
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
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The success of the Workshop was due to the combined efforts of many people. We would like to recognize and thank them for their contributions:

Dr. Daniel Bullen, for his spirited and knowledgeable facilitation of the entire Workshop.

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

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Mr. Scott Ford, an independent contractor who has carefully and accurately transcribed and recorded Board meetings for more than a decade, for recording and transcribing (and sometimes deciphering) the Workshop so that a faithful public record would be available.

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, Cragolino, 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.

A. A. Sagüés
C. A. W. Di Bella

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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. Cragolino: 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 electrodisolution 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., NO₃⁻).

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 90°C. 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 (96°C at the repository elevation) within a few weeks after closure, peaks at approximately 160°C 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 96°C. 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 120°C (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 160°C (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 160°C 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 96°C; (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 96°C, 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 96°C 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 $\mu\text{m}/\text{y}$ 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 $\sim 0.1 \mu\text{m/y}$. 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 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 $\sim 0.1 \mu\text{m/y}$ (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., NO₃⁻). 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 $\sim < 0.1$ $\mu\text{m}/\text{y}$. 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., $> 10\mu\text{m}$).

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 $\mu\text{m}/\text{y}$? (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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LONG-TERM PASSIVE DISSOLUTION AND LOCALIZED CORROSION OF ALLOY 22

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Long-term passive dissolution

Transition metal oxides of the alloying elements of Alloy 22, such as chromium (III) oxide (the predominant oxide contributing to the passivity of the alloy), are thermodynamically stable with respect to the metal. However, the passive film, few nanometers thick, is an intrinsically dynamic network of metal cations and O^{2-} and OH^- anions, that reaches a steady-state (non-equilibrium) condition in contact with an aqueous electrolyte. Such steady state condition is characterized by a constant value of the corrosion current density. This current density is the combined result of a presumably constant dissolution rate of the passive film in the electrolyte and transport of cations and oxygen vacancies through the film contributing to its ionic and electronic conductivity.

We have measured the passive current density of alloy 22 in fully deaerated chloride-containing solutions at various applied potentials within the passive region (-0.2 to 0.4 V_{SCE}), covering a range of chloride concentrations (0.028 to 4.0 M), temperatures (25 to 95°C), and pHs (0.7 to 8.0), and found that the current density is slightly dependent on potential and such environmental variables (Cragolino et al., 2000; Dunn et al., 2001). However, an apparent passive current density was measured in these potentiostatic tests that lasted for 48 hours because more prolonged tests (15-day duration) show that a truly steady state value, measured with a resolution of 1.25×10^{-10} A/cm², only can be attained after approximately 150 hours (Dunn et al., 2001). In this case, using a mechanically polished specimen of the as-received alloy exposed to a 0.028 M Cl^- solution at 95°C under an applied potential of 0.1 V_{SCE} , a current density close to 1.0×10^{-8} A/cm² was obtained. Invoking Faraday's law and assuming congruent dissolution (i.e. the alloying elements dissolve in proportion to their atomic concentration in the alloy), the above current density corresponds to a corrosion rate close to 0.1 $\mu\text{m}/\text{yr}$. If this corrosion rate is assumed to be constant with time as the dissolution of the container progresses through the wall thickness, then for a 2 cm wall thickness, a container life of more than 100,000 yr can be estimated. Such an extrapolation, that goes far beyond any engineering application of Ni-Cr-Mo alloys or similar ones, ignores other unpredicted processes, which may lead to higher corrosion rates or even to a breakaway kinetics (corrosion rate increasing rapidly with time).

As discussed in my presentation, we have approached this problem by modeling the long-term passive behavior on the basis of the point defect model (Macdonald, 1992). Following the initial formulation of the model (Pensado et al., 2000, Cragolino et al., 2000), a more detailed analysis was conducted recently by Pensado (Brossia et al., 2001), and the main assumptions and results can be summarized as follows: (i) passive dissolution of Alloy 22 is controlled by a protective Cr_2O_3 -rich film; (ii) the conduction through the film is mainly by interstitial cations, or oxygen vacancies or both carriers; (iii) the film contains Cr, Ni, and Mo as interstitial defects, Ni as a substitutional defect, and oxygen and Cr vacancies; and (iv) as a results of constraints in estimated values of rate constants for the elementary reactions associated with the creation of interstitials (Cr, Ni and Mo) and substitutionals (Cr and Ni) at the metal/film interface, it is concluded that charge transport through the film is mainly due to interstitial species and injection of vacancies occurred at the metal/film interface. Assuming that no efficient vacancy sink exists at the oxide

film/metal interface, it is postulated that spalling of the passive film caused by vacancy accumulation at that interface occurs at a certain critical value of the vacancy concentration. A heuristic model is used to calculate container lifetime as a function of the critical vacancy concentration fraction. A typical result included in my presentation reveals that the container life increases monotonically with increasing values of the critical vacancy concentration fraction. It is recognized, however, that not only dislocations in the metal, but also high-angle grain boundaries, pre-existing voids, and suitable regions at the metal-scale interface could act as vacancy sinks. Incorporation of vacancy sinks into the model will yield extended container lifetimes. Nevertheless, the accumulation of vacancies in the alloy/passive film need to be verified experimentally to provide support to this model. Although this phenomenon has been observed in the oxidation of Ni-base alloys in high temperatures (see references in Brossia et al., 2001), it is difficult to design an experiment to reveal the accumulation of vacancies at low temperatures.

One important implication of this model is that if vacancy diffusion coefficient in the alloy is very small ($< 10^{-30} \text{ cm}^2/\text{s}$), alloy dissolution is stoichiometric in the long term. Non-stoichiometric dissolution may be observed in the short term, but the model suggests that a non-stoichiometric process cannot be maintained because it would require rapid solid state transport of the preferentially dissolving component (i.e., Ni). Hence, it is important to conduct sufficiently prolonged experiments in which preferential dissolution of alloying elements can be measured by analyzing the solution composition (e.g. using capillary electrophoresis or other high-sensitivity technique) coupled to high resolution passive current density measurements. If non-congruent dissolution occurs, it could be an indication of fast penetration paths in the corrosion front (i.e., due to enhanced transport along grain boundaries) or morphologic changes of the dissolving surface that would lead to current increases with respect to the steady-state passive current density. In particular, segregated impurities in grain boundaries, either preexistent as a result of annealing heat treatments or segregated as a result of anodic dissolution as discussed by P. Marcus for the case of sulfur in nickel and nickel-base alloys, may be involved in the generation of preferential paths for anodic dissolution and film formation. Another process, suggested by J. Scully et al., is the occurrence of metastable passive film breakdown and repassivation events, that could become more pronounced and frequent with increasing potentials within the passive range. This process may lead to a small but sustained increase in the passive current density with time.

Nevertheless, as noted in my presentation, a critical assessment of other mechanistic models such as the semiconductive oxide model or models based on film breakdown/repair processes is necessary. The approach should be based on the possibility of conducting experimental measurements that test the main hypothesis or assumptions in the model, in particular if it is possible to use high temperature (200 to 350 C) experiments in aqueous systems as accelerated tests for extrapolations to low temperature conditions. This approach, despite its potential advantages, may have limitations that should be evaluated because chemical composition and other properties of the passive film on Alloy 22 could change at temperatures above 150 to 200°C as in the case of austenitic stainless steels. However, this temperature effect may be limited to the outer deposited layer and not to the inner barrier layer which is mainly composed of Cr(III) oxide, as previously discussed (Dunn et al., 2001; Brossia et al., 2001) on the basis of literature data for Ni-Cr, Ni-Cr-Fe, and Ni-Cr-Mo alloys.

On the basis of the information currently available from experiments and modeling, it can be expected that a low, stable passive current density can be maintained for many thousands of years on a well prepared surface of mill-annealed alloy 22. Unless a substantial alteration of the environmental conditions occurs, such as an increase in the redox potential to values promoting transpassivity or a sufficiently high concentration of chloride ions in combination with high redox potentials that could promote crevice corrosion, it appears that an Alloy 22 container fabricated with tight specifications can last many thousands of years. However, several conditions associated with physical metallurgical changes of the alloy occurring during container fabrication and closure (e.g., precipitation of TCP phases along grain boundaries) can alter significantly this conclusion, as discussed during the workshop, and require a more

extended experimental evaluation of their effects.

In addition to a better characterization of the passive films in term of chemical composition, including crystallinity versus amorphous character and the effect of aging, as discussed in the workshop, a better understanding of the kinetics of the cathodic reactions on passive surfaces for the reducible species present in the aqueous environment contacting the waste package (i.e., O_2 , H_2O_2 , Fe^{3+}) is necessary. This understanding is important to define the electrochemical conditions, including surface reactivity effects, that balance the cathodic with the anodic reactions and provide the driving force to sustain passivity in the long term.

Localized Corrosion

During the workshop I presented a schematic plot of the hypothetical evolution of the corrosion potential (E_{corr}) and the repassivation potential (E_{rp}), showing the time span over which pit growth occurs before it can be arrested. In our investigations of Ni-Cr-Mo alloys we have used the criterion that sustained (or stable) localized corrosion only occurs at potentials above E_{rp} (Dunn et al., 2000). I would like to emphasize that crevice corrosion instead of pitting is the predominant form of localized corrosion exhibited by Alloy 22. Using specimens with a well defined geometric crevice, the repassivation potential for crevice corrosion (E_{rcrev}) can be defined and determined experimentally in a similar fashion as E_{rp} (Dunn et al., 2000). It can be inferred, hence, that passivity can be maintained if $E_{corr} < E_{rcrev}$. On the contrary, if $E_{corr} > E_{rcrev}$, either as a result of an increase with time in E_{corr} or a decrease in E_{rcrev} , crevice corrosion will initiate.

We have demonstrated (Dunn et al., 2000) for Alloy 825, a less localized corrosion resistant Ni-Cr-Mo alloy than Alloy 22, that E_{rcrev} is the critical potential that should be used to predict the occurrence of crevice corrosion instead of the initiation potential, commonly defined in the case of pitting corrosion as pitting potential or pit initiation potential (E_p), because E_p does not represent a lower bound for the occurrence of localized corrosion. The same argument is valid for the initiation potential for crevice corrosion (E_{crev}). Both E_{crev} and E_{rcrev} , as well as E_p and E_{rp} can be considered as distributed parameters; however, the distribution is significantly narrower for E_{rcrev} and E_{rp} than for their respective initiation potentials. Limited results have shown also that the width of the distribution increase with decreasing chloride concentration and, in general, with the decrease in the aggressiveness of the environment.

I have listed in Table 1 many environmental and metallurgical variables that can alter both potentials. It is essentially the same table shown in my presentation with some additions which are the result of the workshop discussions. The signs (+) and (-) indicate the expected increase and decrease of E_{corr} or E_{rcrev} with the evolution of the environmental variables as noted, while (0) indicates that no significant variation can be expected. Questions marks (?) are added when there is no experimental evidence of the effect of a given variable. Most of these environmental variables will vary with time and the concentration of the various species listed be will extremely important in determining the tendency toward the occurrence of localized corrosion. Aging of the passive films and formation of an oxy-hydroxide deposit layer are also time-dependent processes affected by the evolution of the aqueous environment in contact with the containers. This aqueous environment can be a thin liquid film formed by condensation of water vapor on a metal surface eventually covered by hygroscopic salts or the result of dripping of groundwater, modified by evaporation and concentration caused by the radioactive decay heat, and flowing through rock fractures towards the emplacement drifts when the rock temperature decreases below boiling isotherm (Brossia et al., 2001).

Table 1. Qualitative description of the expected effect of environmental and metallurgical factors on the corrosion potential and the repassivation potential for Alloy 22 in the aqueous environments in contact with radioactive waste packages

Environment or Metallurgical Factors	E_{corr}	E_{rrev}
T decrease	(+)	(+)
pH increase	(-)	(0)
$[Cl^-]$ increase	(-)	(-)
$[NO_3^-]$ or other inhibitors increase	(0)	(+)
$[HCO_3^-]$ increase	(-)	(0)
$[F^-]$ or other activators increase	(-)?	(-)?
$[S_2O_3^{2-}]$ or other reduced sulfur species (from SRB*) increase	(-)	(-)
Minor environment impurities (i.e., Pb, Hg, As)	(0)?	(-)?
E_h^\dagger (from air and radiolytic species) decrease	(-)	(0)
Aging of passive film	(+)	(0)
Outer oxy-hydroxide deposit layer with accumulation of dust, impurities, and salts from environment	(+)?	(-)
Precipitation of intermetallic phases at g.b. [‡]	(0)	(-)
Depletion of alloying elements in welds	(0)	(-)
Segregation of impurities at g.b.	(0)	(-)

*SRB—sulfate reducing bacteria; [†] E_h —redox potential; [‡]g.b.—grain boundaries

It is expected that metallurgical factors, such as precipitation of TCP phases or segregation of impurities, are not going to change with time after waste package emplacement because, according to the current design, the operating temperatures in the repository are not sufficiently high to accelerate diffusion controlled processes responsible of segregation or precipitation. However, fabrication or closure processes such as welding and post-welding treatments may have a significant effect, promoting the precipitation of intermetallic phases, depletion of alloying elements, and segregation of impurities that may have a detrimental effect when aggressive environmental conditions develop. The anticipated effects of these physical metallurgical processes on E_{rrev} are indicated in the table. It should be emphasized, however, that there is no detailed study available for Alloy 22 in which a specific process (i.e., segregation of sulfur to grain boundaries) has been related directly to an effect on E_{rrev} . Nevertheless, it is well established (Brossia et al., 2001) that short (few minutes) thermal treatments at about 870°C promote a significant decrease in E_{rrev} for Alloy 22 even in relatively dilute chloride solutions at 95°C. This decrease in E_{rrev} is accompanied by intergranular corrosion in the creviced area. Although the resulting microstructural and microchemical modifications along grain boundaries have not been investigated, the decrease in E_{rrev} is presumably related to grain boundary precipitation of μ and P phases.

As a result of the metallurgical process discussed above, intergranular corrosion of Alloy 22 may occur in certain aggressive aqueous environments at potentials within the passive range. In response to one of the

questions, it can be said that intergranular corrosion may not be amenable of a description in terms of a critical potential as is the case for localized corrosion. The evaluation of plausible environments that may promote this form of attack for thermally treated Alloy 22 is important because intergranular corrosion may be a precursor to stress corrosion cracking.

Assuming that these detrimental physical metallurgical processes can be controlled or mitigated, the main concern is the evolution of the aqueous environment in contact with the waste packages to a regime in which localized corrosion may occur. I believe that the chemical composition of the aqueous environments derived from the groundwater percolating through rock fractures or evaporated from pore water in the unsaturated zone can be properly bound by using an adequate combination of modeling and experiments. The effect of the waste package as a heat transfer surface promoting evaporative concentration of solutions cannot be neglected. This is being considered in experiments conducted by Greg Gdowski at LLNL that require additional modeling to increase our understanding of complex salt precipitation and ion complexation processes that may sequester or not detrimental anionic species such as fluoride. It should be noted that fluoride increases significantly the rate of uniform dissolution of Ti-0.15Pd (Brossia et al, 2001), but in conjunction with chloride it may also affect the localized corrosion of Alloy 22, as noted in the workshop discussions. On the other hand, nitrate can mitigate localized corrosion, provided the nitrate/chloride ratio is sufficiently high. However, the conjoint action of nitrate and chloride on localized corrosion is not clear and needs to be better established through experiments and modeling. By measuring the E_{rrev} of Alloy 22 in these environments, potential-temperature-anion concentration regions of localized corrosion susceptibility can be mapped. A combination of modeling and experiments designed to evaluate the evolution of E_{corr} in the same environments will be necessary to define with sufficient margin of certainty that the electrochemical conditions required for the occurrence of localized corrosion cannot be attained under radioactive waste disposal conditions.

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LONG TERM PASSIVITY AND LOCALIZED CORROSION OF ALLOY 22

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INTRODUCTION

The selection of Alloy 22 for the outer shell of waste packages for the Yucca Mountain repository is based on its extremely high resistance to both general and localized corrosion. Assessment of the risk of “failure” by corrosion during the long storage life required in the repository requires examination of the following issues:

1. What are the criteria for “failure”?
2. What are the “worst” conditions likely to be experienced by the packages?
3. How might packages fail by general corrosion?
4. How might the packages fail by localized corrosion, with particular reference to metallurgical factors in the alloy?
5. What factors might increase the cathodic reaction and thus the open circuit potential sufficiently to drive general or localized anodic attack?

Each of these questions will be examined in turn, and the implication for future work will be discussed.

CRITERIA FOR “FAILURE”

The approach to assessment of the risk of corrosion failure of waste packages depends critically on the criteria for failure. During the Workshop, it was established “failure” involves corrosion penetration of a significant number of the >10,000 packages rather than one or two. This suggests that extreme and unusual events can be neglected: an example of such an effect might be a highly localized heterogeneity in the rock that leads to the presence of very damaging solution species over one package but no others. Another might be the presence of an unusually large defect in the alloy or in one of the welds. The following discussion will therefore consider “typical” behavior that might affect a significant fraction of the packages.

The risk of catastrophic failure by stress corrosion cracking (SCC) is being assessed by another workshop, so will not be assessed here. However, it should be noted that the

forms of localized attack discussed below might act to form stress-raisers and/or hydrogen penetration into the metal that could contribute to SCC.

The rate of corrosion attack will always be greater in a wet environment than in a dry one at the temperature levels expected in the repository. The following discussion will therefore assume that the titanium drip-shield has failed, and that water will drip onto the containers

REPOSITORY CONDITIONS

One of the more significant debates to emerge from the Workshop concerns the degree to which the likely range of environmental conditions in the repository can be predicted. As the failure criteria involve a number of packages, then it is reasonable to consider “typical” solution compositions in the repository. These are given in the background information supplied for the Workshop and in documents on the web site <http://www.ymp.gov/>. Confidence in the prediction of long-term corrosion behavior will be enhanced by an improved understanding of the range of water chemistries likely to be encountered in different regions of the repository.

The water found in the repository itself is far too dilute to cause corrosion of Alloy 22. However, the heat generated by the packages themselves can cause significant concentration of the water. Even so, simple concentration of the solutions is unlikely to lead to localized attack as the concentration of less aggressive species is comparable with or greater than that of chloride ions. In order to sustain a localized corrosion site such as a pit or crevice, the concentration of chloride ions must be significantly greater than that of species such as nitrate, sulfate and carbonate.

The conditions that are most likely to lead to failure of passivity and localized attack are those where a saturated salt solution, for example magnesium chloride just below its boiling point, is formed on a hot waste package. It is possible that as water trickles down the surface of a hot canister, then different salts might crystallize out at different times and locations, leaving a damaging hot solution on the package surface. In this way, the ratio of anions in the remaining concentrated solution might be different from that in the starting water. This possibility should be investigated experimentally.

GENERAL CORROSION

The rate of general corrosion of Alloy 22 is controlled by the rate of dissolution of the passive film. At steady state, the passive film lost as a result of dissolution will be replaced by film thickening under the influence of the electric field across the metal/solution interphase. Data presented by Cragolino at the Workshop indicated that the rate is equivalent to $\sim 0.1 \mu\text{m}/\text{year}$, suggesting a lifetime of 100,000 years for continuous immersion.

Few factors are likely to increase the rate of general (as opposed to localized) corrosion of the alloy. One possible route is the transpassive dissolution of molybdenum. This is likely to occur only under alkaline conditions when the open circuit potential of the alloy

is significantly elevated. The formation of suitable alkaline conditions is possible but unlikely. Factors that might increase the open circuit potential of the alloy will be considered below.

LOCALIZED CORROSION

It was pointed out at the Workshop that metastable pitting of Alloy 22 can occur under some conditions. Metastable pits are highly unlikely to grow into stable pits on an exposed surface under the probable conditions of solution and potential. Furthermore, the rate of metastable pitting should decrease dramatically with time as susceptible sites are exhausted. Therefore metastable pits themselves are unlikely to contribute to significantly to penetration of the alloy. However, underneath surface deposits, for example corrosion products or scale from the external environment, it is possible that metastable pits may be able to grow into stable pits. This may be facilitated if the deposits show any ion selective behavior, for example favoring accumulation of chloride ions adjacent to a corrosion site.

The development of localized corrosion is more likely at crevices in the structure. However, this is only likely to take place at elevated potentials (see below). The stability of corrosion within crevices depends upon the maintenance of a critical solution chemistry adjacent to the dissolving interface. This is an issue where modeling of the evolution of solution chemistry is likely to be a valuable tool for assessing the risk of crevice propagation.

Localized attack is most likely to take place at a metallurgical heterogeneity. This highlights the importance of quality assurance of both the alloy itself, and also the welding process and post-weld heat treatment. If it is assumed that quality assurance is tightly controlled, there are two long-term problems that might occur. One is in the formation of intermetallic phases, leading to regions in the alloy that are depleted in chromium and/or molybdenum. The other is segregation of elements such as sulfur or phosphorus to grain boundaries. Sulfur can be particularly damaging: it is known that dissolution of nickel can be catalyzed by a monolayer of sulfur. If relatively small amounts of sulfur can segregate to grain boundaries, then it is possible that it could accumulate during long periods of passive dissolution or metastable pitting, leading to catalyzed intergranular attack.

In order to assess whether precipitation of intermetallic species and grain boundary segregation are possible, it is necessary to obtain full details of the thermodynamic and kinetic parameters associated with these processes. Such reactions can in principle be enhanced by radiation damage, but it has been suggested that the nature of the radiation involved is likely to be insufficient to cause damage that would significantly increase the rate of diffusion to boundaries.

CATHODIC KINETICS

Both passive dissolution and localized attack depend critically on the open circuit potential. Factors that could increase this include the presence of peroxide as a result of

radiolysis of water, enhanced oxygen transport through very thin layers of solution, the catalytic effect of deposits from the environment, and the catalytic effects of microbially active layers. Discussions at the Workshop tended to suggest that most of these factors should not enhance the open circuit potential sufficiently to cause problems, but this should be confirmed

SUMMARY

Alloy 22 is a highly corrosion-resistant alloy that is unlikely to corrode under the likely repository conditions. Factors that could pose problems include

- formation of unusually corrosive solutions as a result of selective crystallization of water running down a hot package
- transpassive dissolution of Mo from the alloy
- localized attack at metallurgical heterogeneities
- formation of ion-selective membranes promoting pit stability
- enhanced cathodic reactivity as a result of factors such as radiolysis or the deposition of catalytically active layers

Such phenomena can be investigated experimentally and combined with long-term models.

POSSIBLE PROCESSES AND MECHANISMS THAT COULD LEAD TO UNIFORM OR LOCALIZED CORROSION OF CANISTER ALLOYS OVER VERY LONG TIMES

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ABSTRACT

Two possible processes that may lead to an increase in the corrosion rate of alloy C-22 over very long times are: (a) a change in the open circuit potential to values above the transpassive potential which would result in the dissolution of the Cr and Mo in the passive film; and (b) a change to a less protective passive layer because of gaseous oxidation in the air and/or steam atmospheres that can exist at the elevated temperatures in the repository environment. A mechanism that can lead to localized corrosion at potentials below the critical potential over long times is the metastable pitting that occurs below this potential.

INTRODUCTION

Changes can arise in the repository environment over the very long times that the canister alloy C-22 must resist penetration by corrosion at temperatures that reach values as high as 160C. Possible alterations in the environment could include the radiolysis of water, the introduction of various impurities, changes in the composition of the alloy surface by diffusion of alloy components, wet-dry cycles, as well as others anticipated and not anticipated. This discussion will cover a few of the possible processes and mechanisms that may lead to uniform passive corrosion, localized corrosion or both in the repository over very long times.

PROCESSES LEADING TO UNIFORM PASSIVE CORROSION

Two possible processes will be discussed: (a) a change in the open circuit potential to values above the transpassive potential resulting in the dissolution of the Cr and Mo in the passive film and (b) the change to a less protective passive layer because of gaseous oxidation in the air and/or steam atmospheres that can exist at the temperatures in the repository environment.

Open Circuit Potential Moves above Transpassive Potential

Thermodynamics predicts that if potentials become transpassive, the film's Mo and Cr dissolve—leading to an unprotective film. As the Pourbaix diagrams for the major components of alloy C-22, Ni,

Cr, and Mo, at 25C show, this process is promoted as the pH increases. This could be a possibility at the higher temperatures expected in the repository.

What can bring the open circuit potential above the potentials where the Cr and Mo in the passive film will be oxidized and become the possible soluble species for Cr, $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , or CrO_4^{2-} , and for Mo, HMoO_4^- , or MoO_4^{2-} ? One possibility is the production of H_2O_2 by radiolysis. The thermodynamic expression given in the Pourbaix Atlas for the oxygen diagram (1) for the reaction, $\text{H}_2\text{O}_2 = \text{O}_2 + \text{H}_2 + 2 e^-$, is

$$E_0 = 0.682 - 0.0591 \text{ pH} + 0.0295 \log p\text{O}_2/(\text{H}_2\text{O}_2). \quad [1]$$

Using Equation [1], Table I gives the concentration of H_2O_2 at 25C in equilibrium with a partial pressure of oxygen of 1 at the potentials and pH's where the Cr and Mo in the passive film are oxidized and become soluble species.

Table I The Concentration of H_2O_2 at 25C in Equilibrium with a Partial Pressure of Oxygen of 1 at the Potentials and pH's where the Cr and Mo in the Passive Film Dissolve.

