nominal composition: Ni59, Cr20.4, Mo14.1, W3.2, Fe2.3). A 50-mm-thick inner shell of type 316NG stainless steel is included in the design for mechanical strength.

Nuclear waste generates heat by radioactive decay. After emplacement of the waste packages and before closure of the repository, most of the heat would be removed by ventilation with outside air. After the last waste package is emplaced, there would be a period of ventilation lasting at least 25 years and as much as 300 years or more. At the end of the ventilation period, a decision would be made to close the repository, titanium (grade 7) drip shields would be placed over the waste packages, and all penetrations (e.g., ventilation shafts, entrances, exits) from the surface to the repository would be sealed permanently. Backfilling the tunnels before closure is not necessarily included in the design concept considered here.

Waste Package Environment

Yucca Mountain is in a desert environment. The water table is approximately 300 m below the tunnels of the conceptual repository; thus the repository would be located in what is known as the "unsaturated (vadose) zone." The pores in the rock in the unsaturated zone contain water and air, and the relative humidity at the level of the conceptual repository before any tunneling operations take place is higher than 90%. Gas pressure in the vadose zone is essentially atmospheric. The climate at Yucca Mountain has been wetter in the past and is likely to become wetter at some time in the future, but a rise of the water table that would be sufficient to flood the repository is unlikely.

The rocks from the surface down to somewhat below the water table are varieties of tuff, a high-silica rock deposited as a fine ash from volcanic eruptions and then welded together to

varying degrees by heat and the weight of overlying ash. The rock is fractured, and many of the fractures can transmit water. The composition of water from below the water table and water from rock pores at the proposed repository level (the latter based on limited data) is shown in Table 1. The many minor species in these two waters are not shown. Both waters are slightly oxidizing, near neutral, bicarbonate-type waters with low-level concentrations of anions normally considered aggressive. However, the nature of the waters could be changed greatly by evaporative concentration, as shown in Table 1 by the composition of brines formed by evaporating >99% of the mass of synthetic samples of each water at ~80°C in an open system. Of interest from a localized-corrosion standpoint, evaporation of both waters to near dryness seems to result in appreciable enrichment of not only aggressive anions (e.g., Cl^-, F^-) but also of beneficial anions (e.g., NO_3^-).

Table 1. Composition of waters and concentrated brines from synthetic waters.

Major Species	Nominal Composition (mg/L)			
	Water below the water table (based on many samples)	Brine formed by evaporating water from below the water table to near dryness	Water in rock pores at repository level (based on few samples)	Brine formed by evaporating water from rock pores to near dryness
Na^+	45	850	60	500
K^+	5	700	8	500
Ca^{++}	10	1	100	200
Mg^{++}	2	<.1	17	300
SiO_2	60	760	70	60
Cl^-	7	850	120	500
SO_4^{--}	18	850	115	15
HCO_3^-	130	300	220	<3
NO_3^-	9	860	8	500
F^-	2	700	1	100?

During the preclosure, ventilated period, the relative humidity of the air in the emplacement tunnels would be very low and the WP surface temperatures would be somewhat lower than approximately 90ºC. Corrosion occurs under these conditions but at such an infinitesimally slow rate that it is not considered an issue in comparison to aqueous corrosion.

After the preclosure period, representative temperatures at the WP surface would increase with time and later decay. The peak temperature and duration of the high-temperature period depend on design options, such as how close the packages are placed next to each other in the drifts, the horizontal distance between the drifts, and the duration of the preclosure period. For the purposes of the Workshop, the participants were asked to consider a scenario representative of repository operating alternatives in which the surface temperature of a typical WP rises to above the boiling point of pure water (96ºC at the repository elevation) within a few weeks after closure, peaks at approximately 160ºC in a few years, and remains above boiling for 500-1,000 years. Individual packages may deviate significantly from this schedule depending on the nature of the waste and WP location within the repository. In such a scenario, the rock to a depth of

several meters surrounding the tunnels is projected also to experience a heat pulse with above-boiling temperatures for a long time period, with consequent water evaporation and movement through the rock matrix and the fracture network.

From a corrosion perspective, it is important to know whether there is *liquid* water on the WP surface and, if so, the temperature of the water and the chemical species in it. Also important are the solid materials that may be in contact with waste packages, because these solids could influence the composition of the water and could form crevices and local occluded zones. For example, during the preclosure period, dust would be deposited on the waste packages. The composition of the dust is unknown and is a matter being studied by DOE. If the dust contains deliquescent salts and the relative humidity is above the deliquescence point of the dust, deliquescence could cause liquid water to form on the WP at temperatures well above 96ºC. For example, if the dust has a composition similar to the brine that would result by evaporating water from below the water table, then liquid water could form on the waste package at temperatures as high as 120ºC (a temperature corresponding closely to the deliquescence point of sodium nitrate). If the dust has a composition similar to the brine resulting from evaporating water found in rock pores at the repository level, then liquid water could form at temperatures as high as 160ºC (a temperature that may correspond to the deliquescence points of calcium chloride or magnesium chloride).

