Journal of Nuclear Materials 379 (2008) 33–41

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Understanding long-term corrosion of Alloy 22 container in the potential Yucca Mountain repository for high-level nuclear waste disposal

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ABSTRACT

Alloy 22 (Ni–22Cr–13Mo–3W–4Fe) is the candidate material for the waste package outer container in a potential geologic repository for high-level nuclear waste disposal at Yucca Mountain, Nevada. This alloy exhibits very low corrosion rates in the absence of environmental conditions promoting crevice corrosion. However, there are uncertainties regarding Alloy 22's corrosion performance when general corrosion rates and susceptibility to crevice corrosion are extrapolated to a geological time period (e.g. 10^5 years). This paper presents an analysis of available literature information relevant to the long-term extrapolation of general corrosion processes and the crevice corrosion behavior of Alloy 22, under potential repository environments. For assessment of general corrosion rates, potential degradation processes causing the loss of the long-term persistence of passive film formed are considered. For crevice corrosion, induction time, and the extent of susceptibility and opening area, are considered. *Disclaimer*: The US Nuclear Regulatory Commission (NRC) staff views expressed herein are preliminary and do not constitute a final judgment or determination of the matters addressed nor of the acceptability of a license application for a geologic repository at Yucca Mountain. The paper describes work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for NRC under Contract Number NRC-02-02-012. The activities reported here were performed by CNWRA on behalf of the NRC office of Nuclear Material Safety and Safeguards, Division of High Level Waste Repository Safety. This paper is an independent product of the CNWRA and does not necessarily reflect the view or regulatory position of the NRC.

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1. Introduction

The level of robustness of the outer container of a waste package (WP), in a potential geologic repository for high-level nuclear waste (HLW) disposal at Yucca Mountain, Nevada, is an important factor in successfully achieving the goal of long-term HLW isolation from the accessible environment. The outer container may be constructed of Alloy 22, a corrosion–resistant Ni–22Cr–13Mo–3W–4Fe alloy, that exhibits very low corrosion rates in the absence of environmental conditions promoting localized corrosion. General corrosion rates could increase substantially in the case of passive film instability, depending on environmental conditions and material alteration states during the HLW disposal period. Similarly, localized corrosion, in the form of crevice corrosion, could occur because of passive film instability in occluded environments in the crevices. Higher general corrosion rates or increased susceptibility to crevice corrosion may lead to a shorter WP lifetime and associated increase in radionuclide release potential. This paper presents technical issues relevant to: (i) long-term persistence of passive film; (ii) susceptibility and propagation of crevice corrosion; and (iii) effects of these processes on the WP lifetime and radionuclide release rates. The technical assessments presented in this paper are intended to help prepare for reviewing the US Department of Energy's (DOE's) license application for a potential Yucca Mountain repository.

2. Persistence of passive film

Based on available information, total-system performance assessments (e.g. [42]) normally use a constant general corrosion rate (e.g. 10^{-5} cm/year [3.9×10^{-6} inch/year]) for the WP outer container of Alloy 22, over a 10000-year performance period. This rate is based on the long-term persistence of passive film that gives low general corrosion rates for the WP outer container. The low constant general corrosion rates provide a very long WP lifetime, containing radionuclides in the WP. The persistence of passive film is of high significance to waste isolation, relative to other corrosion modes [60].

Potential degradation processes causing the loss of persistence of passive film on Alloy 22 can be categorized into three areas: (1) enhanced dissolution by anodic sulfur segregation; (2) alteration of passive oxide film (e.g. chromium oxide); and (3) other degradation processes [2].

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0022-3115/$ - see front matter Published by Elsevier B.V.
doi:10.1016/j.jnucmat.2008.06.031

Marcus [34] postulated that sulfur enrichment at the interface of passive film and base alloy (i.e. metal–film interface) may cause passivity breakdown or alteration of passive current density in nickel-based and related alloys. Numerous studies show the detrimental effects of sulfur on persistence of passive film on nickel-based alloys, through relatively short-term (e.g. hours to days) laboratory tests, by accelerating corrosion processes. They are for Ni [38,41,46], Ni–Fe alloys [39,40], Ni–Mo alloys [37], and Fe–Cr–Ni–Mo alloys [19]. Additionally, the induction time for passive film break-down by anodic sulfur segregation could be very long, compared with laboratory test times. Assuming that the sulfur content in Alloy 22 is 5 parts per million (ppm) by weight and the passive current density is 1 nA/cm^2 ($\sim 10^{-6}$ cm/year [3.9×10^{-7} inch/year]), Marcus [33] estimated the induction time of about 900 years for passivity breakdown, if 100% of the sulfur atoms are retained at the metal–film interface.

Chromium oxide is generally considered to be responsible for the high corrosion resistance of nickel-based alloys (e.g. Alloy 22) through the formation of a thin and conformal layer on the metal surface. It is necessary to evaluate the long-term behavior of the chromium oxide or potential changes of this barrier affecting the corrosion performance of Alloy 22, under potential HLW disposal conditions.

Additional degradation processes can also lead to loss of passivity of Alloy 22. These processes can include [26]: (i) mechanical spallation of passive film by void formation at the metal–film interface or film overgrowth [49]; (ii) porous film development by episodic dry–wet process [26,44,16]; (iii) anion-selective sorption into the porous outer layer of passive film, promoting localized corrosion by changing local chemistry [50]; and (iv) increased cathodic kinetics (e.g. large cathodic surface area development) [26,27]. Although these processes appear less likely to occur, during HLW disposal, than sulfur segregation or passive film alteration, they warrant additional consideration because of potential effects on passive film persistence.