Alloy Component	pH	Oxidation Potential, V(SHE)	Relatively Predominant Soluble Species	H_2O_2 concentration at $p\text{O}_2 = 1$
Cr	9	0.3	CrO_4^{2-}	10^5
	7	0.45	CrO_4^{2-}	10^6
	5	0.7	$\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^-	$10^{10.6}$
Mo	9	-0.5	MoO_4^{2-}	$10^{-0.65}$
	7	-0.1	MoO_4^{2-}	$10^{-12.5}$
	5	0	HMoO_4^-	10^{-13}

It can be seen from the calculations given in Table I that at 25C the concentrations of H_2O_2 that must be produced by radiolysis are much too large to dissolve the Cr in the passive layer. On the other hand, the H_2O_2 concentrations at the potentials and pH's at which the production of soluble species of Mo are possible are at the low levels that may result from radiolysis. Over long times at the repository temperatures these low levels of H_2O_2 that could result from radiolysis could raise the open circuit potential to a value where Mo would dissolve and thereby result in an increase in passive corrosion.

Change in the Passive Layer by Gaseous Oxidation

Over long times at temperatures as high as 160C the repository environment could experience wet-dry cycles. Under these conditions the passive layer, originally formed in an aqueous solution, is exposed to a dry gaseous (steam and/or air) environment. This exposure of the passive film could lead to a number of changes as a result of the oxidation mechanisms that occur in gaseous environments—especially over the long times, even at the temperatures that are lower than those usually investigated in gaseous oxidation studies. The changes that could be foreseen would be: (a) an increase in film thickness, (b) diffusion of species from the alloy, (c) diffusion of vacancies and impurities (such as sulfur) from microstructural

features, and (d) precipitation of new phases in the film and (e) modification of the film's structure by, for example, recrystallization.

This alteration in the passive layer, probably requiring very long times of exposure to gaseous oxidation, may result in the formation of a passive film that is unable to prevent passive corrosion when wet conditions exist in the repository.

MECHANISMS LEADING TO LOCALIZED CORROSION

Two mechanisms will be proposed that can lead over long times of exposure to forms of localized attack at open circuit potentials below the critical localized potentials or when the gap between the open circuit potential and the critical localized potential vanishes. They are: (a) small rapid breakdown-repair events below the critical localized potential, and (b) the change in the protective ability of the passive layer and the alteration of the alloy surface by exposure to wet (aggressive anion solutions)-dry (air-steam) cycles at repository temperatures.

Metastable Pitting

Small current fluctuations that have been observed in systems that exhibit pitting have been attributed to initiation-repassivation events. These fluctuations which have been termed metastable pitting can take place below the critical potential for pitting (E_{crit}). Metastable pitting is considered by some of workers (2,3) to be the kinetic precursor to stable pit growth.

Fig. 1 shows that the frequency of these rapid initiation-repassivation events are orders of magnitude lower below E_{crit} than they are above (4). Therefore at potentials below E_{crit} very long times are required before any mechanism leading to stable pitting can be operative. Burstein et al. (2) have proposed one mechanism that describes the events of metastable pitting that lead to stable pit growth as follows:

(a) anion (e.g. Cl^-) movement through the passive film at local sites under an electric field; (b) formation of metal chloride at discrete sites at the passive film-alloy interface; (c) initiation upon rupture of the film at metal-chloride sites; and (d) pit growth at exposed sites sustained when Cl^- ions under diffusion control can prevent repassivation. Impurities such as sulfur from the environment can over time also play a role in this mechanism by entering the passive film before repassivation takes place.

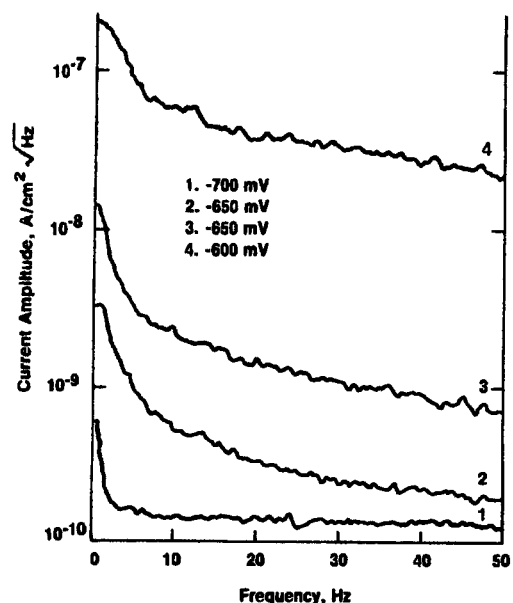


Fig. 1. Noise current spectra of 6061 Al in borate-buffer +0.01 NaCl. Potentials are vs. SCE. The -700mV spectrum is below E_{crit} . The -650mV is taken after 10 min. From Bertocci and Kruger (4).

The mechanism for crevice corrosion may also be associated with metastable initiation-repassivation events because the induction time for the initiation of stable crevice corrosion should decrease as the frequency of these events increases (3,5).

As discussed in the section on uniform corrosion, the passive layer can be modified by exposure to gaseous environments over the very long times and temperatures in the repository. Such exposure can lead to the changes in the passive layer (listed in detail above) such as the introduction of impurities, especially S, defects, and new phases as a result of gaseous oxidation mechanisms. Such a process may then result in the formation of a non-protective layer.

Effect of Alternating Wet-Dry Cycles

When the passive film modified during a repository dry cycle is then exposed to a change in conditions during a wet cycle to aqueous solutions that contain aggressive anions, e.g., chloride-ions, localized corrosion can occur if the altered passive film has an open circuit potential below E_{crit} . This becomes a possible localized corrosion mechanism whereby the passive film is altered by exposure to a gaseous environment—air and/or steam—resulting in the disappearance of the gap between the open circuit potential and the critical localized potential in an aqueous environment.

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The Deterministic Prediction of General Corrosion Damage in HLNW Canisters

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Introduction

Because of the extraordinarily long service life (up to 10,000 years), assurance that the proposed disposal technologies will effectively isolate high level nuclear waste (HLNW) from the biosphere requires the development of methods for predicting the rate of degradation and the accumulation of corrosion damage to the waste containers over times into the future that are twice that over which recorded human history is in the past. These times are such that they exceed the total time of the longest, controlled experiment in which corrosion rates have been measured experimentally by a factor of about 1000. Accordingly, empirical methods and models are incapable of providing the accuracy and confidence of prediction to assure container integrity over the design life. In particular, empirical models, which are best expressed in statistical form (e.g., in the form of extreme value statistics), require a large database of “identical systems”, whose relationships are governed by some underlying distribution function (e.g., Poisson’s distribution). However, in the case of HLNW isolation, no such systems or associated databases exist, so that the application of empirical statistical methods for predicting damage is moot.

The alternative strategy is determinism, which is the philosophy that future events can be predicted on the basis of the natural laws that are invariant in space and time. These models require that the path over which the system evolves into the future be specified in sufficient detail to provide a prediction of the desired accuracy. Furthermore, the process(es) by which degradation occurs must be described in terms of physically realistic mechanisms, the quality of which ultimately governs the accuracy and veracity of the prediction. Nevertheless, the deterministic prediction of corrosion damage is now well established and has been applied in the prediction of both general and localized corrosion damage in a variety of systems, including condensing heat exchangers¹ and water-cooled nuclear reactors². Deterministic methods are also being used to predict the evolution of localized corrosion damage to HLNW containers within the simulated Yucca Mountain repository [DOE NERI project at SRI International, to which the author acts as a consultant].

All deterministic models comprise “constitutive” equations, which describe relationships between components and parameters in the mechanisms, and “constraints” that constrain the solution to that which satisfies the relevant natural law(s). Because corrosion is an electrochemical process, the relevant natural laws are the conservation of charge, the conservation of (equivalent) mass, and Faraday’s law, which specifies the

equivalence of mass and charge (96,487 C/equivalent). In light of the fact that the natural laws are the summation of previous scientific experience, much of which is not directly related to the mechanism of interest, deterministic models are broadly based and are extraordinarily resilient. Most importantly, they require little “calibration” and then only to derive values for poorly known model parameters, if these parameters cannot be determined by independent experiment.

This report describes the development of two deterministic, general corrosion models for predicting corrosion potential and mass loss for HLNW containers in a simulated Yucca Mountain repository. The first model, the General Corrosion Model (GCM), is based on two models that have been developed previously by the author; the mixed potential model (MPM)³ for predicting the electrochemical corrosion potential (ECP) and the Point Defect Model⁴, which describes the growth and breakdown of the passive film that exists on the alloy surface and which can be used to predict the corrosion current density (i_{corr}). Because both the MPM and the PDM are deterministic, as defined above, the resulting general corrosion model is also deterministic. The second model, the Accumulated Damage Model (ADM), employs the GCM to calculate the corrosion rate at closely spaced state points along the corrosion evolutionary path (CEP), which is defined by the temperature of the repository over a million year period, as calculated by the Lawrence Livermore National Laboratory and as provided to the author by Dr. Joon Lee of Sandia National Laboratory. The ADM then integrates the temperature dependent corrosion rate to yield the loss in canister wall thickness as a function of time. For example, the model predicts that the loss in wall thickness will be about 1.65 mm after 10,000 years and a little less than 9-cm after one million years. These predictions are considered to be eminently reasonable, considering the paucity of information of the repository chemical conditions.

The General Corrosion Model (GCM)

As noted above, the General Corrosion Model (GCM) is based upon two previously developed constituent models, the Mixed Potential Model (MPM)³ and the Point Defect Model (PDM)⁴. Both models are highly developed and have been used extensively to predict corrosion phenomena in a wide variety of systems. Accordingly, a brief description of each of the models is given below in order to acquaint the reader with the fundamental principles upon which the codes are based.

Mixed Potential Model

The MPM³ is based on the physical condition that charge conservation must be obeyed in the system. Because electrochemical reactions transfer charge across a metal/solution interface at rates measured by the partial currents, the following equation expresses the charge conservation constraint

$$\sum_{j=1}^n i_{R/O,j}(E) + i_{corr}(E) = 0 \quad (1)$$

where $i_{R/O,j}$ is the partial current density due to the j-th redox couple in the system and i_{corr} is the metal oxidation (corrosion) current density. These partial currents depend on the potential drop across the metal/solution interface.

The current density ($i_{R/O}$) for a redox couple (e.g., O_2/H_2O , H^+/H_2)



(where R is the reduced species and O is the oxidized species) can be expressed in terms of a generalized Butler-Volmer equation as

$$i_{R/O} = \frac{e^{(E-E_{R/O}^e)/b_a} - e^{-(E-E_{R/O}^e)/b_c}}{\frac{1}{i_{0,R/O}} + \frac{1}{i_{i,f}} e^{(E-E_{R/O}^e)/b_a} - \frac{1}{i_{i,r}} e^{-(E-E_{R/O}^e)/b_c}} \quad (3)$$

where $i_{0,R/O}$ is the exchange current density, $i_{i,f}$ and $i_{i,r}$ are the mass-transfer limited currents for the forward and reverse directions of the redox reaction, respectively, and b_a and b_c are the inverse anodic and cathodic Tafel constants. $E_{R/O}^e$ is the equilibrium potential for this reaction as computed from the Nernst equation:

$$E_{O/R}^e = E_{O/R}^0 - \frac{2.303RT}{nF} \log\left(\frac{a_R}{a_O}\right) \quad (4)$$

where a_R and a_O are the thermodynamic activities of R and O, respectively, and $E_{O/R}^0$ is the standard potential. In the present model, general corrosion is considered to occur under a thin liquid electrolyte film on the canister surface. In the present analysis, the film is assumed to be saturated in NaCl, although the algorithm allows any concentration of this electrolyte to be specified. Assuming that the film is sufficiently thin that the film thickness is equal to the ideal Nernst diffusion layer thickness, the limiting currents are calculated using the equation:

$$i_i = \pm nFD C_{O/R}^b / d \quad (5)$$

where the sign depends on whether the reaction is in the forward (+) or reverse (-) direction, F is Faraday's constant, D is the diffusivity of the redox species, $C_{O/R}^b$ is the bulk concentration of O or R , as appropriate, and d is the electrolyte film thickness. The concentration $C_{O/R}^b$ is calculated using Henry's Law with appropriate corrections being made for salting in/salting out (Sechenov's equation).

The corrosion potential is calculated by solving Equation (1) for E , but it is first necessary to specify the form of the alloy oxidation current, $i_{corr}(E)$. This is done by using the Point Defect Model, as described below.

The Point Defect Model

The Point Defect Model was developed by the author to provide a mechanism-based description of the growth and breakdown of the passive oxide films that form on metal surfaces when in contact with oxidizing environments⁴. A full discussion of the model is beyond the scope of the present paper, and the reader is referred to the above citation for detailed accounts of the model and its applications. It is sufficient to point out here that the PDM is based upon a number of postulates and assumptions, some of which are given below:

1. The passive film is a bilayer structure, comprising a highly defective barrier layer that forms from the metal and an outer layer that forms by the hydrolysis of cations ejected from the barrier layer, or of cations produced by the barrier layer itself, and the subsequent precipitation of an oxide, oxyhydroxide, or hydroxide. The outer layer has a low, inherent defect concentration and, generally, contains species that are co-precipitated from the solution.
2. The defects contained within the barrier (inner) layer include cation vacancies (V_M^{\prime}), cation interstitials ($M_i^{\prime+}$), and oxygen vacancies ($V_O^{\bullet\bullet}$). These point defects are generated and annihilated at the metal/barrier layer (m/bl) and barrier layer/solution (bl/s) interfaces in a series of elementary reactions as summarized in Figure 1.
3. The electric field strength within the barrier layer is assumed to be constant and independent of the applied voltage and film thickness. This is so, because the electric field strength is buffered by Esaki tunneling⁴.
4. In the steady state, the rate of growth of the barrier layer into the metal at the metal/film interface is balanced by the dissolution of the film at the film/solution interface; these processes being lattice non-conservative. All other elementary interfacial reactions that generate and annihilate point defects are lattice conservative.
5. Except for some notable cases (e.g., the valve metals), the barrier layer is responsible for the phenomenon of passivity. In the case of the valve metals, and possibly even for some transition metals (e.g., Fe), the outer layer may contribute significantly to the total interfacial impedance and hence may control the rate of charge transfer.
6. A single metal oxidation state exists within the barrier layer. Clearly, this assumption is too restrictive to accommodate all systems, including iron where the barrier layer comprises magnetite containing both Fe(II) and Fe(III) species. A more general model that recognizes the presence of multiple oxidation states in the barrier layer is now under development.

By applying the appropriate mass and charge conservation constraints, it is possible to express the steady state current density due the generation and annihilation of the point defects at the m/bl and bl/s interfaces in the form

$$i_{corr} = \delta F \left[k_2^o e^{a_2 V} e^{b_2 L_{ss}} e^{c_2 pH} + k_4^o e^{a_4 V} e^{c_4 pH} + k_7^o e^{a_7 V} e^{c_7 pH} (C_{H^+} / C_{H^+}^o)^n \right] \quad (6)$$

where $a_2 = \alpha_2(1 - \alpha)\chi\gamma$, $b_2 = -\alpha_2\chi\varepsilon\gamma$, $c_2 = -\alpha_2\chi\beta\gamma$, $a_4 = \alpha_4\alpha\delta\gamma$, $c_4 = \alpha_4\beta\delta\gamma$, $a_7 = \alpha_7\alpha(\delta - \chi)\gamma$, and $c_7 = \alpha_7\beta(\delta - \chi)\gamma$. The parameters in the model are as follows: α is the polarizability of the bl/s interface, β is the dependence of the potential drop across the bl/s interface on pH, α_i is the transfer coefficient for the i -th reaction in Figure 1, χ is the barrier layer oxide stoichiometry ($MO_{\chi/2}$), δ is the oxidation state of the metal species in the solution, and $\gamma = F/RT$. The three terms in the parentheses on the right side of Equation (6) arise from the generation/annihilation of cation interstitials, cation vacancies, and oxygen vacancies (film dissolution), respectively. In general, it is expected that one defect will dominate the defect structure of the barrier layer, so that one term in the parentheses on the right side of Equation (6) is expected to be dominant. The physics governing the identity of the dominant defect has been discussed in some depth elsewhere⁴, so that only a brief account will be given here.

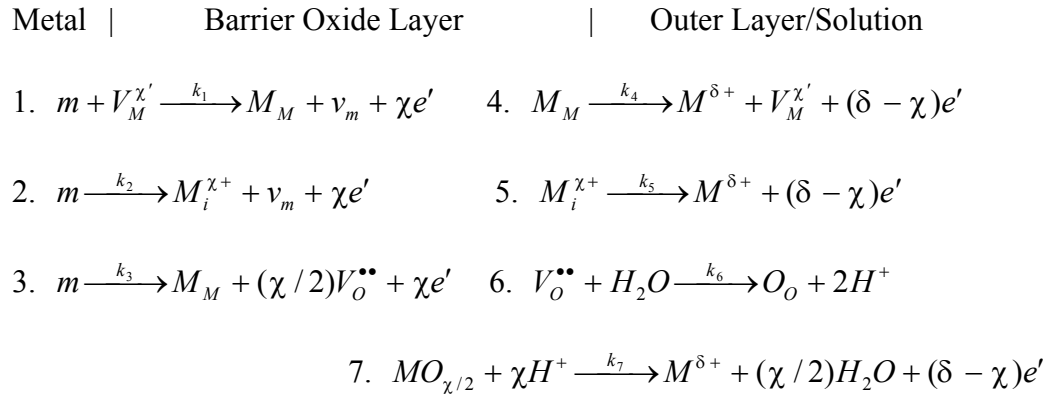


Figure 1. Elementary interfacial reactions that are postulated in the PDM to generate or annihilate point defects in the barrier layer of a passive film.

Briefly, the identity of the principal defect is determined by the relative energies of formation of the defects themselves in the barrier layer. For a barrier layer with a high cation oxidation state (e.g., WO_3 on W) the energies of formation of cation vacancies and cation interstitials are much greater than the energy of formation of an oxygen vacancy, so that the passive film on tungsten (for example) is an oxygen vacancy conductor and the third term on the right side of Equation (6) dominates the current. On the other hand, for systems with low cation oxidation states, such as Ni and Zn, the energies of formation of cation vacancies and cation interstitials are lower than the energy of formation of the oxygen vacancy. Accordingly, the barrier layers on these metals are expected to be cation vacancy or cation interstitial conductors. Experimentally, it is found that the barrier layer on Ni is a cation conductor, while that on zinc is consistent with the dominant defect being a zinc interstitial⁴. The passive film on Alloy C-22 is presumably defective Cr_2O_3 , which occupies a position that is between the two extremes outlined above. Accordingly, it is not possible to predict, *a priori*, the dominant defect in the barrier layer. However, electrochemical studies suggest that the passive current is independent of voltage, which is consistent with the dominant defect being a cation

interstitial or an oxygen vacancy. While this issue must be resolved by experiment, we will assume that the dominant defect is the cation interstitial, so that the first term on the right side of Equation (6) is postulated to dominate the current (see later).

Likewise, the steady state thickness of the barrier layer is easily expressed in terms of the same parameters as

$$L_{ss} = \frac{1}{\varepsilon} \left[1 - \alpha - \frac{\alpha\alpha_7}{\alpha_3} \left(\frac{\delta}{\chi} - 1 \right) \right] V + \frac{1}{\varepsilon} \left[\frac{2.303n}{\alpha\chi\gamma_3} - \beta - \frac{\alpha_7\beta(\delta - \chi)}{\alpha_3\chi} \right] pH + \frac{1}{\alpha_3\chi K} \ln \left(\frac{k_3^o}{k_7^o} \right) \quad (7)$$

where k_i^o is the standard rate constant for the i^{th} reaction and $K = \varepsilon\gamma$. It has been previously postulated (and shown experimentally)⁴ that the voltage of zero thickness of the barrier layer may be equated with the equilibrium potential for the formation of the barrier layer phase E_{bl}^e . This postulate results in a somewhat simpler form of the steady state thickness expression as

$$L_{ss} = \frac{1}{\varepsilon} \left[1 - \alpha - \frac{\alpha\alpha_7}{\alpha_3} \left(\frac{\delta}{\chi} - 1 \right) \right] (V - E_{bl}^e) \quad (8)$$

For the particular case of $\chi = \delta$, this expression reduces further to read

$$L_{ss} = [1 - \alpha] (V - E_{bl}^e) / \varepsilon \quad (9)$$

Note that the pH dependencies in Equations (8) and (9) are contained within the term E_{bl}^e .

The PDM recognizes that the anodic partial current must go to zero at sufficiently negative voltages. This is because the minimum voltage at which the oxidation of chromium to form the barrier layer can occur is given by the equilibrium voltage for the Cr/Cr₂O₃ reaction, E_{bl}^e . In order to describe the variation of the current with potential within the neighborhood of E_{bl}^e , it is assumed that the current density can be described by a Tafel relationship of the form

$$I_{act} = I_{act}^o \exp[1.5\gamma (E - E_{bl}^e)] \quad (10)$$

where the value for the pre-exponential factor ($I_{act}^o = 10^{-12} \text{ A/cm}^2$) has been chosen arbitrarily (the choice does not impact the final result). The total metal oxidation current is then given by

$$I/I_{ss,total} = I/I_{ss} + I/I_{act} \quad (11)$$

Note that for potentials slightly larger than E_{bl}^e , the current is dominated by the passive current.

The GCM developed in this study essentially modifies the MPM that enjoyed great success in the modeling of corrosion processes in BWR primary coolant circuits, by introducing the PDM to calculate the partial anodic current density and by modifying the Butler-Volmer equation for the redox reactions to recognize that the corrosion processes occur on the surface under a thin electrolyte film. Thus, the partial anodic current is calculated using Equation (6), which together with the Butler-Volmer expressions for the two cathodic reactions of interest



and



are substituted into Equation (1) and the resulting expression is solved for the potential, E , corresponding to the electrochemical corrosion potential (ECP).

As noted above, the GCM (general corrosion) model differs in a number of important respects from the earlier MPM³ that was used to model the electrochemical properties of nuclear reactors. The most important of these differences are as follows:

- The GCM incorporates the Point Defect Model⁴ to describe the anodic processes occurring at the metal surface using Equations (6) and (7). In the present version of the model, we assume that the barrier layer is a cation interstitial conductor, but other conduction mechanisms are readily assumed by changing parameter values. Recent work by Bojinov, et al.⁵, using a modification of the PDM, suggests that the barrier layer on Fe-Cr-Mo alloys is an oxygen vacancy conductor, but it should be noted that it is not possible to distinguish between cation interstitials and oxygen vacancies on the basis of current/voltage data. The assignment of the cation interstitial, rather than the oxygen vacancy, as the dominant defect is made on the bases that: (1) Oxygen vacancies are normally dominant in systems of high cation oxidation state ($\chi \geq 4$); and (2) the corrosion rate may not be controlled by the barrier layer dissolution rate (although the dissolution rate imposes a lower limit). However, it is not known whether this conclusion also applies to Alloy C-22, which is a nickel-base alloy. Finally, in applying the PDM to the MPM, it is assumed that the temperature dependencies of the standard rate constants in the model can be described by Arrhenius factors of the type $\exp[-E_a(1/T-1/T_0)/R]$, where E_a is the activation energy, T is the Kelvin temperature, and $T_0 = 298.15$ K.
- The GCM considers corrosion beneath a thin liquid film that forms on the surface through boiling and evaporation. The thin electrolyte film is considered to contain a single electrolyte, which for the present purposes is assumed to be NaCl, plus the requisite H^+ and counter anion as determined from the pH. The NaCl concentration in the electrolyte film may be specified in the input, or the saturated condition for the temperature of interest may be specified. The solubility of oxygen and the mean molal activity coefficient of a univalent ion are calculated from the NaCl concentration; the former by using Sechenov's coefficients for CO_2 (which are assumed to hold for O_2) for temperatures up to 200 °C, as given by Naumov, et al.⁶, and the latter from the extensive data of Liu and Lindsay⁷ on the thermodynamics of the NaCl- H_2O system. The saturation NaCl concentration

and solution density at temperatures up to 200 °C are calculated from the data of Liu and Lindsay and the empirical model of Haas⁸, respectively. The oxygen concentration, mean molal activity coefficient of the solute (NaCl), and the activity of water are calculated using Henry's law data from Naumov, et al.⁶ and the osmotic coefficient data for the NaCl-H₂O system given by Liu and Lindsay⁷, respectively.