Besides dust, other solid materials close to the WP would include carbon steel (used to support the walls of the tunnels), hydrated cement (used in grout for rock bolts), stainless steel (used in the pallet that supports the waste package), titanium (used in the drip shield), and tuff. Over time, as degradation of the engineered barrier system progresses, all of these materials are likely to come into contact with some parts of some waste packages for extended periods. A particular concern is very high pH (i.e., 12-13+) deriving from water in the pores of cementitious grouts. Another concern is low-pH, oxidizing environments caused by iron corrosion products. (The buffering nature of and reactivity of carbon dioxide in the air would bring both high and low pH's closer to neutral if there is chemical equilibrium.)

As noted above, titanium drip shields would be placed over the waste packages shortly before closure of the repository. The primary purpose of the drip shields is to deflect water that may drip from the roof of the emplacement tunnels. However, there are at least two reasons that drip shields would not necessarily ensure that liquid water and WP surfaces would not be in contact. One reason is that any deliquescent salts in the dust on WP surfaces could form brines if the relative humidity is higher than the deliquescence point of the salt. The other reason is that very thin layers of liquid water can form on clean metal surfaces in conditions of less than 100% relative humidity if the relative humidity is high enough.

In addition to considering the temperature schedule indicated above, the workshop participants were asked to assume for the postclosure period that (*i*) some parts of the surfaces of some waste packages may be in contact with liquid water at temperatures up to 160ºC and that the composition of the water could range from pure condensate to concentrated brine; (*ii*) contact between liquid water and WP surfaces may be episodic, particularly at temperatures above 96ºC; (*iii*) anions in the water would include those in Table 1 but not necessarily in the same ratios; (*iv*) when temperatures in the tunnels are at or below 96ºC, the composition of the gas phase is

essentially that of atmospheric air with relative humidity in the range of 90-100% and slightly elevated carbon dioxide content; and (*v*) above 96ºC the gas phase is steam mixed with amounts of air that may range from only traces (as may be expected from ideal equilibrium considerations) to a substantial fraction of the total gas content. This range of air content must be considered because the mountain is permeable and buoyant forces due to heating or barometric pressure changes outside the mountain could lead to air or other gases from another part of the mountain flowing to the repository area. In addition, the repository tunnels, although sealed from the surface, would remain more-or-less connected to each other, and differences in temperatures in and between tunnels would cause convective flow in and between tunnels.

BACKGROUND ON CORROSION ISSUES

Desired Corrosion Performance

In the present repository design approach, the corrosion resistance burden in the 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 higher than very low rates would be very detrimental. Research sponsored by DOE has aimed at ascertaining that for periods far 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.[2]

The requirement for a uniform dissolution rate is particularly severe, because it implies that the time-averaged rate of corrosion should not exceed a small fraction of 1 μm/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 the Workshop. Because the thermal pulse takes place early, projecting localized corrosion behavior projection may be challenging over a shorter time frame than the time frame for passive corrosion. The absolute time scale is nevertheless still very large, so the localized corrosion issue is addressed in the second question.

Recent findings of research on both modes of corrosion under conditions relevant to the repository are highlighted below. Examples of corrosion scenarios that may apply to the questions for the participants also are presented. As for the previous Background section,

[2] 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. Although potentially important, SCC issues were not discussed in the Workshop in the interest of focusing on the other agenda issues.

participants were directed to the YMP web site for detailed information and bibliographic sources.

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 μm/y. Gravimetric tests using corrosion-test coupons were started by DOE approximately four years ago in a facility that consists of aerated bathtub-size tanks that are maintained at either 60ºC or 90ºC. 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 μm/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 gravimetric test facility, which is consistent with the expectations from the electrochemical testing findings discussed below under "Localized Corrosion."

Speculative scenarios

Some speculative scenarios, given below, have been proposed by various investigators for consideration as possible ways that passivity might degrade over long time periods under repository environments that over a shorter time frame would have supported instead very low metal-dissolution rates. These items are presented only for illustration. Workshop participants could address any or all of these scenarios if they wished but were under no obligation to consider them. In the following, the assumption is 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 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 have 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 microscopically 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 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 and 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^- concentration in the bulk solution was greatly in excess of that of beneficial anions (e.g., NO_3^-). However, environments with high ratios of Cl^- 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^- 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 months-to-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 also has been expressed about possible localized corrosion of Alloy 22 from elements such as

As, Hg, and Pb, which are present at very low 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) in comparison to the repository time frame. At present, OCP values on the order of ~ -50 to -200 mV (Ag/AgCl/KCl sat.) are considered likely. Efforts are being made to measure the 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 is 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.

QUESTIONS TO WORKSHOP PARTICIPANTS

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 of ~< 0.1 μm/y. Those observations have led to predicting times on the order of >~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., > 10μm).

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 μm/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 under "Background on Corrosion Issues," 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 parts 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?

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