- No redox species other than hydrogen and oxygen are considered in the model. This assumption reflects the general opinion that the radiation dose rates at the surface are not sufficiently large to produce significant amounts of radiolysis products, such as H₂O₂. However, radiolysis products are considered in the thin layer mixed potential model (TLMPM) that was developed by Macdonald and Urquidi-Macdonald⁹ about a decade ago to explore the impact of radiolysis on the electrochemical and corrosion properties of a HLNW canister. That study, which focused on copper alloys, suggested that there should be observable radiolysis effects, but of course that finding depends strongly upon the dose rate that is assumed to exist at the canister surface. In this regard, it is important to note that the radiation dose rate at the surface of the C-22 canister is likely to be significantly higher than that assumed for the copper canister, because of the smaller wall thickness of the former. Accordingly, the issue of radiolytically-generated redox species should be revisited.
- As noted above, the MPM was originally developed for describing electrochemical and corrosion processes in the heat transport circuits of Boiling Water Reactors³ and hence assumed that pH was not a variable. However, in the present application, the pH is a system variable and hence the expressions for the exchange current densities of both the hydrogen electrode reaction (HER) and the oxygen electrode reaction (OER) have been modified by inclusion of the factor $(C_{H^+} / 10^{-pK_w/2})^{\text{expon}}$, where $pK_w = -\log(K_w)$, K_w is the activity product of water at the prevailing temperature, and C_{H^+} is the concentration of hydrogen ion, which is calculated from the known pH. The exponents (exponHER and exponOER for the HER and OER, respectively) are set equal to 0.5 without theoretical or experimental justification for Alloy C-22. We also introduce a similar factor for the dependence of the exchange current density on the activity of water (a_w), in this case in the form of a_w^p , where $p = 1.4$ for the HER¹⁰ and equal to 1.0 for the OER. The latter value was assumed *in lieu* of experimental data for C-22. Finally, we assume that the temperature dependencies of the exchange current densities for the HER and the OER can be described by an Arrhenius factor of the form $\exp(-14244/RT)$, where T is the Kelvin temperature, as per the original MPM³.
- The potential scale that is employed in this work is the standard hydrogen scale, but that scale is not particularly useful for comparison with experimental data, which are commonly reported on the saturated calomel electrode (SCE) scale or the saturated silver/silver chloride electrode (sssc). However, the conversion factors from one scale to another are temperature dependent. The conversion factors were calculated using the HSC thermodynamic code¹¹ and are calculated internally in the codes.

Accumulated Damage Model

The Accumulated Damage Model employs the GCM to calculate the corrosion rate at closely spaced state points along the Corrosion Evolutionary Path (CEP). As noted in the Introduction, one requirement of a deterministic model is that the CEP be specified and be continuous (i.e., that it contain no discontinuities or singularities). In the present work, the temperature versus time data predicted by LLNL for three scenarios, the Base Case (BC), the Low Temperature Operating Mode (LTOM), and the High Temperature Operating Mode (HTOM), were adopted as describing the CEP. The pH was then calculated by assuming that the water is neutral, that is $pH = pK_w/2$, with appropriate corrections being made for the activity coefficient of H^+ in saturated brine. The integrated damage is then calculated via the recursion formula

$$L_{j+1} = L_j + (dL/dt)\Delta t \quad (14)$$

where dL/dt is the corrosion rate and L is the corrosion loss.

Application of the Models

The codes for the General Corrosion Model (GCM) and the Accumulated Damage Model (ADM) developed in this work **have not been fully optimized**, due to the unavailability of input data for some model parameters for Alloy C-22 under thin electrolyte films in simulated Yucca Mountain environments. Accordingly, the parameter values employed in the calculations described below generally refer to stainless steels, as used in previous applications of the MPM³, or are best estimates (sometimes “guesstimates”). The actual parameter values are contained in the code, together with appropriate comments. One of the principal reasons for developing the codes, in their present forms, is to focus attention on those parameters that need to be experimentally measured. Future work will prioritize these parameters by using the present code to perform extensive sensitivity analyses.

Finally, and as emphasized above, these codes still requires considerable development before they can be considered to be reasonably complete. Nevertheless, as shown below, the codes are capable of yielding realistic values for the output parameters (corrosion potential, transpassive dissolution potential, corrosion rate, and corrosion loss) and future optimization is expected to produce predictions that will be in even better accord with experiment, a view that is based on our previous experience with the ECP code in predicting corrosion potentials in the primary coolant circuits of water-cooled nuclear reactors.

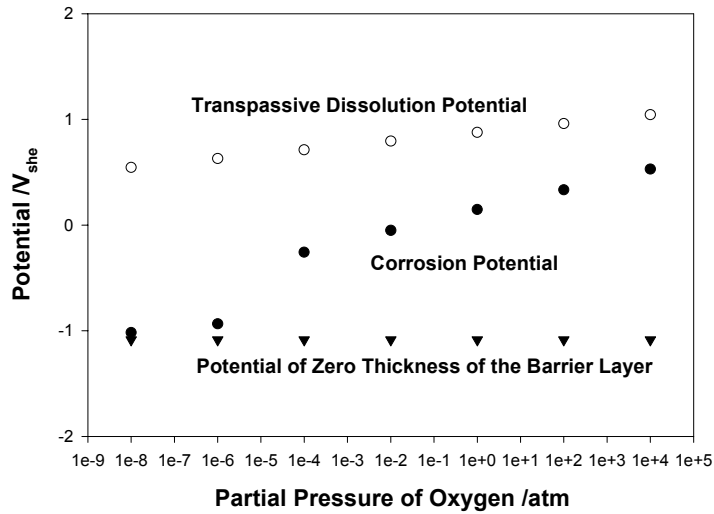


Figure 2. Dependence of the corrosion potential on the partial pressure of oxygen and temperature. pH = 3, saturated NaCl solution, electrolyte film thickness = 0.01 cm.

General Corrosion Model

By way of illustration, the HLNW_ECP code has been used to calculate the ECP (corrosion potential) and the corrosion current density as a function of oxygen partial pressure and temperature, and the results are given in Figures 2 and 3. The thin electrolyte film on the metal surface is saturated in NaCl. The data plotted in Figure 2 show that the ECP (corrosion potential) displays a typical sigmoid variation with log of the oxygen partial pressure. Also plotted in Figure 2 are the transpassive dissolution potential (E_{trans}) and the potential of zero thickness of the barrier layer. Both of these potentials are predicted not to be strong functions of the partial pressure of oxygen (although the transpassive dissolution potential does increase significantly with p_{O_2} , due primarily to the increase in the activity of chromate in the electrolyte film). Accordingly, the difference between the transpassive dissolution potential and the corrosion potential is predicted to decrease substantially as the partial pressure of oxygen increases, but at no practical pressure does the corrosion potential exceed (become more positive than) the transpassive dissolution potential.

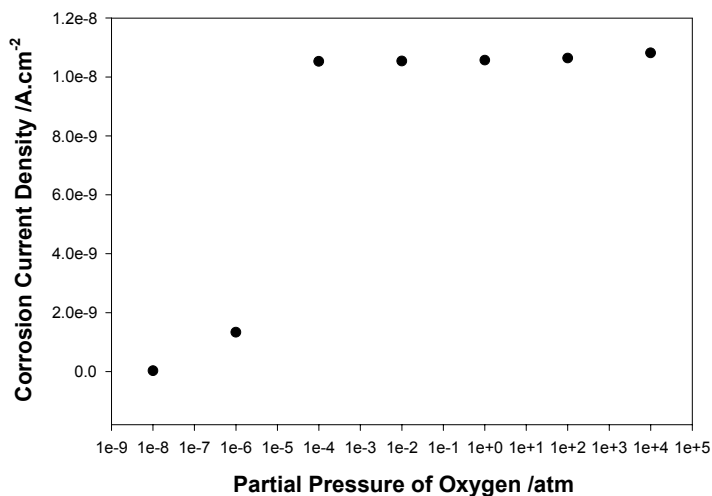


Figure 3. Corrosion current density as a function of the partial pressure oxygen and temperature. The following parameter values were assumed: pH = 3.0, electrolyte film thickness = 0.01 cm, [NaCl] = sat.

With regard to the corrosion current density, i_{corr} is predicted to increase strongly with p_{O_2} at low partial pressures, but then it is predicted to become constant once the partial pressure of oxygen exceeds 0.0001 atmospheres. The initial increase in i_{corr} with p_{O_2} is somewhat artificial, in that it is assumed that the current increases exponentially with voltage until the passive current density is reached [Equation (10)]. This treatment assumes that an “active dissolution” region does not exist for Alloy C-22; an assumption that must be checked, if possible, by experiment. Thus, to all intents and purposes, the ambient partial pressure of oxygen is predicted not to be an important parameter in determining the general corrosion rate of C-22 in contact with saturated NaCl, although it is important in determining the value of the corrosion potential. Because the nucleation rate of localized corrosion is a sensitive function of the corrosion potential⁴, the partial pressure of oxygen would become an issue in analyzing the occurrence of pitting corrosion and stress corrosion cracking, but only if the partial pressure of oxygen was predicted to vary significantly over the life of the repository. It is important to note that the lack of a dependence of i_{corr} on p_{O_2} at oxygen partial pressures above 0.0001 atm is a consequence of assuming that the passive film is a cation interstitial conductor and that no change in oxidation state occurs on ejecting a cation from the barrier layer into the solution. This same relationship holds if the oxygen vacancy was assumed to be the principal defect in the barrier oxide layer, provided again that no change in oxidation state occurred upon film dissolution or ejection of a cation from the barrier layer at the barrier layer/solution interface. On the other hand, if the principal defect is the cation vacancy, or if the oxidation state of chromium changes upon barrier layer dissolution (Reaction 7, Figure 1) or upon cation ejection (Reactions 4 and 5), the corrosion current density becomes potential dependent, as shown below.

The predicted variation of the corrosion potential (ECP) with pH and temperature is shown in Figure 4. The corrosion potential is predicted to increase slightly with increasing temperature, as has been observed experimentally for this Alloy C-22 in sulfuric acid solutions¹², with the greatest dependence being predicted for the lowest pH. This behavior is the reverse of that which is predicted and observed for Type 304 SS in pure water¹³ and in dilute NaCl solutions¹⁴, where the corrosion potential is found to shift strongly in the negative direction as the temperature is increased, at least for temperatures up to 250 °C. The fact that the model predicts the inverse behavior, which is observed experimentally, is encouraging evidence that the MPM is capable of providing an accurate account of the corrosion potential in saturated NaCl electrolyte. However, the author cautions that a rigorous comparison between theory and experiment must await the measurement of values for key model parameters, including the kinetic parameters for the hydrogen and oxygen electrode reactions on Alloy C-22. These measurements are underway and experimental data are expected to be available over the next twelve months.

The corrosion current density predicted by the GCM is plotted as a function of temperature and pH in Figure 5. As expected, i_{corr} is predicted to increase with increasing temperature at all pH values, with the greatest dependence being predicted for the most acidic solution. Furthermore, the corrosion current density is predicted to decrease substantially with increasing pH for any given temperature. These relationships, including the relatively small dependence of i_{corr} on temperature at high pH, are in keeping with experimental observation, although a detailed comparison must await the availability of accurate values for various model parameters. It is important to note, however, that the corrosion current density is one to two orders in magnitude lower than that for Type 304 SS in comparable environments, attesting to the extraordinary corrosion resistance of Alloy C-22.

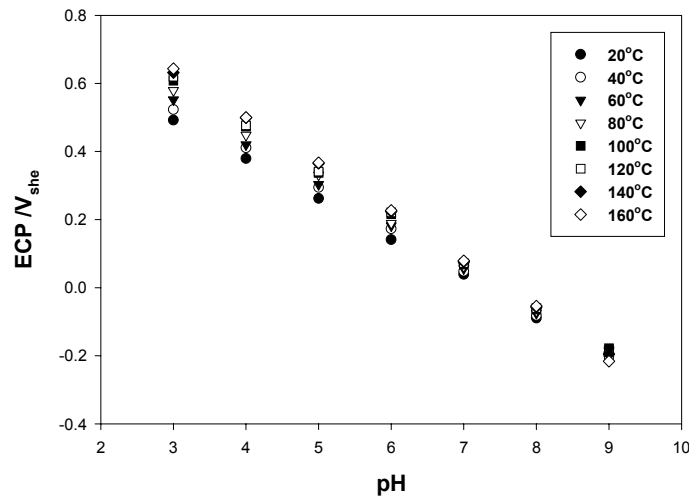


Figure 4. Plot of calculated corrosion potential (ECP) versus pH of the thin electrolyte film on the alloy surface. $T = 100\text{ }^{\circ}\text{C}$, $p_{\text{O}_2} = 0.21\text{ atm}$, electrolyte film thickness = 0.01 cm, $[\text{NaCl}] = \text{sat}$.

An important aspect of the GCM, conferred upon it by the use of the Point defect Model (PDM) to describe the anodic (alloy oxidation) partial current, and by the use of the Butler-Volmer equation to describe the kinetics of the hydrogen and oxygen electrode reactions that occur on the alloy surface, within the framework of the mixed potential model (MPM), is that it is possible to calculate the current that would be observed in the external circuit if the current/voltage curve for the alloy was measured in a normal, controlled potential experiment. A set of such “polarization curves” is shown in Figure 6 for different temperatures ranging from 20 °C to 120 °C at a pH of 7. In constructing these curves, the oxidation state of the metal species being ejected from the barrier layer or resulting from dissolution of the layer (see Figure 1), was allowed to change from 3 (corresponding to Cr in Cr_2O_3) to 6 (corresponding to chromate, CrO_4^{2-}) as the potential became greater than the equilibrium potential for the reaction

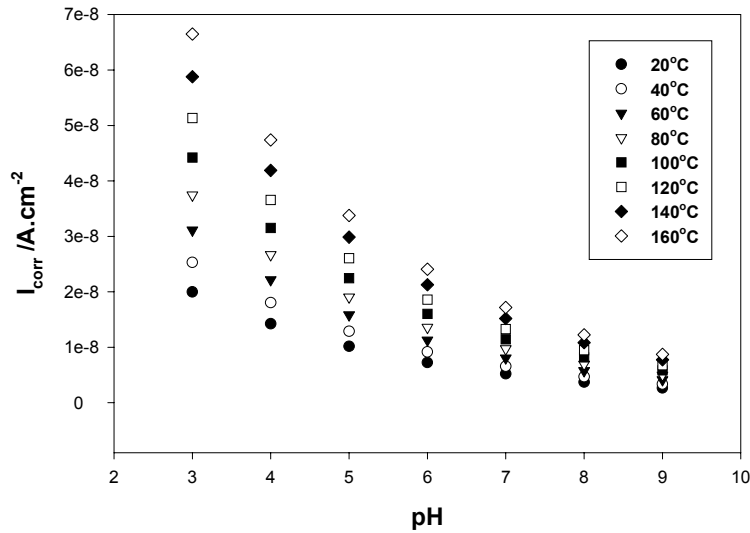
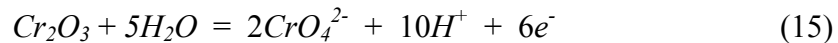
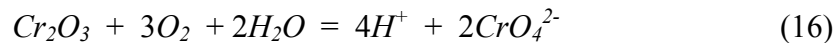


Figure 5. Plot of calculated corrosion current density versus pH of the thin electrolyte film on the alloy surface. $T = 100\text{ }^\circ\text{C}$, $p_{O_2} = 0.21\text{ atm}$, electrolyte film thickness = 0.01 cm, $[\text{NaCl}] = \text{sat}$.



where the activity of chromate in the thin electrolyte layer is assumed to be established by the reaction



Subtraction of Reaction (16) from Reaction (15) yields the reaction (written in the reduction sense)



Thus, the assumption that the activity of chromate ion in the thin electrolyte film is determined by Reaction (15) and that the system is in equilibrium is tantamount to assuming that transpassive dissolution is due to barrier layer dissolution [Reaction (15)] and that it coincides with the equilibrium potential for the oxygen electrode reaction. This assumption may not be completely justified at lower temperatures in light of the high overpotential that is required to affect oxygen evolution on stainless steels and other chromium-containing alloys, but it is expected to become increasingly valid as the temperature is increased. Furthermore, the equilibrium assumption is expected to lead to a conservative result; that is to an estimate of E_{trans} that is more negative than the kinetically controlled, observed value. In any event, the GCM predicts that transpassive dissolution as a sudden increase in the current as the potential is increased through the passive region.

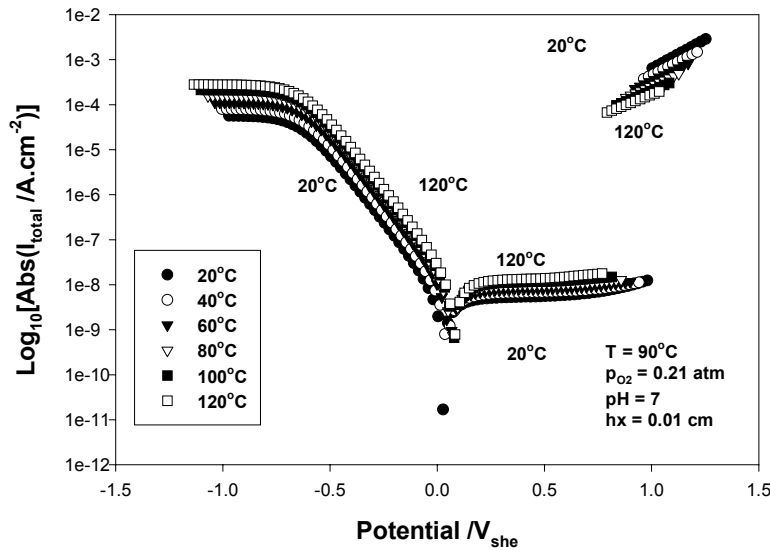
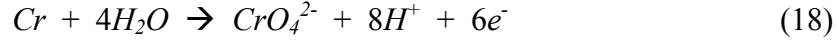


Figure 6. Predicted polarization curves for Alloy C-22 in contact with a thin electrolyte film (saturated NaCl) on the surface as a function of temperature. $p_{O_2} = 0.21$ atm, electrolyte film thickness $hx = 0.01$ cm, $pH = 7$.

The fundamental origin of the sudden increase in current can be gleaned from a consideration of Equations (6) and (7). Thus, from Equation (7) we see that as δ becomes greater than χ , corresponding to the increase in oxidation state of the metal species that is ejected from the film or that results from film dissolution, the last term in the square brackets on the right side becomes positive, thereby contributing to a decrease in the barrier layer thickness. This effect is shown in Figure 7 as a sudden decrease in L_{SS} ; in this case to zero thickness (the calculated thickness for $E > E_{trans}$ was negative, which is

non-physical and hence L_{ss} was set equal to zero). From Equation (6), it is evident that the sudden decrease in L_{ss} induces a corresponding increase in I_{ss} , which is shown in Figure 6. If the film thickness goes to zero then Reactions (1) and (4), Reactions (2) and (5), and Reactions (3) and (7), Figure 1, all collapse to



corresponding to metal dissolution. To the author's knowledge, the PDM is the first (and only) model to predict this important result.

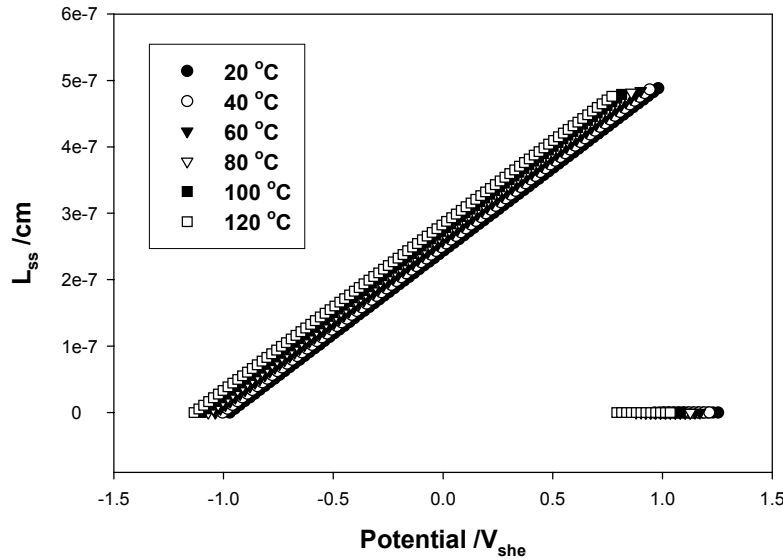


Figure 9. Predicted barrier oxide layer thickness for Alloy C-22 in contact with a thin electrolyte film (saturated NaCl) on the surface as a function of temperature. $p_{O_2} = 0.21$ atm, electrolyte film thickness $h_x = 0.01$ cm, $pH = 7$.

The GCM also predicts that the transpassive dissolution potential shifts in the negative direction with increasing temperature, which is generally observed for stainless steels and other chromium containing alloys. Finally, it should be noted that the cathodic branch of the polarization curves shown in Figure 6 is due entirely to oxygen reduction; this being a consequence of the kinetic parameter values chosen for describing the hydrogen evolution reaction and the potential range over which the calculations are performed.

The predicted polarization curves and steady state barrier layer thickness versus voltage behavior for C-22 as a function of pH at a temperature of 90 °C are shown in Figures 8 and 9. The transpassive dissolution and corrosion potentials are predicted to shift to more negative values as the pH increases (c.f., Figure 4 for the ECP), which again is in general agreement with experimental observation for many alloys.

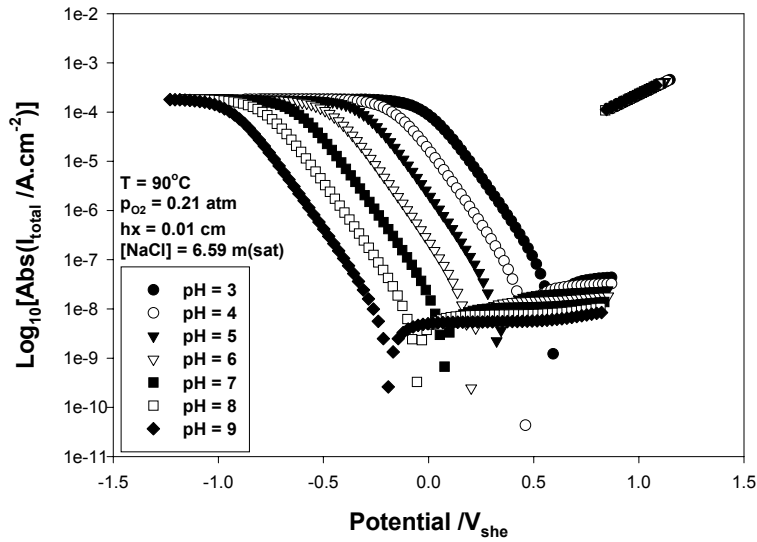


Figure 8. Predicted polarization curves for Alloy C-22 in contact with a thin electrolyte film (saturated NaCl) on the surface as a function of pH. $p_{O_2} = 0.21$ atm, electrolyte film thickness $h_x = 0.01$ cm, $T = 90$ °C.

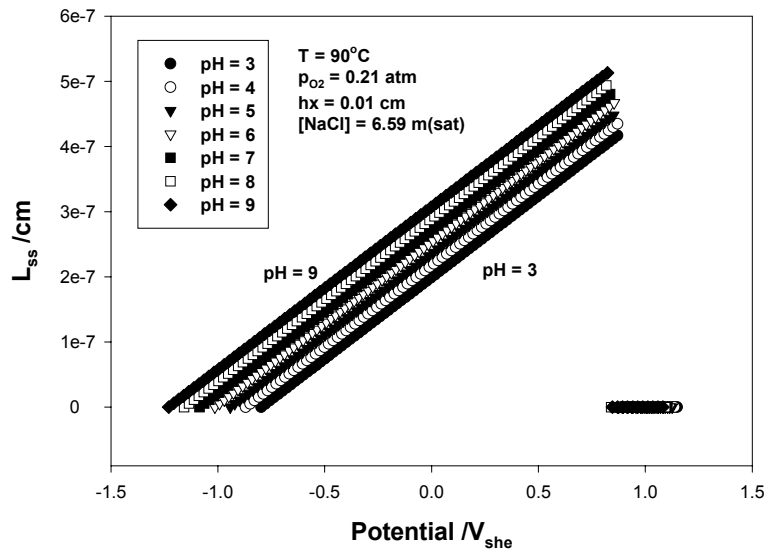


Figure 9. Predicted barrier oxide layer thickness for Alloy C-22 in contact with a thin electrolyte film (saturated NaCl) on the surface as a function of pH. $p_{O_2} = 0.21$ atm, electrolyte film thickness $h_x = 0.01$ cm, $T = 90$ °C.

Experimental data for the general corrosion of Alloy C-22 in well-defined aqueous solutions under prototypical repository conditions are not available. The data that have been reported for “similar conditions” report corrosion current density values ranging over one to two orders in magnitude, depending on who performed the measurements and how they were made. The primary sources of data considered in the brief analysis reported here were taken from reports from the Center for Nuclear Waste Regulatory Analysis, South West Research Institute (SwRI)¹⁵, the University of Western Ontario, Canada¹⁶, the Lawrence Livermore National Laboratory^{17,18}, and the University of Virginia¹⁹. The corrosion current density data used for calibrating the GCM were taken from the SwRI reports¹⁵, but only to the extent that they gave general guidance to the magnitude and the temperature dependence of the passive current density. Thus, it was found from these reports that the passive current density at 25 °C was of the order of a few tens of nano-amperes per centimeter squared and that it does not increase significantly with temperature, at least at temperatures of up to 90 °C. After the present study was underway, the author’s attention was directed to a study by Lloyd, et al.¹⁶, who reported “steady state” polarization data for Alloy C-22 in 1.0 M NaCl solution with the pH adjusted to 1.0. The data are plotted in Figure 10, together with the experimental data of Lloyd, et al.¹⁶ Note that the data all correspond to a potential of 0.350 V on the saturated silver silver chloride scale, although this scale was not specifically identified in the work of Lloyd, et al. (They identified the potential scale as being the “Ag/AgCl” scale without apparently specifying the activity of chloride ion). The calculated data were obtained from the GCM by adjusting the partial pressure of oxygen at each temperature, so as to obtain a corrosion potential of 0.35 V_{SSCE}.

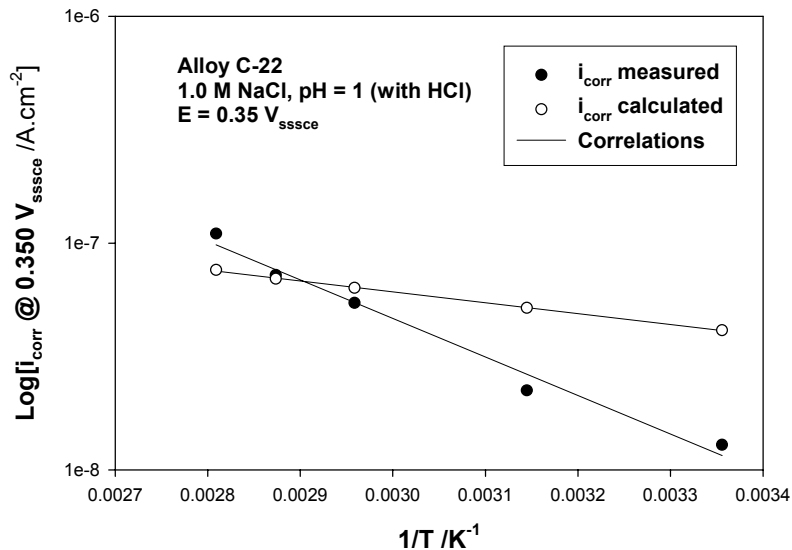


Figure 10. Arrhenius plots for the passive dissolution of Alloy C-22 in 1.0 M NaCl solution adjusted to a pH of 1.0. The measured data were reported by Lloyd, et al.¹⁶

Comparison of the two data sets plotted in Figure 10 shows that the temperature dependence of the experimental data of Lloyd, et al.¹⁶ is much greater than that assumed in the model. Nevertheless, the two data sets are within a factor of three at all temperature and within a factor of two over the critically important temperature range of 40 °C to 120 °C, which would seem to lend credence to the calculations reported in this study. An attempt was made to use the data reported by Farmer, et al.^{17,18}, and by Scully and co-workers¹⁹, but it is evident that the passive current density was measured using a potentiodynamic technique and that the authors had not determined the voltage sweep rate at which the system could be considered to be in a quasi steady state. The use of potentiodynamic techniques, while automated and hence convenient, presents a particularly important problem related to the confluence between theory and experiment, because the theory currently exists only for the steady state. For this reason, the passive current density data of Scully, et al. were not used in the present analysis. Likewise, the data reported by Farmer, et al. cannot be employed, also because of their use of a potentiodynamic technique. In particular, the “corrosion potential” data reported by Farmer, et al. correspond to the “zero current” values recorded on potentiodynamic scans. The “zero current” condition is a necessary, but not a sufficient, condition for defining the free corrosion potential; the other condition being that the system is in its natural state (i.e., it is not polarized). This latter condition cannot be achieved with a potentiodynamic scan, unless it is demonstrated that the same values for the corrosion potential and the passive current density are obtained on the reverse scan. This is generally not the case.

Accumulated Damage Model

The Accumulated Damage Model (ADM) is demonstrated by calculating the corrosion rate and accumulated corrosion damage (thickness loss) for C-22 alloy in contact with a saturated brine electrolyte layer over a one million year repository exposure period. Three cases that have been previously defined by personnel at the Lawrence Livermore National Laboratory were explored: (1) Base Case, (2) Low Temperature Operating Mode (LTOM), and (3) High Temperature Operating Mode (HTOM). The evolutionary paths with respect to temperature are shown in Figure 11. The Base Case and the HTOM display similar temperature evolutionary paths, in which the temperature rises to a maximum of about 160 °C. On the other hand, the LTOM, which corresponds to the scenario where closure of the repository is delayed until considerable decay of the most active radioisotopes has occurred, displays significantly lower temperatures, with the maximum reaching to a value that is a little over 85 °C.

The parameters assumed for the calculation of the corrosion rate and accumulated corrosion damage are as follows: $p_{O_2} = 0.21$ atm, h_x (thickness of the electrolyte layer) = 0.01 cm, $pH = pK_w/2$, and $[NaCl] =$ saturated at the corresponding temperature, where K_w is the dissociation product for water. It was further assumed that equilibrium exists between the electrolyte film and the ambient atmosphere and that the concentration of oxygen in the layer at the layer/atmosphere interface could be calculated using Henry’s law together with appropriate Sechenov (salting in/salting out) coefficients⁶.

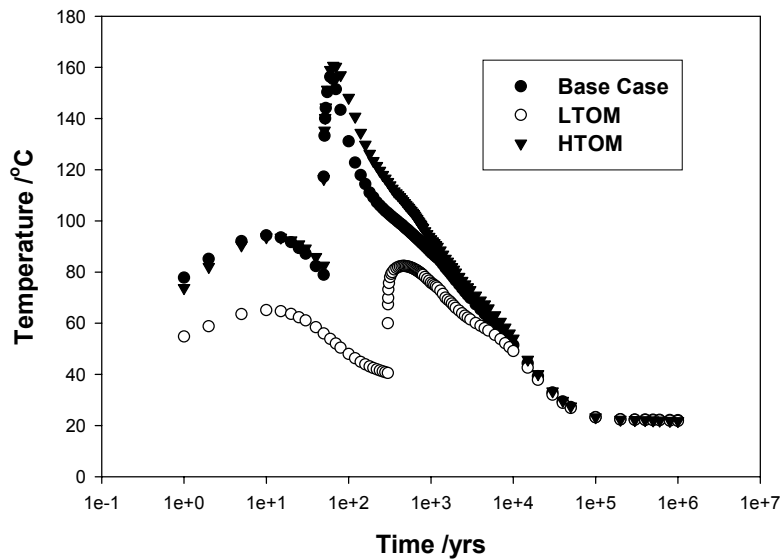


Figure 11. Evolutionary paths with respect to temperature for the Yucca Mountain HLNW repository for the three scenarios defined by the LLNL.

The predicted corrosion rate evolutionary paths are displayed in Figure 12 for the three scenarios defined by the LLNL. As expected, little difference is predicted to exist between the corrosion rate evolutionary paths for the Base Case and the HTOM scenarios, except that the Base Case corrosion rate is predicted to be slightly lower than that for the HTOM in the 100 to 1000 year period. On the other hand, and paralleling the behavior of temperature, the corrosion rate for the LTOM is predicted to be significantly lower than that for the Base Case and the HTOM for the first ten thousand years. At longer times (10,000 years to 1,000,000 years) the corrosion rate evolutionary paths are predicted to coincide.

Although the predicted corrosion rate displays considerable variation with time, because of the concomitant variation in temperature, the accumulated damage (corrosion loss) is predicted to increase monotonically with time. Furthermore, the three scenarios are essentially coincident, leading one to conclude that little difference may exist between the three cases as far as corrosion performance is concerned. (Note that there may exist other reasons for choosing one scenario over another that are not considered in the present analysis). However, the near coincidence of the corrosion loss evolutionary paths is somewhat illusory, in that the time in Figure 12 is expressed on a log scale whereas that in Figure 13 is linear. Thus, the integrated corrosion rate at long times dominates more in the corrosion loss behavior than it appears to do so in the corrosion rate behavior. To illustrate this point, the corrosion loss for the three scenarios defined above is plotted as a function of linear time over the first ten thousand years in Figure 14. In this case, the integrated corrosion rate (corrosion loss) for the low temperature-operating mode (LTOM) is distinctly lower than those for the other scenarios, as expected. Even so, the maximum difference in corrosion loss between the three modes is predicted to be little more than 10 %.

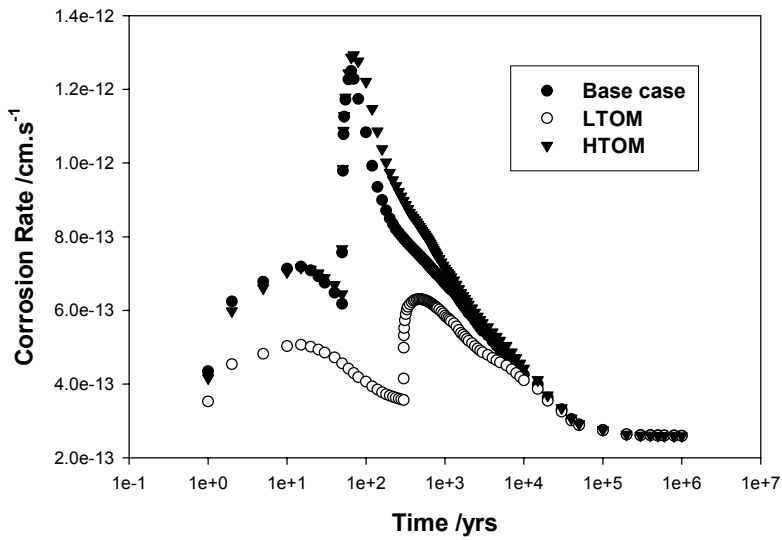


Figure 12. Evolutionary paths with respect to corrosion rate for Alloy C-22 in contact with saturated NaCl for the Yucca Mountain HLNW repository for the three scenarios defined by the LLNL.

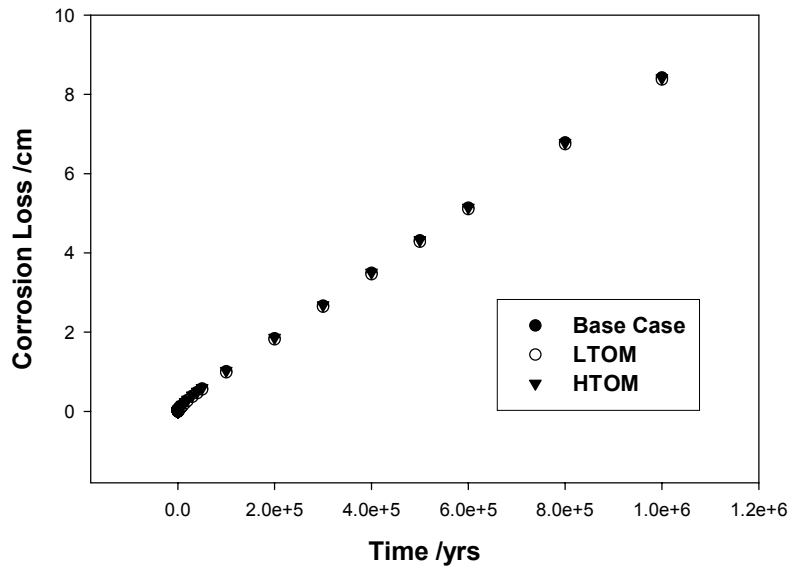


Figure 13. Evolutionary paths with respect to corrosion loss for Alloy C-22 in contact with saturated NaCl for the Yucca Mountain HLNW repository for the three scenarios defined by the LLNL.

At this point, it is worth commenting on the value of the corrosion loss predicted by the ADM. As seen in Figure 13, the corrosion loss after one million years is predicted to be almost 9-cm, which is considerably greater than the 2-cm wall thickness of the Alloy C-22 canister. Clearly, the ADM predicts failure if the service life is set at 1,000,00 years. On the other hand, the predicted corrosion loss for a 10,000-year service life is about 1.6 mm, which is considerably smaller than the designated wall thickness. In this case, no failure by general corrosion is predicted. Indeed the calculations shown in Figure 13 indicate that general corrosion failure will not occur over the first 200,000 years of storage, which represents a significant corrosion allowance over the design life.

Finally, concern has been expressed that the corrosion potential may drift in the positive direction over time, to the extent that it could exceed (become more positive than) the transpassive dissolution potential. If this did occur, then it is possible that the corrosion rate could increase by several orders in magnitude and hence lead to rapid

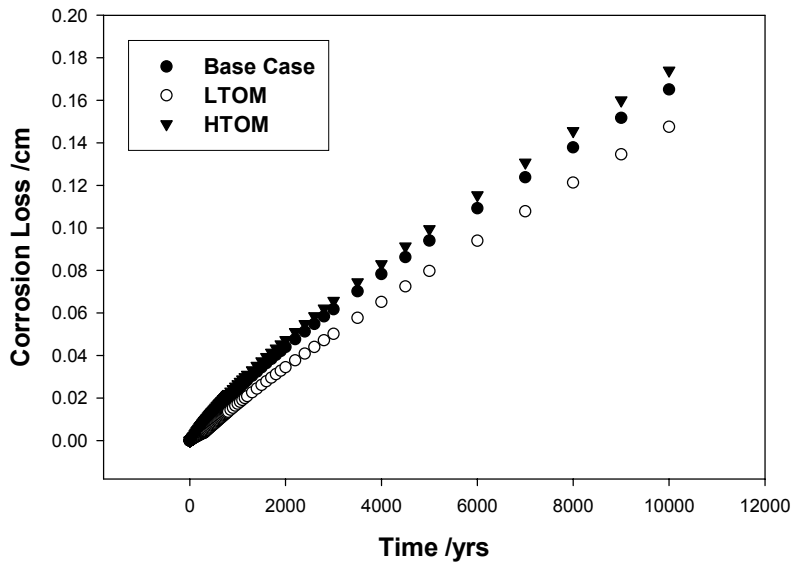


Figure 14. Evolutionary paths with respect to corrosion loss over the first ten thousand years for Alloy C-22 in contact with saturated NaCl for the Yucca Mountain HLNW repository for the three scenarios defined by the LLNL.

failure. This possibility has been explored in Figure 15 for the three scenarios defined by the LLNL. Both the ECP and the transpassive dissolution potential, E_{trans} , are predicted to vary significantly over the evolutionary path of the repository, but at no time is the ECP predicted to become comparable to E_{trans} . Indeed, the closest that the two potentials are predicted to come to one another is after about seventy years, at which time the transpassive dissolution potential is predicted to exceed the corrosion potential (ECP) by about 400 mV. Based on these results, the likelihood that the canisters will suffer transpassive dissolution along the evolutionary path is considered to be extremely low.

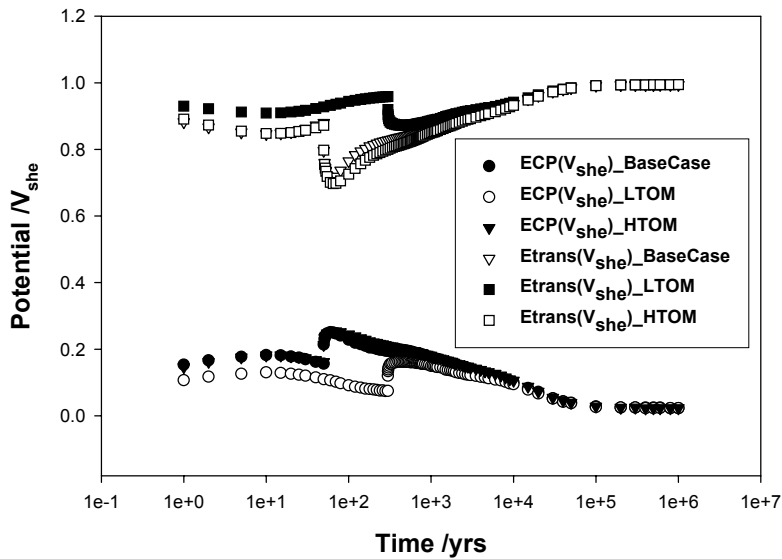


Figure 16. Predicted evolutionary paths with respect to corrosion potential and transpassive dissolution potential over one million years for Alloy C-22 in contact with saturated NaCl in the Yucca Mountain HLNW repository for the three scenarios defined by the LLNL.

Summary and Conclusions

The work described in this report has resulted in the development of two deterministic models for predicting the corrosion behavior of Alloy C-22 canisters in the Yucca Mountain HLNW repository. Thus, the general corrosion model (GCM) calculates the corrosion potential, the trans passive dissolution potential, and the corrosion current density for the alloy in contact with a thin electrolyte film containing a specified concentration of NaCl (including the saturated, default system), which in turn is in contact with the ambient atmosphere. The second model, the accumulated damage model (ADM), then employs the CGM to calculate the corrosion loss over a specified evolutionary path for the repository. The models are deterministic, in that the predictions are based upon specific corrosion mechanisms, as described by the Point Defect Model (PDM) for the passive current density and the Butler-Volmer equation for the partial cathodic processes that occur at the surface, that the predictions are constrained by the appropriate natural laws (the conservation of charge and Faraday's law), and that the route to the future is described in terms of a continuous evolutionary path. The models have not been fully optimized, because of the lack of data for key model parameters. Nevertheless, the models:

- Account for the existence of the transpassive state in terms of known electrochemical phenomena [oxidation of Cr(III) to Cr(VI)]. In fact, the PDM predicts the existence of the transpassive state without the need to adjust the theory in any manner whatsoever.

- Predict accumulated general corrosion damage (corrosion loss) values for the three scenarios proposed by the LLNL (Base Case, LTOM, HTOM) that are eminently reasonable. Thus the ADM (Accumulated Damage Model) predicts that the corrosion loss to the Alloy C-22 canister after 10,000 years in contact with saturated brine over the specified evolutionary paths will be of the order of 1.6 mm, compared with a wall thickness of 2-cm. Consumption of the wall thickness is predicted to take about 200,000 years, whereas the general corrosion loss after a million years exposure in the repository is estimated to be slightly less than 9-cm.
- Predict surprisingly little difference between the total corrosion loss for the three evolutionary paths examined in this work (Base Case, LTOM, HTOM).
- Predict that at no time during the evolution of the repository will the corrosion potential become more positive than the transpassive dissolution potential. Indeed, the prediction of the models is that the ECP will remain more negative than the transpassive dissolution potential by at least 400 mV at all times. Accordingly, the threat of transpassive dissolution to the integrity of the canister is considered to be highly unlikely.

Acknowledgments

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REPLY TO QUESTIONS ON LONG-TERM PASSIVITY AND LOCALIZED CORROSION OF ALLOY 22

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QUESTION 1 a) The Ni-Cr-Mo alloy [known as 22] will almost certainly have a thin passive oxide layer which confers corrosion resistance. Its thickness is probably in the neighbourhood of 10A-20A, this being typical of passive oxide layers on either Ni or Cr. We will assume that in the early stages of corrosion, uniform dissolution is occurring at a slow [possibly decreasing] rate giving rise to the so-called "passive" current. The magnitude of this current will depend on a number of inter-related factors such as: the nature of the oxide film, the environmental conditions [T, pH, Anions, etc.], nature of alloy because of repassivation, reaction driving force [open-circuit potential]. I believe that to answer this first question in an intelligent way, we should know what processes are giving rise to the passive current, ie. is it uniform metallic cation dissolution through the oxide film, a non-uniform version of this at defects or weak points in the film, uniform chemical dissolution of the oxide followed by film repair, non-uniform dissolution of the film at defects followed by local repair, or some other mechanism. Based on my own research with Ni and Fe, using oxygen-18 SIMS, XPS, Auger Spectroscopy, replica TEM, as well as electrochemistry, my suggestion is non-uniform dissolution of the oxide at defects but the defects are not "static" with time but randomly sweep across the entire surface. The effect of this is that the whole film eventually sees such breakdown [this mechanism is strongly supported by the O16/O18 results in the case of Ni; see eg. B. MacDougall, D.F. Mitchell and M.J. Graham, J. Electrochem. Soc.132, p. 2895 [1985]]. A very important fact is that with increasing time of anodic polarization, the density of film defects decreases and simultaneously the passive current decreases since there are fewer and fewer weak points at which breakdown can occur. It is unlikely that there will ever be "no" defect sites in the film, and these sites will be prone to Cl-induced localized corrosion [pitting]. Upon film breakdown at the weak points, the film needs to repair itself [if possible]; the current efficiency of this repair [defined as 100% if no parallel metal dissolution occurs, ie. only reformation of the oxide, but actually may be much less] dictates the "activity" of the defect. As an aside which is outside the scope of this abstract, there may actually be a increase in the activity associated with the film defects as the number of defects decreases, ie. as the film becomes more perfect in terms of number of defects. This could have profound implications on the resistance of the film towards localized corrosion as it ages and becomes more defect-free, and should be at least considered when thinking about how "perfect" a passive film really is, and what we actually mean by "perfection".

I am pleased that short-term polarization experiments have been performed in Cl-containing solutions in order to test alloy-22 under these conditions; however, I am quite concerned that no experiments appear to have been performed in Cl- plus F- solutions [since both anions will almost certainly be present in the Yucca mountain environment]. From my extensive experience with Ni and Fe, the simultaneous presence of Cl- and F- in solution can be extremely detrimental for local breakdown and corrosion. The Cl- appears to mainly operate via a competitive adsorption route, interfering with oxide film formation at those sites where the passive film has locally broken down. The F- does not operate in this way at all, but rather is able to incorporate

in the passive oxide film lattice at sites previously occupied by oxygen, thereby greatly decreasing the stability of the film [B. MacDougall and M.J. Graham, J. Electrochem. Soc. 132, p. 2553 [1985]]. The reason that F⁻ is able to do this so effectively appears to be related to the fact that the ionic radius of F⁻ is almost identical to that of O²⁻ at 1.3Å. In comparison, the Cl⁻ is about 50% larger and not so easily accommodated. Consistent with this, Auger analysis of oxide films on Ni indicates that large amounts of F⁻ can be incorporated in the oxide lattice [15 or more at. %] while only small amounts of Cl⁻ can be incorporated [a few at. % at most]. It appears that the F⁻ is thus able to weaken the passive film and give rise to much more local film breakdown; at this point the Cl⁻ in solution interferes with local film repair so that many pits are generated on the surface. Under applied anodic potential conditions, this can give rise to the metal becoming essentially “swiss-cheese”. In light of these observations, **I think that it is essential to study the anodic behavior of alloy-22 in solutions containing both Cl⁻ and F⁻.** The results obtained in Cl⁻ “only” solutions may have little meaning in terms of the long-term performance characteristics of this alloy. It may also make sense to study the “repassivation” characteristics of this alloy by performing “scratching-type” experiments where the passive film is physically removed in a mixed Cl⁻/F⁻ solution and reformed under anodic conditions at different potentials. I would think that with the very long-term exposure of this alloy under containment conditions, it is not inconceivable that local mechanical disruption of the thin passive film may occur from time to time.

In direct response to Question 1, I believe that the long-term corrosion rate can increase substantially with time if the electrolyte in contact with the WP sees an increase in the F⁻ concentration. The fact that at the same time the Cl⁻ concentration is also increasing is potentially very bad for the integrity of the WP. The potential concentrations of both these anions due to water evaporation is given as ca. 700ppm, a concentration that is certainly not low. It is obviously important to perform the accelerated corrosion experiments under conditions closely related to those which will be experienced in the field. It should be mentioned here that solution pH will play a very major role in the case of the fluoride solution where the possible species go from HF₂⁻ to HF to F⁻ as the pH increases, and the different species can have different influences on passivity development and breakdown. It should also be noted that initiation of localized corrosion can result in a very significant decrease of the pH locally, so that the nature of the anionic species present can change upon initiation of pitting or crevice corrosion.

As an example of just how different the aggressive behaviour of Cl⁻ is from F⁻, reference is made to Fig. 1 where results are presented for the nickel system passivated at a constant potential in the passive region using a pH 3.0 sulfate solution. Either Cl⁻ or F⁻ is added in the mM concentration range after a “good” passive film has been established, and the resulting change of anodic current with time recorded. In the case of Cl⁻ addition, nothing happens until after an induction period, at which point the current increases abruptly as pitting corrosion occurs at a few isolated places on the Ni surface. In the case of F⁻ addition, the breakdown behavior is completely different with the anodic current gradually increasing until passivity has completely broken down over the entire surface [breakdown began in a localized fashion but eventually spread to the entire surface]. While it could be argued that Cl⁻ is more dangerous for localized and F⁻ for general corrosion, both are very aggressive so far as passivity is concerned, and in combination they are potentially even more dangerous.

b) Has the passive film on Alloy 22 been characterized in terms of its thickness, composition, crystal structure? If not, this could be done fairly quickly. Also, how does the stability of the film towards open-circuit decay, cathodic reducibility, and induction time for pitting in Cl⁻, vary with potential of film formation? Cyclic voltammetry and potential step experiments have been done under some conditions, I believe, but these appear to be limited at present. Does the alloy behave in a fashion similar to Ni? Since the Ni, Cr, Fe, Mo, etc. will possibly dissolve at different rates, there will be a “time evolution” of passive film composition, and maybe even morphology. This could be for better or for worse, and should be investigated.

QUESTION 2a) With time, the “electrolyte environment” in the vicinity of the WP can change and this can have major implications for the “effective” electrochemical driving force. Eg., the level of Cl and F in the vicinity of the WP can change with time, and these anions can have a major influence on the potentials at which reactions can occur because of their complexing ability. As a simple and rather famous example, the reversible potential for the conversion of ferric [3+] to ferro [2+] ion is shifted from 0.77V to 0.37V in the presence of cyanide anion, ie. the anodic reaction is now much easier than the cathodic one. So even if the driving force potential remains the same, the rate of the anodic reaction will be much enhanced. Similar trends could well be observed for Ni [as well as Fe and Cr] in the presence of F or Cl. So far as the open circuit potential itself is concerned, changes in this should be mainly due to changes in the electrolyte environment or the anodic and/or cathodic reaction characteristics.

b) I feel more comfortable with the term “**critical potential range**” which would take into account the V-induction time characteristics of localized corrosion, where the t(ind) decreases as the potential increases anodically. This is shown clearly in Fig. 2, where the pitting induction time decreases as the potential at which the pitting experiment is conducted increases. For experimental and other details, see B. MacDougall and M.J. Graham, J. Electrochem. Soc. 131, p. 727 [1984]. In this Fig., it is remarkable that the prepassivated nickel samples containing chloride in the oxide film lattice are actually more resistant to pitting than those preformed in a system where incorporated chloride is avoided. This is an unexpected result that has never been fully explained, but is certainly interesting from the point of view of what gives rise to pitting resistance in an oxide film. Common sense would have suggested the reverse, but the results speak for themselves. An important observation here is the increase in induction time with decreasing potential, possibly suggesting that no matter how low the potential, pitting will occur if one waits long enough? It should be mentioned that the potential range observed here is the one where “sustained” pitting begins; once it does begin, it is quite difficult to arrest because of the “local” conditions within the pit [the so-called hysteresis effect]. The effective potential is always going to influence the tendency for pits to develop and grow, or repassivate; it is just that this potential may not remain the same as the nature of the passive film changes in character, along with the fact that it will also depend on the period of time we are willing to wait?

c) An important question concerns the possibility of the open-circuit [OC] potential increasing during the long term to values which might be dangerous for the induction of pitting or crevice corrosion. The OC potential will be determined by the mixed cathodic/anodic processes occurring, the former likely being some form of oxygen reduction and the latter being [passive] dissolution of the alloy. Polarization of the cathodic reaction should move the OC potential

negatively [if the anodic reaction remains unchanged] while polarization of the anodic reaction should move it positively [if cathodic reaction is unchanged]. Indeed, at the workshop there was discussion about the long-term dangers associated with the anodic reaction slowing down as the passive film becomes more protective with ageing, and the possibility of an associated increase in the OC potential. But the real situation is probably quite complex, especially from the point of view of the oxygen reduction reaction, which occurs in two 2-electron stages, initially to peroxide and then to water. In alkaline solution, the potential of the first is -0.065V , the second is 0.867V , and the overall 4-electron process is 0.401V [remember that in acid solution, the overall process has a theoretical reversible potential of 1.229V , whereas the highest actual potential usually observed is 0.98V , for various reasons]. It should be remembered that the oxygen reduction reaction [ORR] is the critical cathodic reaction occurring in a hydrogen/oxygen fuel cell at a noble metal catalyst; however, in that system the idea is to have the highest positive potential possible for the cathodic reaction, even under current load. While there are distinct differences with the “corroding systems” under discussion here, the fuel cell researchers have made major advances in understanding the kinetics and mechanism of the ORR, and this information is possibly useful for corroding systems. To prevent localized corrosion, it is best to have the cathodic reaction occurring at the least positive potential, in other words one should avoid the peroxide to water conversion from controlling the potential. Now it is known that on bare iron at pH's between 6 and 8, the oxygen reduction goes via 4-electrons to OH^- ; on passive iron, mainly the 2-electron reduction to HO_2^- occurs [V. Jovancicevic and J. O'M. Bockris, *J. Electrochem. Soc.* 133, p. 1799 [1986]; also E. Yeager, *J. Mol. Catal.* 38, p. 5 [1986]]. Indeed, the exchange current for this 2-electron reduction is reported to be 8-orders-of-magnitude higher than that for the 4-electron process, meaning that one can produce a lot of peroxide on the passivated surface. Another publication [H.S. Wroblowa and S.B. Qaderi, *J. Electroanal. Chem.* 279, p. 231 [1990]] suggests that the oxygen reduction reaction on iron in alkaline solution stops at the HO_2^- stage with a passive film but goes completely to OH^- on a surface covered by a prepassive film [ie. the passive film in its very early stages of development]. It thus appears that the reaction mechanism is quite sensitive to the state of development of the passive oxide film on iron. What are the implications of these observations, ie. are there significant changes in the kinetics and mechanism of the cathodic reaction as the reacting alloy-22 surface changes and the passive oxide film develops and ages with time? If nothing else, it certainly does indicate that the condition of the alloy-22 surface is potentially as important for the cathodic reaction as it is for the anodic reaction [perhaps not surprising when one considers that both reactions are occurring on the same surface].

The generation of peroxide during the ORR is usually detected with a rotating ring-disc electrode [RRDE], the peroxide being generated at the disc as working electrode and detected at the ring. At the workshop, there was some discussion of the fact that peroxide was not detected in this system, but my reading of the literature on this subject indicates that peroxide is sometimes generated but not detected simply because the peroxide reaction [either decomposition or further reduction] is quite fast. Also, there was discussion about the level of peroxide possibly being in the ppm level. But one must remember that the solubility of oxygen in water is only 8ppm at its maximum, so we are not dealing with really large amounts of these species dissolved. However, the influence of these small amounts of dissolved species is enormous, as witnessed from the effect that this level of dissolved oxygen has on so many corrosion reactions. It might be an idea to do a few experiments on the oxygen reduction reaction using alloy-22. Both cathodic

polarization and OC potential measurements could be done on well-passivated alloy-22, and this should not take a lot of time. One should compare the results with the classic ones obtained on oxide-free and oxide-covered Pt, as well as Fe in its active and passive state, to see if there are major differences so far as the potential is concerned. One should look for higher potentials than are normally observed.

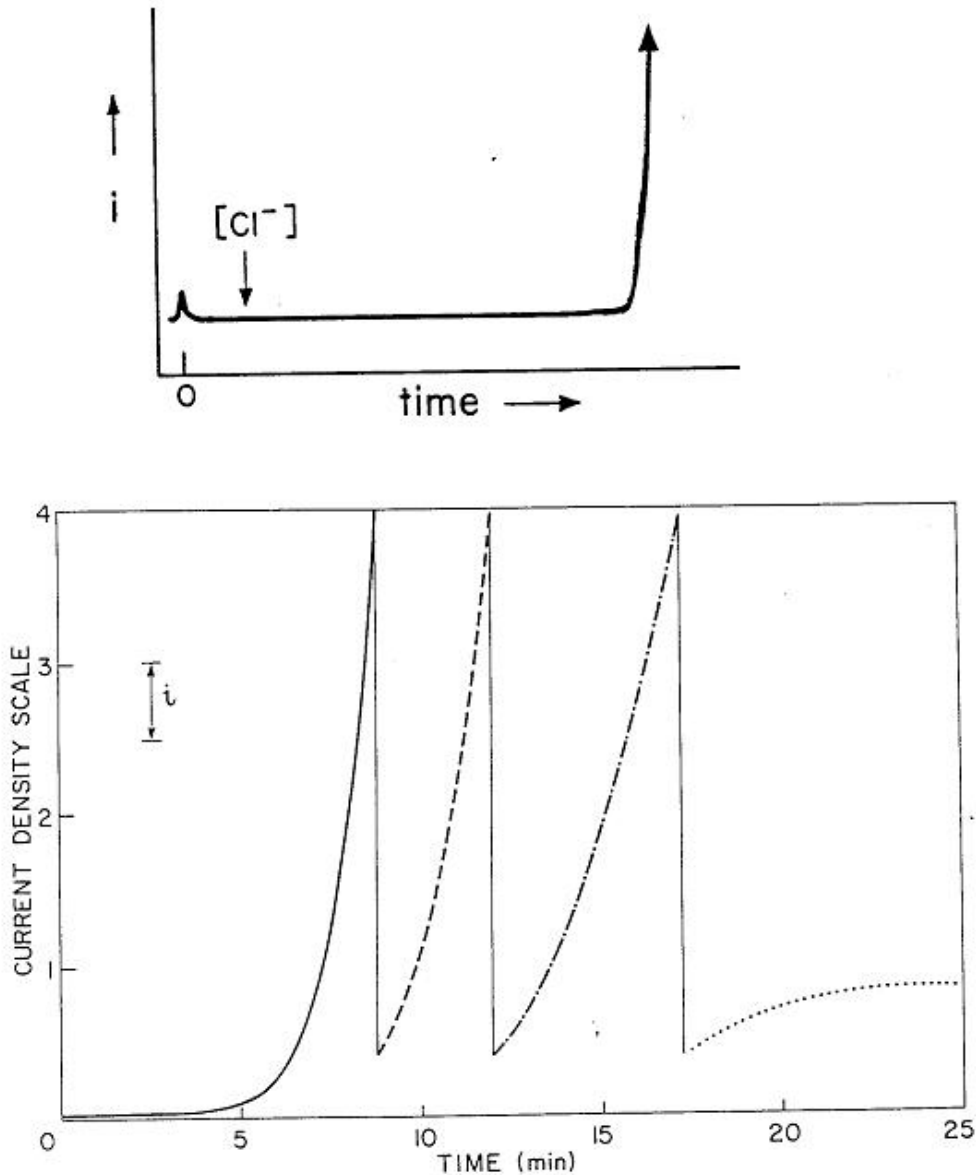


Fig. 1 TOP. Current density vs. time plot for a passivated Ni electrode in pH 3.0 Na₂SO₄ to which chloride ion was injected at time 0; after a certain induction time, the anodic current begins to increase exponentially as pitting corrosion commences. BOTTOM Similar profile but in this case a fluoride solution was injected at time 0; current increase is gradual with time; note that the current sensitivity scale is decreased at various times by a factor of ten so that the current will continue to fall within the scale.

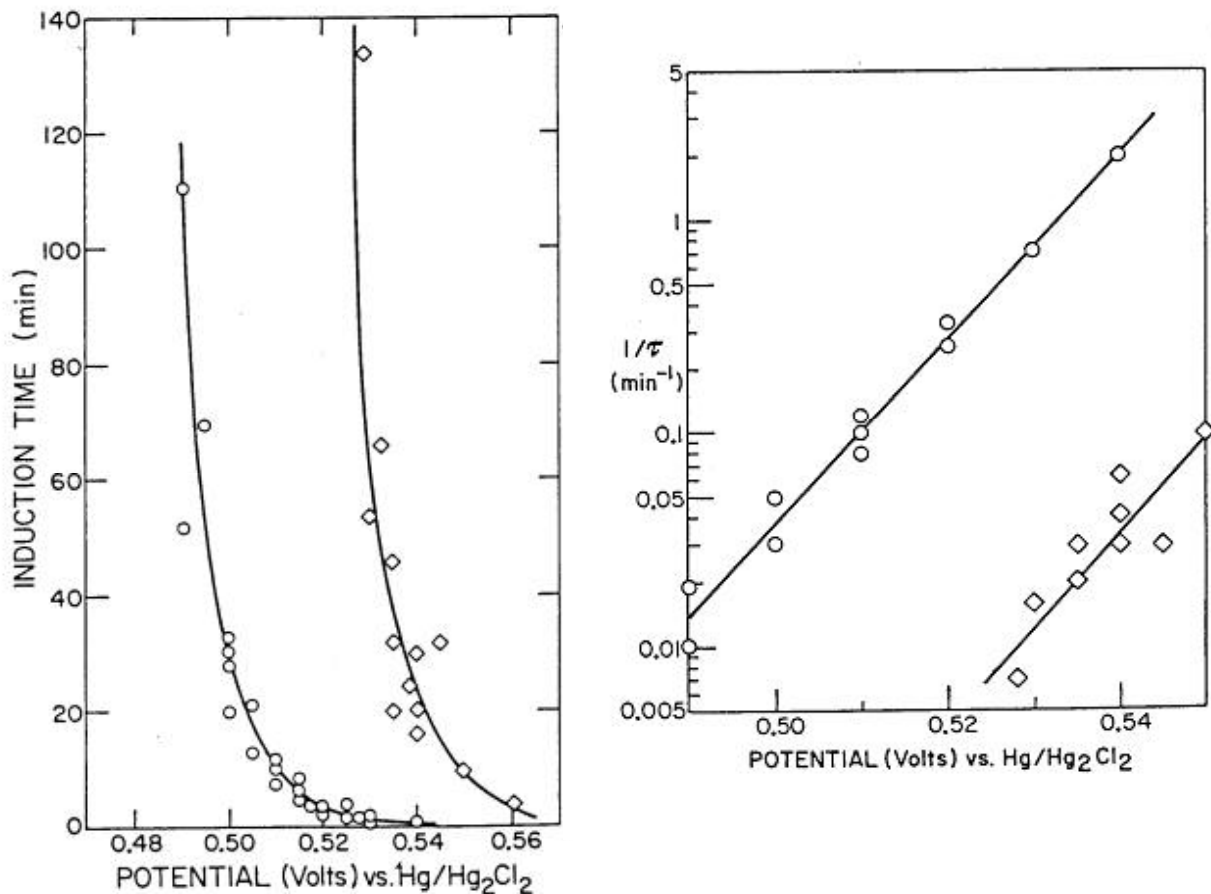


Fig. 2 LEFT. Variation of induction time for chloride induced pitting of previously passivated nickel in pH 4 Na₂SO₄ as a function of anodic potential; circles represent nickel previously passivated in background solution only while diamonds represent results for nickel sample prepassivated in chloride containing solution. In the latter samples, chloride is incorporated in the passive oxide film, however, these samples are actually more resistant to pitting than the ones prepassivated in the absence of chloride. RIGHT. Previous results plotted in a logarithmic fashion showing more clearly the decrease of pitting induction time with increasing anodic potential.

Long Term Extrapolation of Passive Behavior

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Introduction

In the Yucca Mountain project of repository for high-level nuclear waste, the outer shell of the waste packages consists of Alloy 22 (Ni59, Cr20.4, Mo14.1, W3.2, Fe2.3). With a wall thickness of 20 mm, the time-averaged rate of uniform corrosion must be $< 1\mu\text{m}/\text{year}$ in order to ensure a life-time largely exceeding 10 000 years. Alloy 22 is normally protected against corrosion by the presence of a thin passive film. Thus the passive film must be maintained over $> 10\ 000$ years to achieve the desired protection.

This short paper is a contribution to the review of critical issues in the long term extrapolation of passivity breakdown and localized corrosion of Alloy 22, which was the theme of a workshop organized by the NWTRB in Washington DC on 19-20 July 2001.

Nature of the passive film: chemical composition, structure, growth mechanisms

Since the protection of the waste package against corrosion will rest, to a very large extent, on the properties of the passive layer on the outer Alloy 22 shell, it is essential, for the prediction of the long term behavior, to have data on the chemical composition and the structure of the passive layer. A good understanding of the growth mechanisms is also important, not so much for the initial passivation, but rather for the repassivation that would be necessary in case of local breakdown of the passive film (repassivation, or the re-growth of the passive oxide layer, is a major issue in pitting, crevice corrosion, and stress corrosion cracking).

Composition of the film

The passive film formed on nickel base stainless alloys is known to be significantly enriched with chromium oxide with respect to the nominal chromium content of the alloys. As an example, the passive film formed on Alloy 600 in acid solution at room temperature consists of 95 % Cr₂O₃ in the inner oxide layer [1]. The outer hydroxide layer contains a large fraction of Cr(OH)₃ (data obtained by X-ray Photoelectron Spectroscopy). There are, to my knowledge, no published data on quantitative measurements of the composition of the passive film on Alloy 22 under the conditions of the Yucca Mountain repository site. However, SIMS and AES data (sputter depth profiling) presented at the workshop confirm the enrichment of chromium in the passive film. The presence and content of Mo and/or W in the film remain to be investigated.

Composition of the alloy underneath the passive film

Under the passive film, a layer of modified composition is usually present on stainless steels as well as on nickel base alloys [2]. This layer would be exposed to the environment in case of local passivity breakdown, and is therefore important for the repassivation behavior of the alloy. There are no available data on this aspect for Alloy 22.

Structure of the passive film

There is increasing evidence that passive oxide films on Ni, Fe, Cr and stainless steels are crystalline [2-4]. On stainless steels, the preferential growth of the basal plane (0001) of α -Cr₂O₃ has been observed [3,4]. Crystalline films are not formed instantaneously, and it has been demonstrated that crystallisation of passive films is potential and time dependent [2-4]. Crystallisation during ageing of passive films, together with Cr³⁺ enrichment in the passive film, appear to be beneficial for the resistance to localized corrosion in chloride solution, but there are of course no data for time scales of the order of the one of interest for nuclear waste packages.

Dissolution (corrosion) in the passive state

Passive dissolution is thought to be uniform on a macroscopic scale. This is the basis for the extrapolation of material loss over time periods of 10⁵ years and more. Direct dissolution of cations after transport through the passive layer, and dissolution of the oxide at the passive film surface are the two dissolution processes involved in the passive dissolution. On a microscopic scale, it has recently been observed on Ni [5] that the dissolution of the oxide surface is a localized process taking place preferentially at step edges where the atoms have a low coordination. The degree of localisation of the passive dissolution process involving direct dissolution of cations after transport through the oxide layer is not known.

Two points for the prediction of the long term behavior of passive surfaces appear to be important according to the above considerations on the mechanisms of passive dissolution:

- an increase of the surface and interface roughness inherent to the localized passive dissolution,
- an accumulation of vacancies below the passive film, also inherent to the passive dissolution.

Anodic segregation of sulfur at the alloy/passive film interface

Among the mechanisms that may cause the long term corrosion rate to increase or even lead to passivity breakdown and localized corrosion, I would like to emphasize the accumulation of sulfur at the alloy/passive film interface (the so-called anodic segregation of sulfur).

The concept of anodic segregation was first proposed after the discovery that sulfur present as an impurity in the bulk of Ni and of Ni-25Fe alloys is enriched on the surface during anodic dissolution [6-8]. This phenomenon was also observed on Fe-50Ni [9] and on Alloy 600 [10,11].

The mechanism is the following: sulfur present in the bulk accumulates on the surface during the dissolution of the metal. In the active state, the mechanism is schematically represented in Figure 1.

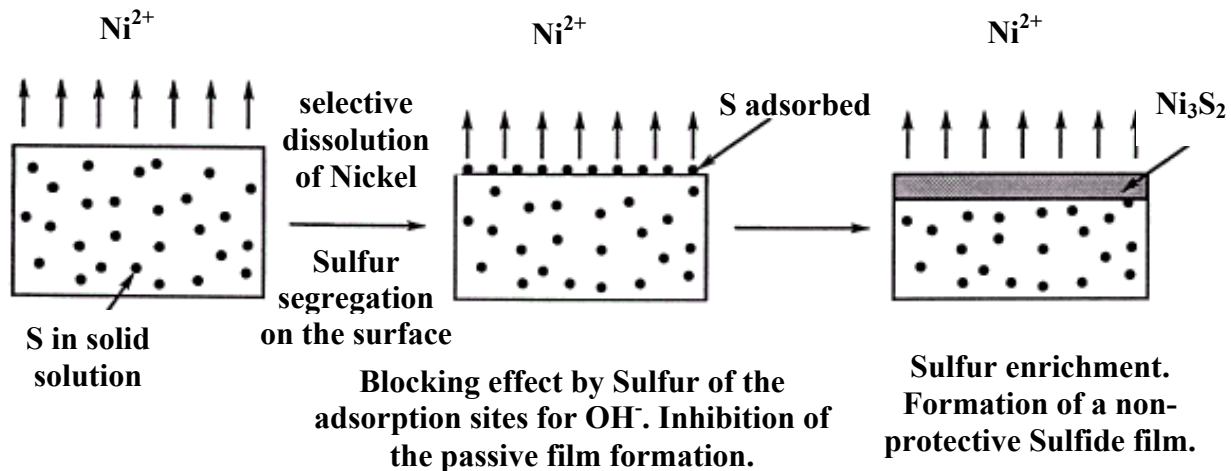


Figure 1: The mechanism of anodic surface segregation of sulfur

Anodic segregation of sulfur also occurs, in the passive state, at the alloy-passive film interface. Indeed, after the formation of the passive film on a bare metal surface, slow dissolution of the metal cations continues, involving dissolution at the passive film surface and transport of ions through the oxide. The question then arises as to where the bulk impurities, e.g. sulfur, go during this process. This question was addressed in a detailed investigation of Ni and Ni-Fe alloys which were doped with radioactive sulfur in order to trace the path taken by the sulfur atoms during the slow dissolution in the passive state [12]. The radiochemical results gave direct evidence that sulfur present in the bulk accumulates at the metal-passive film interface. The enrichment rate was shown to be proportional to the sulfur content in the metal and to the dissolution current density. Above a critical concentration of sulfur at the interface (metal-oxide), breakdown of the passive film was observed. This critical concentration of interfacial sulfur was measured with radioactive sulfur and found to be close to one monolayer of sulfur (i.e. $\sim 40 \times 10^{-9} \text{ g/cm}^2$). The loss of adherence (or decohesion) at the interface for this critical coverage has been attributed to a weakening of the bonding of the oxide to the substrate caused by sulfur. The nucleation of the sulfide which is expected to take place when the sulfur concentration exceeds a complete monolayer may be responsible for the observed local breakdown of the film and pitting. The defects which are likely to exist at the interface could serve as specific sites for the nucleation of the sulfide, once a quasi-complete monolayer of sulfur has been accumulated at the interface. A

schematic representation of the proposed mechanism of the sulfur-induced breakdown of the passive film is shown in the following figure.

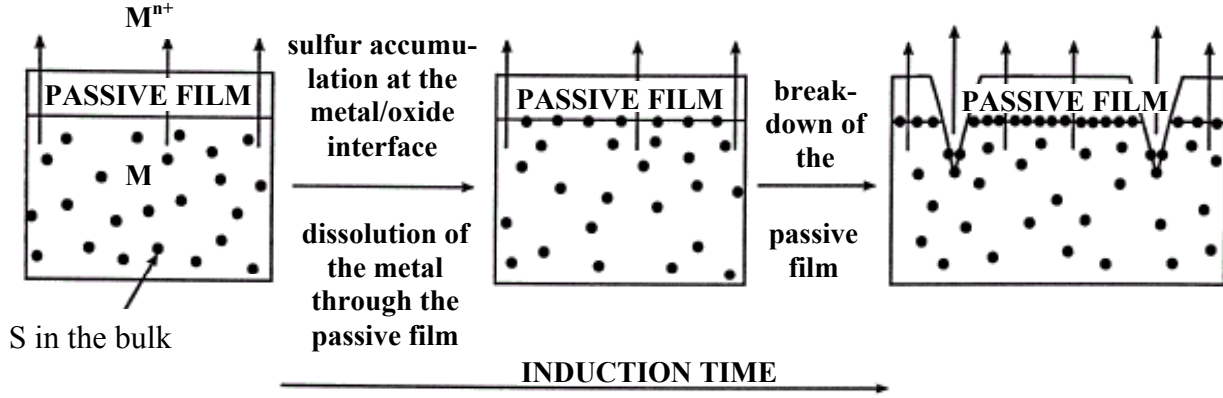


Figure 2: The mechanism of anodic interfacial segregation of sulfur and passivity breakdown

Assuming that all the sulfur present in solid solution in the alloy accumulates at the interface, the concentration of sulphur at the interfaces, $\Theta_s^{\text{interf.}}$, can be expressed in the following way:

$$\Theta_s^{\text{interf.}}(t) = \frac{MS}{nF} \int_0^t i dt,$$

where t is the time, i the current density, n the number of electrons exchanged in the reaction, F the Faraday constant, M the atomic weight of the metal and S the concentration of sulfur in the metal.

The induction period, τ , for passivity breakdown can be defined as the time required to reach a threshold concentration $\Theta_{s, \text{max}}^{\text{interf.}}$ above which breakdown of the film occurs because additional sulphur cannot be accommodated at the interface. The threshold concentration is therefore given by:

$$\Theta_{s, \text{max}}^{\text{interf.}} = \frac{MS}{nF} \int_0^{\tau} i dt.$$

The induction time τ can be expressed as $\tau = (\Theta_{s, \text{max}}^{\text{interf.}} nF)/(iMS)$, assuming that the current density, i , does not change as long as the sample remains passivated. It has been shown for nickel that $\Theta_{s, \text{max}}^{\text{interf.}}$ is in the monolayer range, i.e. of the order of $40 \times 10^{-9} \text{ g cm}^{-2}$. Using this value, the equation above can be used to calculate an approximate value of τ in other systems.

Whether this could occur on Alloy 22 under repository site conditions is not known. If we assume that for Alloy 22 all the sulfur contained in the material that is dissolved during passive dissolution accumulates at the alloy-passive film interface, and that the critical interface concentration causing passivity breakdown is of the order of a monoatomic layer, the time to passivity breakdown can be predicted using the above equation. Assuming that the S content is 5ppm and the passive current density is 1 nA cm^{-2} , the time to passivity breakdown τ , is predicted to be ~ 900 years. The occurrence of repassivation of the depassivated areas or of pitting corrosion would then depend on other factors including the composition of the exposed alloy surface, the presence of corrosive anions in the aqueous layer, the pH and the temperature.

Other aspects

In dry conditions a thicker oxide is likely to be formed at higher temperature ($\geq 160^\circ\text{C}$ i.e. in the “hot” case). A major problem could be the presence of a water layer with high concentration of salts at relatively high temperatures. In addition, the behavior of this thicker oxide, when further exposed to cool and humid conditions, is not known. The lack of data makes it difficult to make a rational comparative analysis of the two situations (hot *versus* cold cases).

There are many other factors that are not examined in this paper, but that other workshop panelists will consider in their reports including the metallurgical factors (inclusions, intermetallic precipitates, microstructure), and crevice corrosion, which may well be the major threat due to the presence of deposits on the waste package surfaces. It is to be noted that stress corrosion cracking was not within the scope of the workshop.

Concluding remarks

In this short paper, critical factors in the long term behavior of passive films on alloys for high level nuclear waste packages have been examined. The emphasis was placed on the chemistry and structure of passive films, on the mechanisms of passive dissolution and on the anodic segregation of sulfur at the alloy/passive film interface, which may be a cause of passivity breakdown after extended periods of time. More data would be necessary for predicting the long term behavior of passive films on Alloy 22.

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WHAT IS THE WORST THAT COULD HAPPEN TO A C-22 CONTAINER DURING 10,000 YEARS EXPOSED TO DRIPPING GROUNDWATER?

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The two questions that were posed to the workshop participants relate to *passive dissolution* and to *localized corrosion*. Essentially we were asked: could either of these modes of corrosion be facilitated by slow processes acting over the 10,000 year performance period of an Alloy 22 nuclear waste container, in ways that would not be apparent in short-term corrosion testing?

There are conventional corrosion processes that could lead to perforation of a waste container, and there are unconventional or even fantastic ones. Our problem, in part, is that few of the latter are directly testable. However this should not deter us from recommending a vigorous program of electrochemical evaluation of samples that have been immersed for several years in relevant environments. Five years is a lot shorter than 10,000 years, but we should remember that most corrosion kinetics slow down with time: pit depth (h) is commonly reported to increase with time as $h \sim t^m$, with $m = 0.3-0.5$. If we take $m = 0.33$, just for illustrative purposes, then after 5 years h would already be more than 7% of its value after 10,000 years! Admittedly this is for immersed conditions, and we can anticipate that atmospheric pitting would grow more linearly with time, especially as the growing corrosion product layer traps electrolyte and might reduce the solution resistance between anode and cathode (but since this scenario is for unrestrained dripping on to the container, the evaporite layer would be massive anyway). Some Japanese work suggests that this speculation may be valid¹.

Uniform Corrosion

The long-term passive dissolution of an alloy like C-22 in an immersed situation could produce a redeposited corrosion product layer at least on the order of microns in thickness, since Cr(III) has significant solubility at the relevant pH values (significant in this context being anything greater than ca. 10^{-14} M). It is possible that this layer will suppress cathodic activity, but we have no data on that. In a thin-film electrolyte there would be rapid saturation with Cr(III) and the passive current would be correspondingly lower (although the solubility would be higher for most models of the thin-film chemistry, which would balance the situation somewhat).

¹ T. Yoshii, M. Nishikawa and K. Hayashi, Atmospheric Corrosion Resistance of Stainless Steels Evaluated From Ten Years Atmospheric Exposure Tests, *Nisshin Steel Tech. Rep.*, no. 59, pp. 54-67, Dec. 1988.

If I define “increase in passive corrosion rate” as a completely uniform concept, not allowing any separation of anodes and cathodes under the porous outer layer of corrosion product, then I cannot see any way of triggering an alarmingly high uniform corrosion rate except *transpassivity*. There are several ways of looking at this issue, which I summarize briefly below:

Increase of the corrosion potential by the long-term operation of familiar processes

This achieves a high potential by virtue of a steady decrease of the anodic passive current density, without any increase in the oxygen reduction kinetics, which may stabilize or even slow down with time. Clearly the worst that can happen is that the potential will stop rising when the passive current levels out (owing to the onset of a minuscule level of transpassivity).

Progressive catalysis of the cathodic reaction

In this case oxygen reduction remains the predominant cathodic reaction, but is catalysed by substances that short-circuit the passive film. These may be plated out from the environment – e.g. noble metals. A more interesting possibility is that long-term passive dissolution may lead to metallic conduction at discrete sites on the surface. In this respect one can anticipate that transpassive dissolution under open-circuit conditions will have some degree of autocatalytic character, since it may produce a more conducting, catalytic surface.

Presence of peroxide

There is little doubt that peroxide, especially in alkaline media, can promote transpassivity of nickel-base alloys, not at the mm-per-year rates seen in bleach plant in the 1980s, but at rates of microns per year that might present a risk of perforation in 10,000 years.

I defer to radiation chemistry experts as to the amounts of peroxide that can be produced. I believe fluoride, which is present in Yucca Mountain, can stabilize peroxide as it complexes the heavy-metal cations that catalyse peroxide decomposition.

Molybdenum transpassivity

So far we have implicitly been considering chromium transpassivity, in which Cr(III) oxide dissolves oxidatively as Cr(VI). At one time there was controversy in the pulp and paper community as to whether Cr or Mo transpassivity was responsible for uniform corrosion of Alloy C-276, but it now appears that the potential has to rise to the Cr transpassivity region. Mo transpassivity appears to be transient, although it certainly does not do the passive film any good to have persistent dissolution of Mo, and the passive current remains relatively high for a long time. The open-circuit potential will remain for a long time at the knee on the current-potential curve where this Mo transpassivity occurs, then when all the Mo has gone from the surface it may rise to allow limited Cr dissolution.

Needless to say, all these processes will be limited in extent in a thin-film electrolyte.

Localized Corrosion

Essentially we are concerned with any behaviour that might undermine the $E_R(\text{crevice})$ concept developed by Tsujikawa². This is a very powerful approach, especially for austenitic stainless steels where it pertains to stress corrosion cracking as well as localized corrosion failure. In atmospheric conditions near the MgCl_2 dry-out point (about 30% RH) SCC of these materials can occur even at room temperature³. Alloy C-22 is not known to crack under such conditions. I can see several ways in which $E_R(\text{crevice})$ might be non-conservative in the present case:

The “intelligence” of localized corrosion

One should never underestimate the ability of localized corrosion sites to remain stable when a one-dimensional analysis would suggest that they must repassivate because the dissolution rate cannot retain a “critical” chemistry within the site. When I was at Brookhaven National Laboratory we carried out some intriguing experiments with a group of MIT undergraduates⁴. Using artificial pit or “pencil” electrodes, we explored the differences between current control (approximating to open-circuit corrosion) and potential control. We found that there was a large difference in behaviour near the repassivation condition. Potentiostatic experiments showed a sharp repassivation potential and critical current density to maintain stability, but under galvanostatic conditions the corrosion would remain stable at lower currents and potentials. When this happened the surface became porous and the corrosion propagated under the surface. Later I applied the same general thinking to the tunneling corrosion of aluminum, which is another example of a metal “intelligently” using a limited current to grow a convoluted localized corrosion interface⁵. Such phenomena will lower the effective value of $E_R(\text{crevice})$ to essentially the open-circuit potential of the metal in the local environment, in a sufficiently occluded geometry. They may also promote very sharp localized penetrations. At this point we do not know how much such considerations will alter our thinking that is currently based on $E_R(\text{crevice})$.

Surface deposits, corrosion products and membrane effects

Under-deposit corrosion is often assumed to be similar to or less damaging than conventional contact-type crevice corrosion. I cannot agree with this simplification. As argued by Sato, and demonstrated in my own group for FeOOH on stainless steel⁶, there is something peculiarly aggressive about membranous metal hydroxide layers, which seems to be associated with anion-selective properties. Similar properties are exhibited by extracellular polymers, produced by bacteria, and may be implicated in freshwater microbial corrosion. Anion-selective deposits are spectacularly more aggressive than contact crevices in low-chloride media. This “super-crevice”

² Tamaki, K; S. Tsujikawa and Y. Hisamatsu, in *Advances in Localized Corrosion*, pp. 207-214, NACE, Houston (1990).

³ S. Shoji, N. Ohnaka, Y. Furutani and T. Saito, Effects of Relative Humidity on Atmospheric Stress Corrosion Cracking of Stainless Steels, *Boshoku Gijutsu (Corros. Eng.)*, **35**, 559-565 (1986).

⁴ G.T. Gaudet, W.T. Mo, J. Tilly, J.W. Tester, T.A. Hatton, H.S. Isaacs and R.C. Newman: Mass transfer and electrochemical kinetic interactions in localized pitting corrosion, *AIChE Journal*, **32**, 949-958 (1986).

⁵ R.C. Newman: Local chemistry considerations in the tunnelling corrosion of aluminium. *Corros. Sci.*, **37**, 527 (1995).

⁶ M.I. Suleiman, I. Ragault and R.C. Newman: Pitting of stainless steel under a rust membrane at very low potentials. *Corros. Sci.*, **36**, 479-486 (1994).

action seems to be due to the combination of a relatively low solution resistance for current flow out of the corrosion site, coupled with efficient retention of the aggressive anolyte within the site.

The gradual development of a deposited outer hydroxide layer on top of the passive film will promote localized corrosion at potentials significantly below $E_R(\text{crevice})$. The resulting corrosion will resemble either pitting or crevice corrosion depending on the spatial variation of the membrane thickness, location of cathodic sites, variation in the thin-film electrolyte, etc.

Environment development in thin layers resulting from dripping

The investigations carried out to date have not exhausted the possibilities for development of aggressive media locally on the container surface. One can readily imagine water running down the side of a container and depositing different salts at different places. This separation process might even concentrate some trace impurity like bromide, which is very aggressive as it complexes with Mo and eliminates its beneficial effect on localized corrosion. This sounds far-fetched but deserves at least passing attention. In any event, it is not hard to imagine the development of a strong chloride solution by this mechanism, and one might not be able to rely on the inhibiting effect of nitrate.

To the extent that lead or reduced sulfur deposition represents a potential danger, one would have to consider how much could accumulate by this kind of evaporative mechanism, and whether a fractionation process would occur leading to a high local concentration.

To conclude, the most credible dangers for the containers, apart from stress corrosion cracking, are transpassive corrosion and localized corrosion under a membranous metal hydroxide layer. The latter causes me much more concern at present.

REPLY TO QUESTIONS ON LONG-TERM PASSIVITY AND LOCALIZED
CORROSION OF ALLOY 22

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

When the passive current increases with time, one usually attributes it to a change in composition of the electrolyte. This can occur within the service environment for a host of reasons. It is even more likely within confined regions such as under dirt or debris that settles on the material's surface. This behavior is shown during the first 14 hours for iron in Figure 1, during which time the current increases by nearly an order of magnitude but is still quite low in the passive region. The increase in passive current in Figure 1 occurred on the wall of a crevice rather than on the outer (clean) surface of the iron

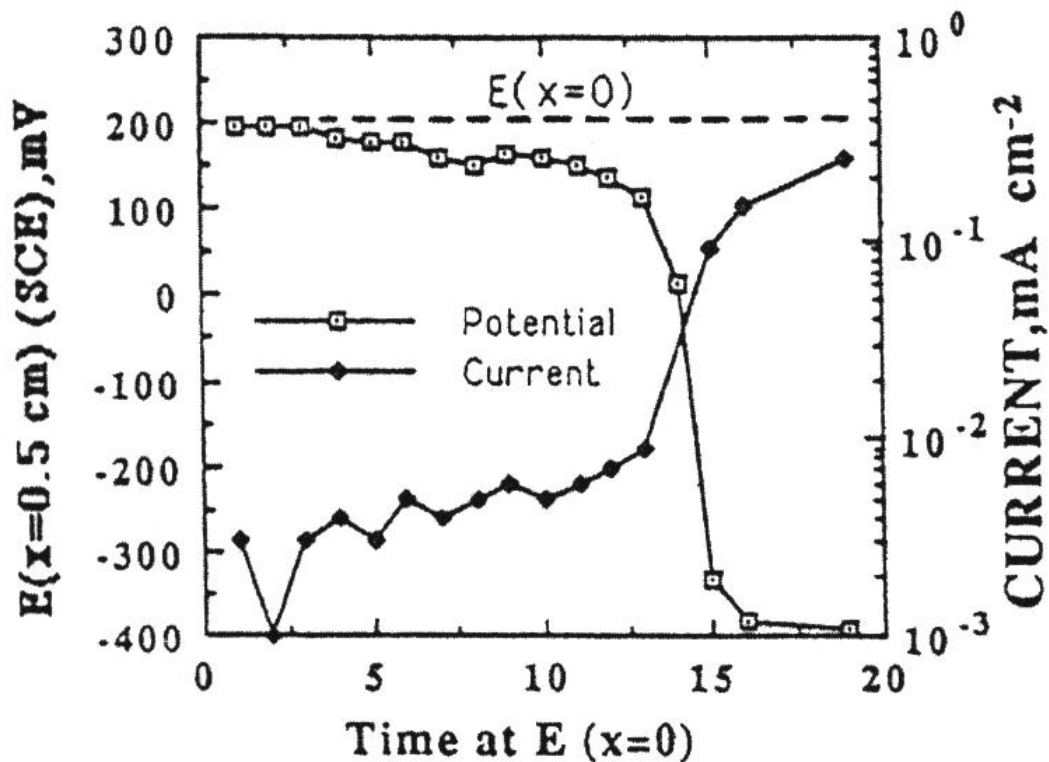


Figure 1. In-situ measured $E(x)$ and I data inside a crevice during the induction (0 to 14 hr) and crevice corrosion (14 to 20 hr) periods using a two-stage crevice design. Iron in pH 10 solution.¹

sample. Only certain chemical species degrade the passive film in this way, and it can take some considerable time to identify these species for any given alloy. Since the mechanism of the degradation is unknown, there are only a few generalizations available to hasten the discovery process. Without a full knowledge of these species, considerable risk can be associated with the use of a newly developed alloy in a particular service environment. In the early days of nuclear reactor construction, Inconel, a nickel based, corrosion resistant alloy, was developed for its better resistance to corrosion and in particular to stress corrosion cracking (SCC), compared to other corrosion resistant alloys of its time such as stainless steel. Safe containment was predicted for the life of the reactor since water was the environment and Inconel had shown excellent resistance to corrosion in some very aggressive environments, including resistance to SCC. It was only a short time into the life of the reactor before cracks developed in the Inconel tubes. This was a serious threat to the continued safe operation of the reactors. The potential for permanent shutdown (or worse) was avoided by improved control of the water's impurities.

At least one species (sulfur) has already been suggested as potentially degrading to the passive film of Alloy 22 at this workshop (P. Marcus). The specter of biological activity adds to the uncertainty. No reassuring data were presented at the work shop to indicate that passive film degradation need not be considered as a major concern, especially when one considers that an order-of-magnitude increase in the passive current means an order-of-magnitude decrease in lifetime due simply to thinning of the container wall. In the next few years much could be learned about the identities of aggressive species for Alloy 22.

However, identifying and testing aggressive species will only be part of the answer, since there remains the uncertainty of extrapolating to exceedingly long times using results from accelerated laboratory tests. This is particularly perplexing since the mechanism of the degradation is unknown. Furthermore, there are at least two known forms of passive film degradation (and thus also two mechanisms) and both have to be considered for Alloy 22. One is the classical random site degradation that occurs at relatively high overpotentials and leads to pitting corrosion. The other is a general degradation. The latter occurs at low overpotentials (as in Figure 1 during the first 14 hours) and leads to the development of an active region in the polarization curve. General degradation is also known to occur at higher overpotentials, in which case a higher general (uniform) passive current density is observed. Both forms can occur (simultaneously) on the covered (crevice) surface, be caused by a change in either or both the local composition of the occluded environment and the local electrode potential between the surface and covering debris, and be readily monitored with currently available laboratory techniques using specially designed crevice systems. In addition to Alloy 22, some data could be obtained for nickel, its major component, in order to obtain a more complete data base. Nickel would allow for the use of more open crevices for which microprobes could be used to obtain data inside the crevice of the kind shown for iron in Figure 2.

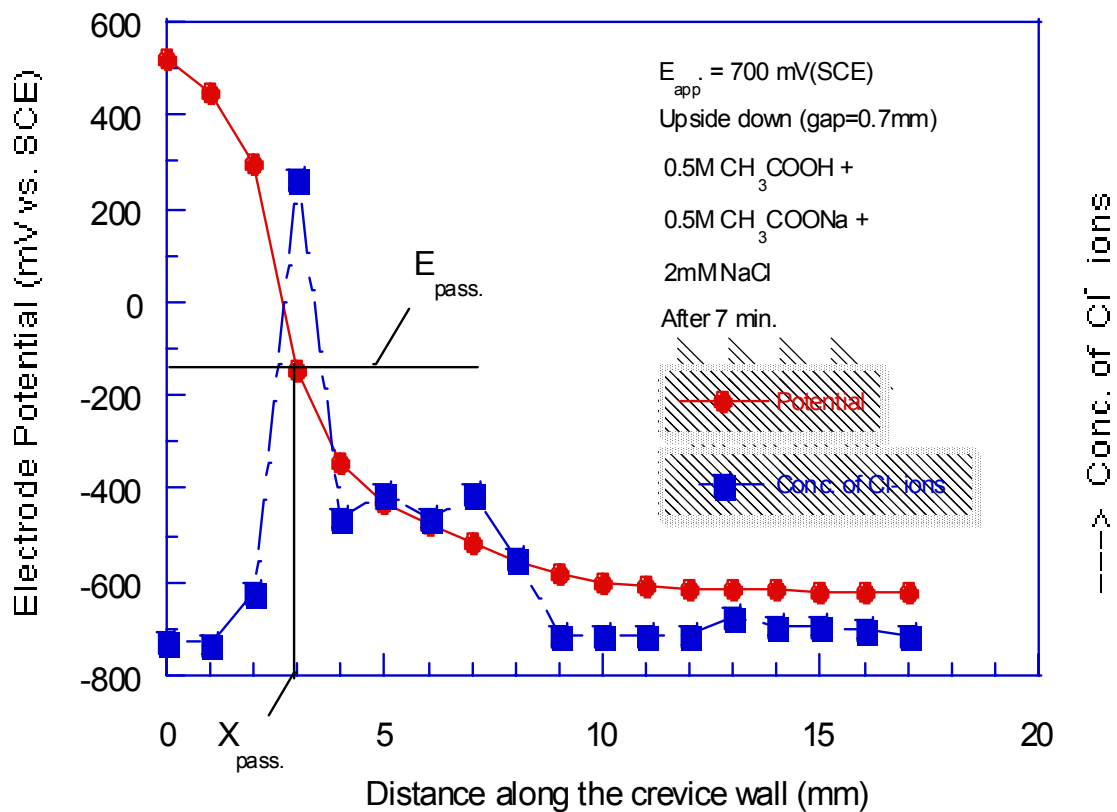


Figure 2. In-situ measured $E(x)$ and $[\text{Cl}^-](x)$ profiles using the potential and chloride microprobes in an iron crevice undergoing crevice corrosion. $E(x)$ varied with distance into the crevice by 1.1 volt. The chloride concentration at one distance into the crevice ($\sim x_{pass}$) was an order of magnitude higher than the lowest measured concentration in the crevice. The bulk solution was 2 mM in Cl^- ion.²

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

The cause of passive film degradation mentioned in No. 1, which leads to progressively increasing passive currents (first 14 hours of Figure 1), can also lead to other forms of corrosion and cracking. After 14 hours of gradually increasing passive current in Figure 1, the current increases much more steeply with time to a much higher (orders of magnitude) value in the mA range. Such a high current is indicative of active dissolution on the crevice surface, i.e., at approximately 14 hours the passive film, on a region of the crevice surface which was at low overpotentials, became completely unstable and crevice corrosion began on this unprotected region of the crevice wall. The occurrence of crevice corrosion was confirmed by observation of the crevice wall in-situ during the experiment and afterwards under the microscope.

The changes in solution composition that caused the gradual degradation of the passive film during the 14 hour induction period presumably also led to the onset of crevice corrosion at 14 hours which continued to the end of the experiment. The other information in Figure 1 is the in-situ, simultaneously measured electrode potential at the halfway distance into the 1.0 cm deep crevice, $E_{x=0.5}$. The $E_{x=0.5}$ value is 600 mV less noble than the applied potential at the opening of the crevice, $E_{x=0}$, the latter of which was set with a potentiostat. Crevice corrosion occurred at the 0.7 to 0.8 cm distance into the crevice where $E(x)$ was equal to or less noble than the measured $E_{x=0.5} = -400$ mV_{SCE}. Thus, passive film breakdown occurred in the low overpotential region where active peaks typically form in the polarization curve, rather than at high overpotentials in the passive region where breakdown occurs at random local sites and leads to stable pitting corrosion. The former (low overpotential breakdown) is not understood, especially when it occurs inside crevices, and has received virtually no attention by researchers compared to the attention given in recent decades to the high overpotential passive film breakdown.

As in question 1, research on two fronts is needed, basic research to understand the low overpotential type of passive film breakdown, and research to determine if any of the chemical species anticipated in the Yucca Mt. repository site can cause passive film breakdown in the low overpotential region for Alloy 22. Some studies of this type have surely been already conducted but a more exhaustive study seems warranted, especially using creviced samples, for Alloy 22.

Part of the basic study would be to determine the role of hydrogen gas that forms inside the crevice where the proton discharge reaction occurs on the crevice wall. The first question to be answered is whether or not hydrogen gas forms inside crevices for nickel-based alloys, as it has been found to occur for other base metals. If it does, then the passive wall current, even at the very low 10^{-8} A cm⁻² value of Alloy 22, is sufficient to generate large IR voltages (10^2 mV) as reported at this workshop (Pickering). The way in which the gas promotes these large IR voltages is by forming especially tight crevices. Gas readily fills the spaces of poorly matching crevice surfaces. The resulting dimension

of the crevice that forms between the gas and the metal can, in principle, be of atomic dimensions. Hence, it is realistic to think in terms of 1, 10, etc., nm gap dimensions for crevices formed by gas. Considering for the moment that the likelihood exists for Alloy 22 to form tight crevices in the repository environment, the spectra of IR induced crevice corrosion becomes one of the more likely scenarios of localized corrosion for Alloy 22. Thus, more needs to be understood about how, and if, the chemical species that have been identified as aggressive to passive films (in the high overpotential region) contribute to passive film breakdown in the low overpotential region. An expanded search for aggressive species could accompany this study since other species (than those that cause breakdown at high overpotentials) could exist or form in the Yucca Mt. environment and cause breakdown at low overpotentials for Alloy 22.

For the basic study, nickel would be a good choice since it is the majority metal in Alloy 22. In addition to obtaining data for nickel as shown in Figures 1 and 2 for iron, the distributions of other potentially aggressive species, e.g., H^+ , S, etc., need to be determined as a function of time inside the crevice, along with the $E(x)$ profile and the location and morphology of the active corrosion on the crevice wall.

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POST-WORKSHOP REPORT ON

LONG-TERM EXTRAPOLATION OF PASSIVE BEHAVIOR

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Prior to analyzing any long-term corrosion rate or predicting a failure mode for Alloy 22 in the repository, one must make some assumptions about or at least provide some description of the chemical and thermal conditions corresponding to the service of the alloy. In that regard, especially since "cost" is essentially not an important issue, one can expect that the initial surface will be prepared in such a way to optimize the passivity and minimize both uniform and localized corrosion. Certainly in the most serious corrosion laboratory studies, alloy coupons are generally prepared by a chemical cleaning and initial passivation prior to electrochemical studies. Mechanical abrasion is not considered an adequate or reproducible initial state. Studies of scale growth on pure iron and steels in dry atmospheres at low temperature (300C) indicate that an abraded initial surface exhibits a parabolic oxidation rate constant which is about an order of magnitude higher than that for a chemically etched surface.¹ The mechanistic interpretation for this "surface preparation effect" involves the preparation of the surface to develop the interfacial dislocation structures for the epitaxially oriented oxide product on the metal.² The climb of these interfacial misfit and misorientation dislocations supports the annihilation of vacancies responsible for the growth rate and adherence of cation-diffusing corrosion product films or scales.³ Since the experimentally established uniform corrosion rate for Alloy-22 is expected to be insignificant, even for 10,000 years, the necessary scale adherence would be best developed by an initial chemical etch (or electropolish) and anodizing treatment. Perhaps during this surface preparation, some cerium oxide could be incorporated into the initial passive film, as even a minute amount of ceria is known to minimize chromia growth in both aqueous and dry oxidation.⁴ If necessary, the canister could be immersed and cleaned prior to loading of the radioactive waste and welding closure.

According to the service conditions for the canister in the repository, depending upon exactly how ventilation will be used to control the temperature, the Alloy-22 should begin service experiencing dry oxidation at a temperature less than 250C. It seems important that any laboratory aqueous corrosion testing (immersion or atmospheric) start from an initial surface with some air-formed film of the relevant thickness (even if its formation temperature is chosen to satisfy an accelerated test). Likewise, since the service conditions are likely to involve atmospheric corrosion with cyclic wetting and drying and the associated concentration of aggressive salts, and since such conditions should outweigh in importance any steady-state uniform corrosion damage for a fully wet surface, the lab testing should emphasize these atmospheric corrosion aspects. Probes have been designed to indicate the instantaneous rate of atmospheric corrosion.⁵ The use of such probes is recommended both for lab testing and later canister monitoring. If the use of ventilation can be manipulated prior to repository closure, one could consider permitting the Alloy-22 surface to remain hot and dry for as long as possible, and then introducing ventilation cooling to achieve surface wetting, with the avoidance of more damaging cyclic wetting and drying. Although I am not familiar with mechanistic studies where an initial chromia passive film is thickened/aged by extended dry oxidation, and then subjected to atmospheric or immersed aqueous corrosion, I would surmise that the warm/dry exposure would strengthen the metal/oxide interface and the associated scale adherence. But if the oxidation stage should result in scale fissures, these could represent preferred sites for pit initiation. The presence

or absence of such pits should be detectable using the logarithmic sensors for atmospheric corrosion.

The remarks presented above are relevant as a response to Question 1. From my knowledge of the laboratory studies completed and underway, I would suggest that the surface preparation and test sequencing may not have received adequate attention, nor has a sufficient effort been made to minimize (as opposed to studying) the expected corrosion.

Relative to the Question 2, concerning the attainment of electrode potentials which would support stable localized corrosion, the point was made that highly energetic gamma rays would escape the capsule and interact with wet debris on the canister surface. Such interactions could presumably create highly oxidizing species, peroxide receiving special mention, which could raise the surface potential. The lab testing seems to rely upon the presence of known buffering anions to limit such an increase in potential. Some future laboratory corrosion testing in which an aqueous film contaminated with representative debris is also subjected to gamma radiation would seem reasonable. Perhaps again, one can remark that the dangerous corrosion process is localized atmospheric corrosion, so that experimentation with coupon immersion is less relevant. Likewise, the weld area would certainly be the local area most subject to localized corrosion because of the variations in composition and structure inherent with welded zones. Often, this problem is compensated by the selection of a weld metal composition which is somewhat more corrosion resistant than the base metal. Since impurity, e.g. sulfur, segregation to grain boundaries and other interfaces must be expected to result from any heat treatment, the acceptance limits for such impurity concentrations must be tight and minimized for the Alloy-22 specification. New techniques have been developed to melt and cast Ni-base superalloys with minimal sulfur content, and these should be applied to the production of Alloy-22.

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ON LONG-TERM EXTRAPOLATION OF PASSIVE BEHAVIOR

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ABSTRACT: Under radiation conditions semiconducting p-type oxides, if formed on Alloy 22, will shift the open-circuit potential of the alloy in the anodic direction and cause passivity breakdown leading to a localized mode of corrosion in the alloy. Semi-conducting n-type oxides will shift the alloy potential in the cathodic direction and prevent the passivity breakdown, though increasing the probability of hydrogen damage in the alloy. In order to prevent the passivity breakdown due to p-type oxides application of the coating of n-type oxide layers such as TiO_2 on the Alloy 22 will be effective.

1. Long-Term Passive Dissolution

The accepted knowledge indicates that the passive dissolution current, i , of metals is controlled by the interfacial potential, $\Delta\Phi_{MO/S}$, between the passive film and the aqueous solution as shown in Eq. (1):

$$i = i_o \exp[(\alpha e \Delta\Phi_{MO/S})/k T] \quad (1)$$

The adsorption of hydrated anions and cations on the passive film changes the interfacial potential, $\Delta\Phi_{MO/S}$, probably forming surface complexes and introducing ionic and electronic defects in the film surface. The long-term change in the ion adsorption will thereby affect the uniform corrosion rate of passive metals. Further, the passive dissolution current will be affected by radiolytically produced oxidizing substances such as hydrogen peroxides in water as well as radiation-damaged solid-state defects in the passive film.

We assume, however, the change in the passive dissolution current due to the ion adsorption and radiation will not be very large, probably less than ten times or a hundred times in magnitude, provided that the adsorbed ions cause no passivity breakdown.

Since the passive dissolution rate is extremely small, no particular trouble may be expected to occur as long as the passive dissolution takes place in a uniform mode in the potential regime of passivity. We may encounter trouble, however, when the open-circuit potential of the passive metal goes up for some reason into the transpassive potential regime where the dissolution rate is much greater and becomes potential-dependent as the interfacial potential of $\Delta\Phi_{MO/S}$ increases with anodic polarization.

In order to measure extremely small corrosion rates in a short period of months or years it is necessary to apply a very sensitive instrument such as QCM (quartz crystal microbalance sensitive to nanograms, a few atomic layers) for infinitesimal amounts of weight change, though the stability of QCM measurements for months is a difficult problem to overcome.

2. Long-Term Preservation of Conditions Preventing Localized Corrosion.

The accepted knowledge predicts that the passivity breakdown occurs only when the electrode potential of passive metals is more anodic (positive) than a critical potential for the breakdown of passivity and subsequent localized corrosion. No alternative localized corrosion mechanisms other than those described in terms of a critical potential will be operative even in the long-term corrosion. For nickel-chromium stainless steels there are two critical potentials, the pit-initiation-repassivation potential and the crevice protection potential, of which the former is more positive than the latter.

The open-circuit potential of passive metals is usually determined by the environment in which they are placed. It is also affected by the presence of solid precipitates in contact with the metal surface. Semiconducting solids, in particular, change the open-circuit potential of passive metals depending on their semiconducting property. Semiconducting solids set their electrode potential close to the flat band potential, provided that no ionic transfer occurs at the solid/aqueous solution interface. For metal oxides the flat band potential is more anodic in case of p-type oxides and more cathodic in case of n-type oxides than the corrosion potential of passive metals.

It might happen during the long-term storage of nuclear wastes that semiconducting oxides are formed for some reasons and brought into contact with the Alloy 22 of the canisters. Then, the open-circuit potential of passive Alloy 22 will change.

As shown in Fig. 1, p-type oxides tend to shift the open-circuit potential of passive metals in the anodic (positive) direction, which is enhanced when radiation produces a sizable sum of excited electron-hole pairs in the semiconducting oxides. A possibility will then arise that, when brought in contact with p-type oxides such as NiO, Alloy 22 shifts its open-circuit potential in the anodic direction beyond the crevice-protection potential or the pit-initiation potential and will suffer as a result a localized mode of corrosion as shown in Fig. 2. Crevice corrosion is more

likely to occur if crevices exist between the alloy surface and the oxide, since the crevice protection potential is usually less positive than the pit-initiation potential.

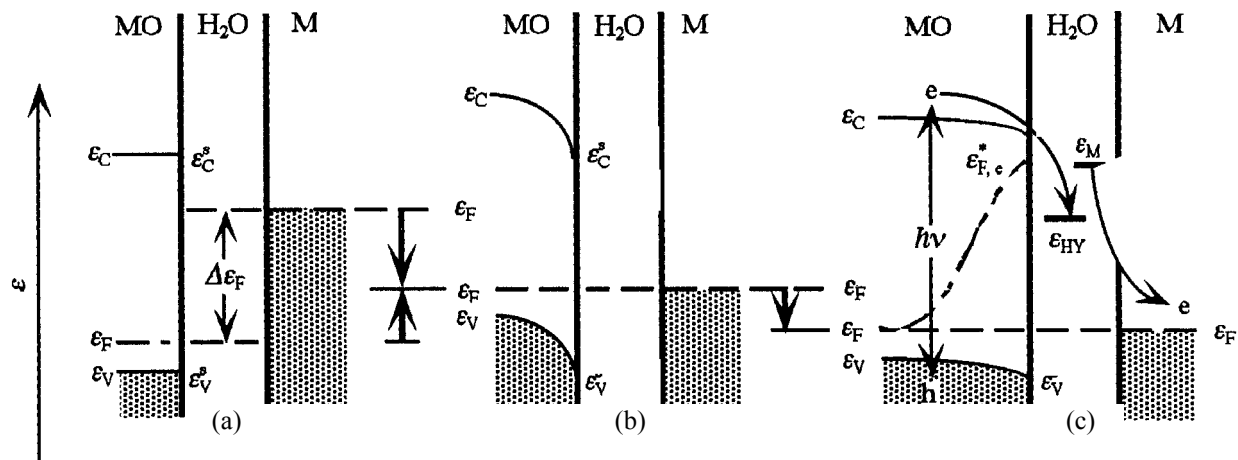


Fig. 1. Electronic energy levels in two electrodes of a metal and a p-type semiconducting metal oxide electrode (a) prior to, (b) posterior to the electronic contact without photoexcitation, and (c) with photoexcitation: $\varepsilon_{F,e}^*$ = quasi-Fermi level of interfacial photoexcited electrons in MO; ε_{HY} = Fermi level of redox electrons in hydrogen reaction [$H_2 = H_{aq}^+ + 2 e_{redox}$]; ε_M = Fermi level of metal dissolution reaction.

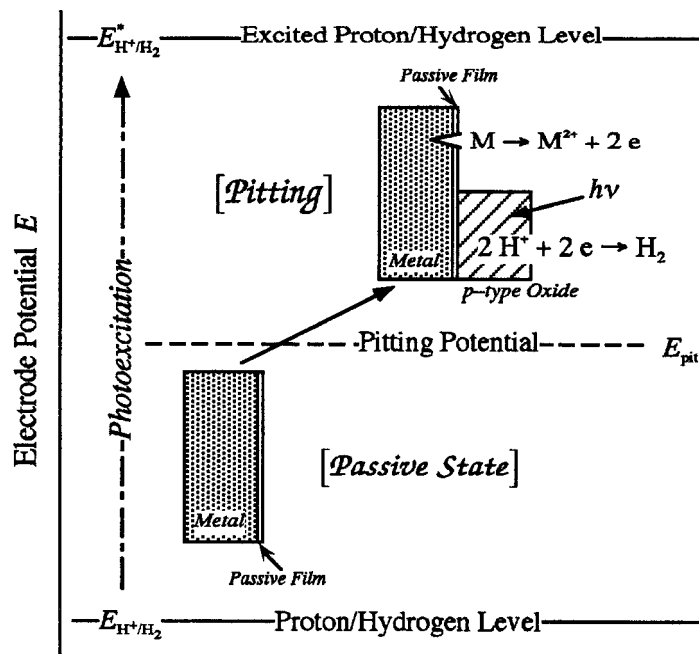


Fig. 2. Anodic shift of the open circuit potential of passive metals in contact with p-type oxides: Photoexcited electrons in the conduction band of the oxide cause the cathodic reaction of hydrogen evolution to occur on the oxide surface, which couples with the anodic metal dissolution to form a local corrosion cell even in the absence of oxygen.

Moreover, the radiation-excited electrons are thermodynamically capable of cathodically reducing water molecules to produce hydrogen gas on the p-type oxide, provided that the

conduction band level of the oxide is higher than the hydrogen reaction level. This cathodic hydrogen evolution on the oxide may be coupled with the anodic metal dissolution at the passivity-breakdown sites as shown in Fig. 3. The localized corrosion thereby goes on running even in the environments free from oxygen.

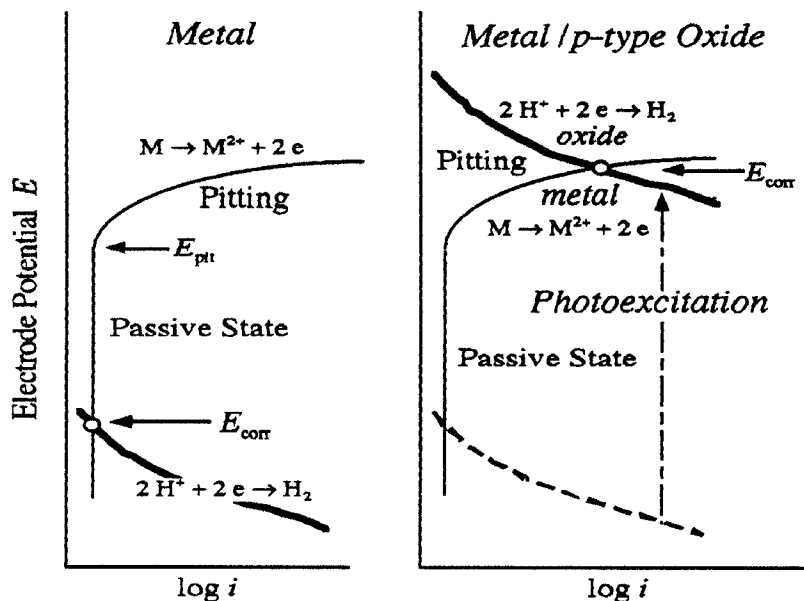


Fig. 3. Polarization curves of a passive metal with or without a p-type oxide in contact under irradiation conditions.

In case of n-type oxides the situation is exactly reverse to that of p-type oxides. The oxide electrode potential is more negative than the passive metal potential, and the open-circuit potential of the oxide-metal mixed electrode accordingly shifts in the cathodic direction, in particular, under irradiation conditions. Shifting the metal potential in the cathodic direction beyond the hydrogen potential has the hydrogen evolution take place on the metal surface. The radiation-excited holes are also thermodynamically capable of anodically oxidizing water to produce oxygen on the n-type oxide, provided that the oxide valence band level is lower than the oxygen reaction level. This anodic oxygen evolution on the oxide may be coupled with the cathodic hydrogen evolution on the metal surface. This local cell then brings about the possibility of hydrogen damage in the passive alloy.

As for the effect of radiation on the long-term corrosion, we have so far been paying attention merely to solid-state radiation damage and water radiolysis that produces oxidizing substances such as hydrogen peroxides, which is one of the oxidizing substances that possibly cause the open-circuit potential to shift in the anodic (positive) direction. Besides, however, we have to keep our eyes on the radiation-excited electrons and holes in the solid oxides, which provide a high reducing and a high oxidizing capacity, respectively. The extremely high energy radiation of MeV from nuclear wastes does not directly affect the corrosion processes, but the secondary low energy radiation produces in semiconducting oxides excited electrons and holes

whose energy is of the same order of a few eV as that of the corrosion reactions. These excited electrons and holes consequently exert influence directly to the corrosion processes.

The suggestion made above for the possible effects of semiconducting oxides on the passivity breakdown is no more than a thermodynamic inference with no direct experimental evidence, except that n-type titanium oxides have been observed to reduce the corrosion of metals [see N. Sato; Corrosion Science 42(2000),1957].

In order to examine whether the suggested matter is really concerned with the long-term storage of waste packages, experiments can be made without difficulty. By measuring the flat band potential of dusts, debris and passive dissolution precipitates, we can make it clear whether they are characterized as p-type or n-type oxides.

3. Concluding Remark:

Under radiation conditions semiconducting p-type oxides, if formed and brought in contact with Alloy 22, will shift the open-circuit potential of the alloy in the anodic direction and cause passivity breakdown leading to a localized mode of corrosion in the alloy. Semiconducting n-type oxides shift the alloy potential in the cathodic direction and prevent the passivity breakdown, though increasing the probability of hydrogen damage in the alloy.

In order to prevent the passivity breakdown due to p-type oxides we can effectively apply the coating of n-type oxide layers such as TiO₂ on the Alloy 22.

In addition, as described elsewhere, the ion-selective property of the surface precipitates formed on the alloy during the long-term corrosion is one of the matters essential to predicting the occluded corrosion environment under the precipitates on the alloy surface.

CONCEPT AND MEASUREMENT OF REPASSIVATION POTENTIAL FOR CREVICE CORROSION

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ABSTRACT

Concept of repassivation potential, $E_{R,CREV}$, for stopping the growth of the crevice and the standardized procedure for measuring $E_{R,CREV}$ has been described. $E_{R,CREV}$ could provide a reliable and conservative measure for accessing the long-term life performance of the waste package material in a repository site.

INTRODUCTION

It is well accepted that the possibility for the initiation and development of localized corrosion could be judged by comparing the open circuit potential, E_{OP} , with the critical potential, E_{CRIT} , as shown in Fig.1. For the waste package, WP, this criterion could be used successfully, but it must be pointed out that the open circuit potential can be easily decided by a conventional method, while there are still many discussions how to decide the critical potential for the localized corrosion, especially for the crevice corrosion. Pitting potential is well accepted as a characteristic potential for generation of pitting on the free surface, the measuring method of which is standardized in JIS, ASTM, and other standards. Pitting potential is a good measure for evaluating not only the order of the pitting

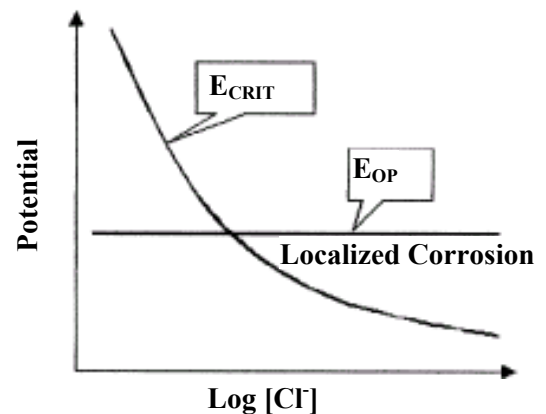


Fig.1 Localized corrosion is possible to occur at $E_{CRIT} < E_{OP}$

resistance of stainless steel in the laboratory, but also practical performance in the field as far as the free surface is concerned. The accumulated field experiences, however, indicate that crevice corrosion which is formed under deposit or contacts between flanges is more important failure mode than pitting corrosion. Stress corrosion cracking which is the other important failure mode of localized corrosion is more likely to be caused after crevice corrosion. It is required to access crevice corrosion behavior more definitely and to establish a measure for characterizing crevice corrosion. Corresponding to this situation, many people from university and

industry in Japan have been devoted to clarifying the mechanism of crevice corrosion since beginning of 1980's. Especially, Professor Tsujikawa has played a major role in understanding basic mechanism of crevice corrosion and proposed a concept of repassivation potential for stopping a growing crevice, providing a most conservative and unique measure for occurrence of crevice corrosion (1).

As shown in Fig.2, we can observe the initiation potential for crevice corrosion, E_1 , on the dynamic anodic polarization curve by using the working electrode with a crevice and also the potential, E_2 , at which the anodic current approaches to zero in the reverse scan. Tsujikawa had found that E_2 depends on the depth of crevice and scanning conditions. His detailed analysis on the conditions of growing and stopping the crevice around E_2 had manifested that a newly defined critical potential, repassivation potential, $E_{R,CREV}$, could provide a conservative and reliable measure for evaluating the susceptibility of passive alloys to crevice corrosion. No occurrence below $E_{R,CREV}$ was confirmed in a large amount of data including the round robin tests. He had revealed that the crevice formation proceeds by two stage process; the first stage near the edge of the crevice shows a higher dissolution rate but not so much depends on potential and alloy composition, followed by the second stage at the more deep depth which depends largely on potential and alloy composition, deciding almost the stable crevice formation (2). This is the reason why the method described in the later requires confirming the existence of 40 μm depth of crevice after the measurement.

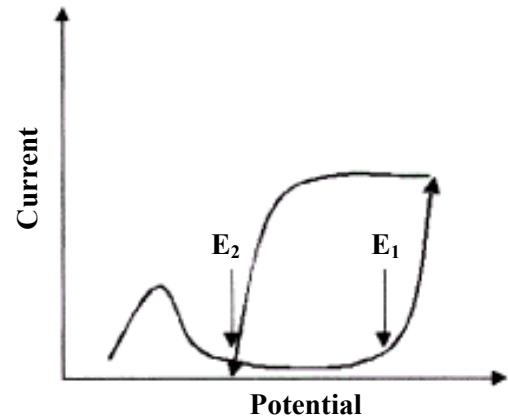


Fig.2 Initiation and termination of crevice growth at E_2 and E_1

DESCRIPTION OF THE METHOD TO MEASURE $E_{R,CREV}$

Electrochemical method is used for determining the repassivation potential with a conventional potentiostat, electrochemical cell, and the specimen electrode with a tight crevice shown in Fig.3 (3). A metal/metal crevice is formed at a contact interface between small area and large area plate specimen which are fastened by a titanium washer and bolt. The contact area is 20x20 mm. Before the measurement, the surface of both specimens should be polished with #600 paper and rinsed with distilled water or alcohol, followed by assembling two plates into the electrode at the

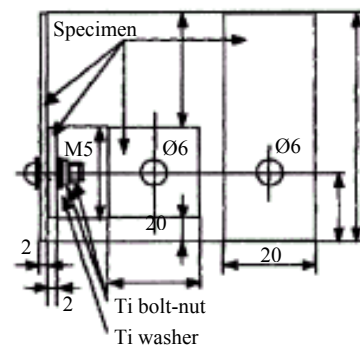


Fig.3 Specimen electrode with a crevice

wetted condition test solution. The test solution in the standard uses sodium chloride solution containing 200 ppm Cl^- at 50 C.

The point is to make a crevice preliminary using the specimen with a tight crevice by anodic polarization over E_1 and holding at a galvanostatic condition and to decide the critical potential to stop the growth of the crevice by using the potentiostatic step down method.

The actual procedure to measure is shown in Fig.4; the plate specimen with a tight crevice is immersed in the deaerated sodium chloride solution, and polarized to the anodic direction from open circuit potential by potentiodynamic method at a constant sweep rate of 30 mV/min to a potential at which 0.2 mA anodic current is observed. At this potential, the potentiostatic control is changed to the constant anodic current control of 0.2 mA which is kept for 2 hours to ensure formation of enough depth of crevice. After making enough depth of the crevice, the potential of the specimen is stepped down by 10 mV under the potentiostatic control, during which the anodic current is monitored. After every 10 mV step down, the anodic current decreases at first, but again increases if the crevice is active. When no increase in the anodic current is observed during 2 hours, indicating death of the active crevice, the potential corresponds to $E_{R,CREV}$. After the measurement, it is required to confirm the formation of the crevice, the depth of which should be more than 40 μm . If the depth of crevice was not found to reach 40 μm , the data has to be discarded.

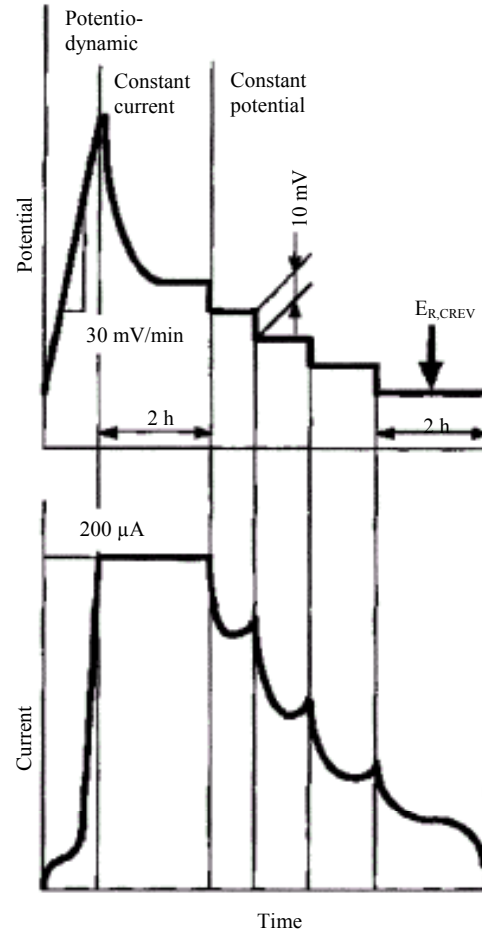


Fig.4 Polarization procedure for measuring $E_{R,CREV}$

DISCUSSION

Some examples of the measurement on Type 304 stainless steel are shown in Fig.5, in which $E_{R,CREV}$ measured by the standardized method described above is plotted as a function of chloride concentration with other characteristic potentials of $V'_{C,CREV}$ (30 mV/min) and $E_{R,CREV}$ (10 mV/min) (4). $V'_{C,CREV}$ (30 mV/min) is obtained for the initiation of crevice by the potentiodynamic method and $E_{R,CREV}$ (10 mV/min)

is obtained for the repassivation of crevice by the potentiodynamic method instead of the standardized method. The discrepancy between $E_{R,CREV}$ and $E_{R,CREV}(10\text{mV}/\text{min})$ becomes larger with decreasing the concentration. $E_{R,CREV}$ is more reliable because a quasi steady state of the solution chemistry within crevice could be maintained due to longer term holding.

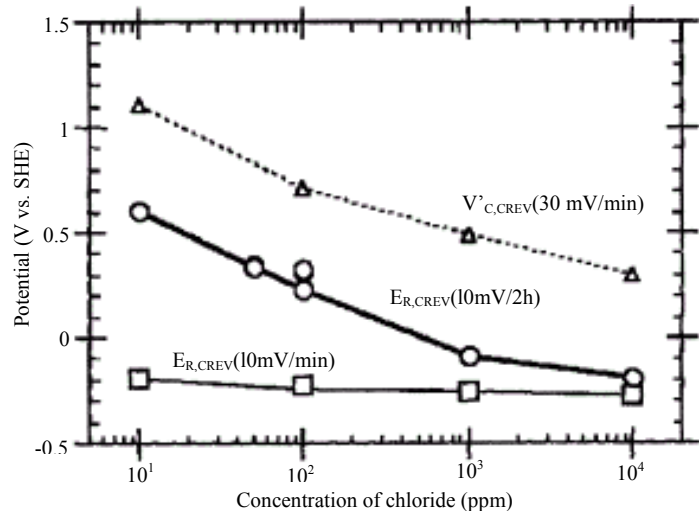


Fig.5 $E_{R,CREV}$ as a function of $[Cl]$

For years in Japan, we have discussed the usefulness and reliability of the method proposed by Tsujikawa (1). Industrial people hesitate to standardize the Tsujikawa method, because the judgment using $E_{R,CREV}$ is too severe and conservative. It was claimed that $E_{R,CREV}$ of common type of stainless steels like Type 304 is sometimes less noble than the open circuit potential in ordinary environments in which the steel even could be utilized. This situation might be judged to be in the incubation stage shown in Fig.6. If stainless steel is used in this condition, we could expect the generation of crevice after some incubation time. At present we could not have any definite model or reliable theory to predict the incubation time and this material should be replaced to the higher $E_{R,CREV}$ material if long time performance would be anticipated.

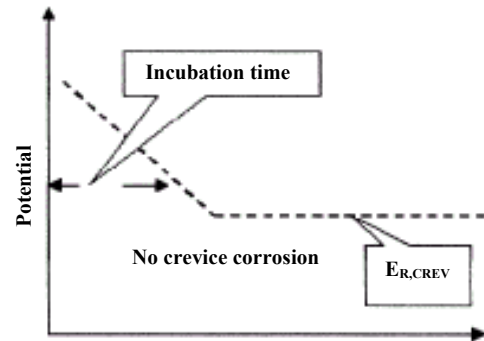


Fig.6 Incubation time exists for initiation of crevice, but is hardly to be predicted

As discussed in the preceding section, the method itself can provide the reliable value which is quite useful for evaluating the susceptibility of stainless steels for crevice corrosion. Then the committee for Japanese Industrial Standard(JIS) decided to standardize a new electrochemical method for the crevice corrosion, that is, "Method of determining the repassivation potential for crevice corrosion of stainless steels".

Because of its conservative nature, I would like to recommend $E_{R,CREV}$ for evaluating the long-term behavior of candidate materials which could be used without crevice corrosion. If $E_{R,CREV}$ of the candidate alloy is above the open circuit potential in the repository environment, we could have a confidence to use the material for the WP for long term without crevice corrosion.

ACKNOWLEDGMENTS

I would like to express sincere thanks to Dr. M. Akashi who made a great contribution for preparing the draft of the JIS of the repassivation potential.

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COMMENTS FOR INTERNATIONAL WORKSHOP ON LONG-TERM EXTRAPOLATION OF PASSIVE BEHAVIOR

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Considerable effort has been undertaken in different laboratories to collect data of uniform and localized corrosion of Alloy 22 in a waste package environment. These data are substantial for predicting the behavior of an alloy during a long period of time (~10,000y). It is not easy to extrapolate the corrosion rate from short experiments lasting several weeks up to 1-2 years to 10,000y with high level of certainty. The extrapolation can be laden with considerable errors. It is difficult to predict how the passive film will alter in time. One can presume that the passive film on an alloy may change its chemical and physical properties, resulting in the changes of the passive dissolution rate. Changes in environment can also occur at the surface of the corroding metal, by possible evaporation and temperature fluctuation. There are two anodic reactions that occur on the passive surface: film formation and passive dissolution. Hence, the measured passive corrosion is the sum of the current consumed for these reactions. It is known that the passive films on metals and alloys are growing according to the logarithmic law. The growth of the passive thin film is initially high and also the general dissolution is high and decreases in time as the passive film becomes more protective. Initially (nonstationary condition) the passive film forms by the selective dissolution of the alloy, and in time a uniform dissolution of the alloy occurs (stationary conditions), and current derives mainly from dissolution. The passive films on alloys are bilayer with the inner oxide barrier layer and outer hydroxide precipitated layer. In the case of alloys containing Cr the inner layer is composed of Cr_2O_3 and the outer layer of is composed of chromium hydroxide. It is believed that a hydroxide layer stabilizes the passive film. There are many data showing that the aging of the passive metals and alloys at low (ambient) temperatures improves the corrosion properties of passive alloys. However, there are no data and predictions on how the passive film will modify in an extremely long time.

To simulate corrosion in a repository condition the measurements of general corrosion were performed in a dilute solution of salts which might exist in repository conditions, in a simulated concentrated solution and in a simulated saturated solution. The measurements of corrosion rate

were made mostly on the specimens fully immersed in the solution (in the presence of air). Some experiments were made also on the specimens exposed to the wet vapor above the water line with only traces of air.

Corrosion of the alloy on the waste package occurs in a liquid-phase layer on metal surface which depends on evaporation, humidity (RH), air flow and temperature. The thickness and composition of this layer would be dependent upon the above parameters. Hence, the corrosion rate obtained from measurements of corrosion rate of specimens immersed in a simulating solution of constant composition will not necessarily represent the real corrosion rate on waste packages. One can expect that in one extreme case a dilute solution would exist in liquid layer on the metal surface, when the supply of water is high. In another extreme case (higher temperature) because of complete or partly evaporation of water, the precipitation of solid salts soluble and insoluble in water will gather on the metal surface.

After evaporation of water the salts might interact with the outer layer of the passive film dehydrating the hydroxide. Hence, the stabilizing hydroxide layer will be destroyed producing an oxide film and water that will be consumed by the hygroscopic salt. Because of the negligible content of water on the metal, electrochemical corrosion will not occur.

These two phenomena: salt precipitation and formation of oxide film as a result of dehydration of the outer layer of the passive film and dissolution of the salts with hydration of an oxide film, probably occur periodically. It is assumed that the alternate dehydration of the passive film ("dry" cycle) and hydration of the passive film (wet cycle) will destabilize the passive film and increase the corrosion rate.

To me it would be useful to design an experiment which alternates wet corrosion in a thin liquid-layer and the drying of a liquid-phase. The more of these wet/"dry" cycles the higher corrosion is expected. The effect of dissolved oxygen needs also be taken into consideration.

The presented (in "Questions to Workshop Participants and Background on Corrosion Issues") models of increasing corrosion after a longer time by vacancy or defects formation are interesting and worth checking. However, it would be difficult to accept these models, assuming that long and short time of aging occurs by the same mechanism. As known in short periods of time (hrs, days) amelioration of resistance to corrosion occurs by a decrease of the structural defects. However, it is

not excluded that a rigid structure of oxide (with low concentration of defects) evolves during short aging leads again to a more defective structure; for example, by formation of stresses in the passive layer weakening the film and increasing corrosion. It is also not excluded (but rather improbable) that corrosion potential (because high concentration of Cr_2O_3 in the film) can increase to the value of critical repassivation potential leading to localized corrosion.

However, it would be difficult to simulate processes occurring during long time of aging. I think, that some kind of aging simulation can be made by measuring the changes in composition, physical properties and passive dissolution of the passive film at different constant potentials below the film breakdown potential.

Concerning localized corrosion I believe that the repassivation potential for crevice and repassivation pitting potential criteria are valid to determine whether localized corrosion will or will not occur in very well defined conditions..

I presume also that some kind of "localized corrosion," namely nonuniform general corrosion, can occur after a longer time of exposure of alloy in the repository conditions when corrosion takes place in the presence of some debris non uniformly distributed.

In conclusion, it needs to be stated that because of lack of our knowledge on behavior of a passive film in time, it is difficult in a changing environmental condition to predict, with confidence, if the corrosion rate will increase or decrease in a long time. Based on available experimental results I believe that corrosion will not significantly increase.

Report on the Predictions of the Stability of Nuclear Waste Containers of Alloy 22 with Respect to Corrosion Failure

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The corrosion stability of alloys of reactive metals is mainly based on their passive behavior. Usually the corrosion rate of passive metals is less than $0.1 \mu\text{A}/\text{cm}^2$ corresponding to ca. $0.8 \mu\text{m}/\text{a}$. The measurement of the corrosion rate of alloy 22 has been determined to less than $0.1 \mu\text{m}/\text{a}$. Due to this passive behavior it is the main hope that containers of alloy 22 with 2.5 cm thick walls will last 100 000 years or at least 10 000 years. Passivity may be determined by dissolution equilibria as described by Pourbaix diagrams in alkaline and weakly acidic solutions. However in strongly acidic electrolytes the anodic oxides are far from their dissolution equilibrium and the stability of the metals is determined by their slow dissolution kinetics and not necessarily by the predictions of the Pourbaix diagrams, i.e. their thermodynamic data. It is the slow transfer rate of cations at the oxide/electrolyte interface of the passivating oxide layer which renders passivity. This transfer causes stationary dissolution rates of $8 \mu\text{A}/\text{cm}^2$ for iron in 0.5 M H_2SO_4 [1] which decrease to ca. $0.1 \mu\text{A}/\text{cm}^2$ in 1 M HClO_4 [2,3]. This example shows already the strong influence of anions to the dissolution rate in acidic electrolytes. This behavior may be related to the complexing properties anions to cations causing an increased rate of dissolution. Furthermore the passive current density does not exceed $0.1 \mu\text{A}/\text{cm}^2$ for passive Cr in 0.5 M H_2SO_4 as determined by rotating-ring-disc techniques including hydrodynamic modulation [4]. This passive corrosion rate has been determined more precisely by radioactive tracer measurements without disturbing parallel reactions for the measurements of these small electrochemical currents [5]. Ni has a relatively high passive current density in 0.5 M H_2SO_4 of several $\mu\text{A}/\text{cm}^2$. It depends also strongly on the electrode potential and achieves much higher dissolution rates in the transpassive potential range. As a consequence Ni base alloys with ca 20% Cr as e.g. alloy 22 are mainly protected against a slow general dissolution due to the beneficial properties of Cr which accumulates within the passive layer especially in acidic electrolytes due to a preferential dissolution of Ni [6]. As a consequence the dissolution rate of Ni/Cr alloys in the passive state are extremely small even in strongly acidic electrolytes.

The composition of passive layers on binary Ni/Cr alloys has been studied in detail in acidic and alkaline electrolytes including a systematic variation of the electrochemical parameters like the potential and the time of passivation and the composition of the electrolyte and the alloy [6]. According to these studies the characteristics of the two metals determine the passive layer and their protecting properties. In alkaline solution a high $\text{Ni}(\text{OH})_2$ content is present as an outer layer which is a consequence of its insolubility at high pH. It will, however, dissolve in acidic electrolytes. In summary one expects a high stability of Ni/Cr alloys like alloy 22 in alkaline as well as in acidic electrolytes mainly due to the beneficial properties of Cr. The Mo content is most likely not beneficial to the slow passive corrosion rate of the alloy and should be seen as an important alloy component with respect to its beneficial properties to the prevention of localized corrosion. Pure Mo has only poor passive properties with relatively high current densities.

All these conclusions from the passive behavior require a homogeneous composition of the metal and still do not include the influence of so called aggressive anions. It is very likely that the alloy

surface contains Cr deficient sites which are less protected due to the minor protecting properties of an excess Ni-content. Besides some local deficiency of Cr due to alloy manufacturing a similar problem might arise due to welding of the containers and failures due to an inappropriate heat treatment. At these defects a higher dissolution rate in the passive state may cause a more intense local dissolution of the alloy as predicted. This is in so far critical as a large surface of all the containers has to be in a homogeneous appropriate state and composition.

Two anions of the concentrated water of the water table or the water of rock pores may be dangerous, chloride and fluoride. It is at least not impossible that these anions may accumulate at the metal surface due to the high temperature of the containers and a continuous access of water. In a wet period these anions may cause an increased corrosion current density when the decreasing temperature allows the formation of a highly concentrated electrolyte due to water condensation. Even in this case Cr is not attacked whereas Ni is not resistant to corrosion. The passive layer on Cr is not attacked by aggressive anions which renders a unique stability of this metal in these environments. Hastelloy C4 (70% Ni, 15% Cr and 15%Mo), a Cr/Ni alloy of similar composition as alloy 22, has been exposed to highly concentrated $MgCl_2$ solutions and showed pitting during passivation transients at $E = 0.2$ V/SHE at elevated temperature (90 °C). However the so called Q-brine used in these studies [7] with 91.9 g/l Mg^{2+} , 71 g/l Na^+ , 31.8 g/l K^+ , 297.3 g/l Cl^- and 14.4 g/l SO_4 is not very likely to occur according to the evaluation of the scenarios which have been summarized by experts. This brine corresponds to a chloride concentration of 8.4 M. It might be realistic for concentrated solutions which might occur in salt stocks which have been proposed as a repository for nuclear waste in other countries as e.g. in Germany. Besides chloride, fluoride should be seen as another aggressive anion which may be accumulated due to the exposure of the containers to the water of the water table. Fluoride is known to cause a general attack of iron and nickel in acidic solutions and localized corrosion in alkaline electrolytes [8-10]. But here again, passivating Cr-oxides are resistant and a high Cr-content should protect the alloy, an assumption which has to be checked. Both anions, chloride and fluoride increase the transfer rate of Ni^{2+} from the passive layer to the electrolyte due to their complexing properties and thus should be seen as aggressive species [11]. This is closely related to localized corrosion which will be discussed in the second part of this report.

A possible shift of the electrode potential to the transpassive range of the polarization curve has to be discussed as a part of the corrosion scenario. For these conditions not only Ni may dissolve as Ni^{3+} [1] but also Cr as soluble CrO_4^{2-} or $Cr_2O_7^{2-}$ in alkaline or acidic solutions. However it seems relatively unlikely that this shift to $E \geq 1.0$ V will occur. The kinetics of oxygen reduction is very slow with a high overpotential so that it will cause a potential in the passive range only. The formation of highly oxidizing species as radicals or H_2O_2 by radiolysis due to the presence of nuclear waste will not lead to a sufficient concentration. The α - and β -radiation of the radioactive waste is mainly absorbed in the wall of the containers and they do not get to the electrolyte at their outer surface. γ -radiation will pass the container walls and thus will enter the electrolyte but has only a small interaction with the solution. This is again a consequence of its low absorption rate. In addition the short lifetime of radicals does not permit their diffusion to the metal surface and thus they will not increase the electrode potential. In conclusion, the formation of oxidizing species to a sufficient concentration does not occur in an outer electrolyte layer of the containers and thus cannot shift the potential in the transpassive range.

In summary Ni/Cr/Mo alloys as alloy 22 are promising materials for nuclear waste containers due to their excellent passive behavior and the protectiveness of their passive layers. Only for very high concentrations of aggressive anions like Cl^- and F^- and at elevated temperature an increase of the dissolution rate is possible. However it is not very likely that this situation due to drying waters will be realized at the surface. At least for the hot scenario with a relatively short cooling period of the containers by air ventilation the temperature will be well above 100°C for the first 1 000 years so that there should not be a water condensation during this time to form an aggressive brine. The localized depletion of Cr due to manufacturing of the alloy may be a problem as only a sufficiently high homogeneously distributed Cr content on the very large surface of all the containers guarantees the all over corrosion resistance in the passive state.

Localized Corrosion

The possible access of aggressive anions like Cl^- or F^- to the metal surface, raises the question of local breakdown of passivity and pitting corrosion. Ni is submitted to localized corrosion by both anions and to a general breakdown of passivity by F^- in acidic electrolytes. Cr has again very specific properties as a corrosion resistant material. Its passive layer remains protective in the presence of both anions and thus does not pit [11]. The resistance of Ni base alloys with a large Cr content are again protected against pitting. Apparently extremely high concentrations of aggressive anions are required to get localized corrosion [7]. In this respect the critical potentials of Ni in solutions of aggressive and inhibiting anions should be discussed again. NO_3^- as an inhibitor is found in the water of the water table and Cl^- as an aggressive anion. A sufficiently large ratio of both anions is required to get localized corrosion. In the presence of both species there exists not only a pitting potential E_p as a lower potential limit but also the inhibition potential E_i as an upper limit, according to Eqs. 1 and 2 and Fig.1. Similar equations are obtained for Fe and all halides as aggressive and ClO_4^- and NO_3^- as inhibiting anions [11,12].

$$E_p = a - b \log [a] \quad (1)$$

$$E_i = a - b \log \{[A] / [B]\} \quad (2)$$

The presence of Cr should shift both lines to higher concentrations or concentration ratios respectively. Thus the V-shaped pitting range as presented in Fig. 1 for Ni is located at high potentials and a large concentration of the aggressive anions is required to get pitting in a potential regime between both lines. In the case of a sufficiently large Cr content as for alloy 22 this apparently requires concentrated brines as has been tested with Hastelloy C4 [7]. For this alloy pitting has been observed during passivation transients in Q-brine at elevated temperature. At 90°C Hastelloy C4 shows pitting at potentials as low as $E = 0.2 \text{ V}$. It might again not be very likely that a concentration increase of the solute of water of the water table will happen to these concentrated brines. At least during the first 1 000 years any deposits on the container walls will be dry for the hot scenario and a brine may form due to water condensation only when progressive cooling will shift the temperature in the vicinity of 100°C . This resistance towards pitting is again an expression of the very high corrosion stability of passive Cr. Therefore it seems that also pitting will not be a major problem for the first 1 000 years.

Careful studies of the current density of Ni/Cr alloys show pronounced current oscillations which are attributed to nucleation, growth and repassivation of pits on Ni/Cr alloy [7]. These frequent

current oscillations are related to small material losses due to localized corrosion. This birth and death of very small pits at the metal surface will cause also some dissolution of the metal which then during $t > 1\ 000$ years with a very large number of instable pits is similar to a general attack of the metal surface. If pit nucleation occurs statistically this kind of attack resembles an increase of metal dissolution which adds to the dissolution current density and causes additional material loss. Looking to the current noise of Hastelloy C4 at $80\ ^\circ\text{C}$ in Q-brine one may estimate a charge of $240\ \mu\text{C cm}^{-2}\ \text{min}^{-1}$. Assuming a decrease of the size of the oscillations with time by 1 order of magnitude only one obtains with $24\ \mu\text{C cm}^{-2}\ \text{min}^{-1}$ or $13.24\ \text{mC cm}^{-2}\ \text{a}^{-1}$ $0.13\ \text{mm}$ material loss per year. However, this estimate requires again the presence of an aggressive brine at the metal surface and it is not at all clear whether the current oscillations will fade out with time. These data refer to a temperature transient test of Hastelloy C4 in Q-brine with a temperature increase from $50\ ^\circ\text{C}$ to $80\ ^\circ\text{C}$.

Another serious problem is crevice corrosion, which has not been discussed to a large extent at the workshop. Ni base alloys are used as corrosion resistant materials for many parts for ship building and other applications in aggressive environments. Its excellent corrosion stability leads to its frequent application for manufacturing of special parts which usually are exposed to sea water. However all these Ni-base alloys are known to be susceptible to crevice corrosion. Currently a large research activity has started due to serious problems with this material in practical service. It is of course a question of the shape of the crevice whether crevice corrosion will occur or not. In laboratory tests this is achieved by an appropriate pressure of a rubber ring to the alloy surface – it should not be too strong or too loose. The electrolyte should enter the crevice but it should be narrow enough to cause a sufficient ohmic drop to shift the potential in the active range of the polarization curve. According to the experts in the field almost all Ni/Cr alloys are susceptible to crevice corrosion in sea water. In some tests $1\ \text{mm}$ local material loss has been found within 1 day. Here again the presence of a highly Cl^- -containing solution is required. This might not be realistic for the first $1\ 000$ years but may be a problem at the cooler period of the T/t diagram when water condensation becomes possible forming an aggressive brine on the container surface. Crevices may form due to deposits of solid material or may start at crevices caused by structural details caused by the construction of the containers.

A final possibility of corrosion failure may arise from activated corrosion in the dry state in the presence of halides, especially chloride. This corrosion mechanism is well known from plants for waste combustion where HCl is a frequent gaseous product when chlorinated organic polymers (PVC) are burnt [13]. Halides may penetrate protecting oxide scales which form at elevated temperature due to oxygen access. This penetration occurs preferentially at defects in these oxide layers. At temperatures $T > 600\ ^\circ\text{C}$ HCl reacts with oxygen and forms a small partial pressure of Cl_2 which is the main aggressive species for this corrosion mechanism. At the metal surface metal halides may form, especially NiCl_2 , which migrate to the oxide/gas interface and reacts with the excess oxygen to NiO . The related release of Cl_2 may enter again the reaction cycle. At the oxide/ metal interface the partial oxygen pressure is sufficiently low due to the presence of the metal surface to permit the formation of chlorides. At regular pressure the oxide is the stable species. Although this mechanism of activated corrosion is effective at elevated temperature there might be a slight chance of damage at some few $100\ ^\circ\text{C}$ during the high temperature scenario within the first $1\ 000$ years which presumably has not been already tested. Here again Cr and the growing Cr_2O_3 -scale is a barrier to avoid the activated corrosion mechanism except at

defects where the attack of the material underneath will occur. At high temperatures the metal attack is serious. However, this high temperature corrosion mechanism requires the presence of halides specifically chloride, which cannot be excluded completely. Furthermore it is not clear whether temperatures in the range of 200 °C will cause damage within long periods of time. Presumably the temperature is too low to cause any damage.

For localized corrosion phenomena Ni/Cr alloys require again a high chloride or fluoride content for the contacting solution. Only for these conditions pitting or activated corrosion at high temperature have a certain probability but are not very likely to occur. Crevice corrosion seems to have a higher probability to occur, if a crevice may form due to special details of the construction of the nuclear waste containers or deposits of solid material.

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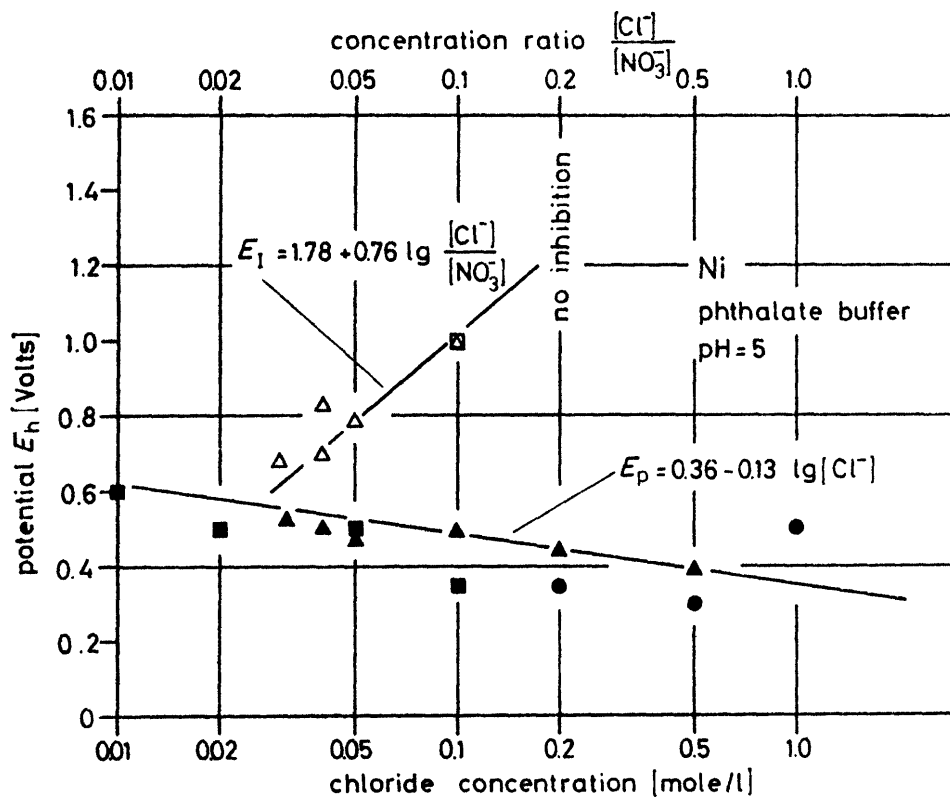


Fig. 1: Pitting potential E_p and inhibition potential E_i of Ni and their dependence on the Cl^- concentration and the concentration ratio of Cl^- to NO_3^- respectively in phthalate buffer pH 5.0 [12].

THE BOARD IN BRIEF

The Nuclear Waste Technical Review Board was created by Congress as an independent agency of the federal government in the Nuclear Waste Policy Amendments Act (NWPAA) of 1987. The Board is charged with evaluating the technical and scientific validity of activities undertaken by the Secretary of Energy within the scope of the Nuclear Waste Policy Act of 1982, including the following:

- characterization of potential repository sites, and
- activities related to packaging and transporting high-level radioactive waste and spent nuclear fuel.

In conjunction with its ongoing evaluation responsibility, the Board has made numerous recommendations intended to (1) enhance the overall technical validity of the Department of Energy's site-characterization efforts, (2) focus and set priorities among research areas, (3) integrate the various components of the DOE program, and (4) identify and characterize uncertainties in performance estimates. The Board's technical and scientific findings, conclusions, and recommendations are included in reports that are submitted at least twice each year to the Secretary of Energy and Congress.

The NWPAA authorizes a Board of 11 part-time members who are eminent in a field of science or engineering and are selected solely on the basis of distinguished service. Board members are appointed by the President from a list of candidates recommended by the National Academy of Sciences. The first members were appointed to the Board on January 18, 1989.

The Board sponsors meetings and technical exchanges with program participants and interested parties, including representatives of DOE and its contractors, the U.S. Nuclear Regulatory Commission, the U.S. Environmental Protection Agency, the State of Nevada, affected units of local governments, the U.S. Geological Survey, the U.S. Department of Transportation, Native American tribes, nuclear utilities, environmental groups, state utility regulators, representatives of high-level waste programs in other countries, and members of the public.

The Board's reports, meeting transcripts, letters to and from DOE, congressional testimony, and all other published documents are available on the Board's web site at www.nwtrb.gov.

SYNOPSIS

The outer part of the conceptual waste package that would contain high-level nuclear waste and spent fuel to be disposed of in a proposed repository at Yucca Mountain, in Nevada, is a 2-centimeter-thick shell of Alloy 22, a very corrosion-resistant material that depends on a nanometers-thick passive layer for its corrosion resistance for at least 10,000 years.

Mankind's experience with Alloy 22 is only a few decades, with alloys like Alloy 22 only a few more decades, and with any metal or alloy that owes its corrosion resistance to a passive layer not much more than a century, at best.

Because experience is limited to a century or so, what are the theories and the assumptions that form the basis for extrapolating for thousands and thousands of years the corrosion resistance of a material that depends on a passive layer for its corrosion resistance? To address that question, the U.S. Nuclear Waste Technical Review Board decided to sponsor a workshop on the question and other issues related to predicting corrosion behavior for periods of unprecedented duration.

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

Fourteen internationally recognized corrosion experts participated in the workshop, which was held on July 19-20, 2001, in Arlington, Virginia. A transcript and other information about the workshop are on the Board's web site. After the workshop, participants submitted brief postworkshop reports. These Proceedings are a compilation of those reports.

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