2.1. Anodic sulfur segregation

Marcus and his coworkers investigated the effects of sulfur, particularly of adsorbed sulfur, on Ni [38,41,46] and Ni–Fe alloys [39,40]. It was demonstrated that a monolayer of adsorbed sulfur on the metal surface enhances the anodic dissolution rate and prevents passivation by anodic sulfur segregation of sulfur present in the metal. Fig. 1 shows the process of passive film breakdown during dissolution as per the mechanism proposed by Marcus [34]. According to this mechanism, most of sulfur in the metal can accumulate on the metal surface by the selective dissolution of the metal elements (e.g. nickel, iron) during a passive dissolution – a process also known as anodic sulfur segregation. In the same reference, three favorable factors for sulfur segregation at the metal–passive film interface are proposed as follows: (i) very strong chemical bond between metal and sulfur, (ii) very low solubility of sulfur in nickel oxide and (iii) the electric field across the passive film, which assists easier transport of the metal cations to the film–solution interface from the metal–film interface, but impede the transport of a mostly negative charged sulfur. Above a critical concentration of sulfur (i.e. one monolayer of sulfur) at the interface and subsequent a formation of metal sulfides, the breakdown of the passive film would occur at the defect sites preferentially, responsible for the observed local breakdown of the film and pitting [38].

On the contrary to the detrimental effects of sulfur on the passivation, addition of an alloy element such as molybdenum is known to counteract the detrimental effect of sulfur in nickel-based alloys. In Ni–2Mo, the adsorbed sulfur on the surface decreased sharply during the active dissolution of alloy, by removing either formed soluble molybdenum–sulfide (e.g. $Mo_2S(O)_x$) or molybdenium-sulfur cluster [37]. Similar effects were shown by Elbiache and Marcus [19] in Fe–17Cr–14.5Ni–2.3Mo stainless steel. In the presence of molybdenum, sulfur accumulation was still observed but decreased compared with alloys without molybdenum [34]. Chromium also counteracts the detrimental effect of sulfur, by promoting the passivation of nickel-based alloy (Ni–21Cr–8Fe). This beneficial effect of chromium in the presence of sulfur has been explained by the formation of continuous layers of chromium oxide (and hydroxide) embedding, considered to be nickel sulfide islands [36,12,13].

Jones and his coworkers conducted corrosion tests in Alloy 22 implanted with sulfur by short-term polarization techniques, finding that with the sulfur content up to 2–3 at.%, the change of general corrosion rate was within the data uncertainty range [24,63]). This low level of sulfur content on the surface, however, increased up to 5 at.% after 29 days in 1 M NaCl solution. Jones et al. [24] estimated that it would take approximately 500 years to form a monolayer of sulfur at the metal–oxide interface in nickel-based alloys containing 100 atomic part per million (appm) sulfur, assuming a general corrosion rate of 10^{-6} cm/year [3.9×10^{-7} inch/year].

Enhancement of the corrosion rate may depend on the persistence of sulfur or its compounds, such as nickel and/or molybdenum sulfide, at the metal–film interface. Due to very low solubility products of metal sulfides in general, the dissolution of metal sulfides exposed to the solution may be thermodynamically limited. Thus, metal sulfides such as Ni_3S_2 could stay on the metal surface during a relatively long period, preventing the formation of protective passive oxide film on Alloy 22. On the other hand, it is kinetically possible that the fast dissolution of metal species from the exposed area could enforce and accelerate the dissolution (or desorption) of metal sulfides by breaking the bonds between metal

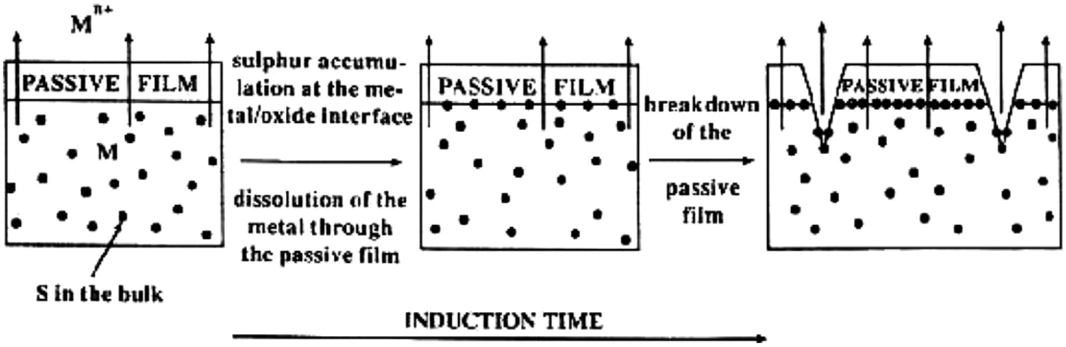

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Fig. 1. Mechanism of the breakdown of the passive film induced by enrichment of sulfur at the metal–passive film interface [34]. (Reprinted from 'Sulfur-Assisted Corrosion Mechanisms and the Role of Alloyed elements' by P. Marcus in *Corrosion Mechanisms in Theory and Practice* edited by P. Marcus and J. Oudar, Marcel Dekker).

matrix and sulfides. The reduction of adsorbed sulfur concentration on the metal surface has been observed in Ni [38] and Ni–Fe alloys [39,40] at high anodic dissolution rates. The presence of molybdenum in Alloy 22 can also counteract the effect of sulfur by reducing sulfur content present on the surface, as mentioned above [34]. The persistence of sulfur or its compounds could be attenuated in the presence of molybdenum. On the other hand, chromium has a low affinity for sulfur, but high affinity for oxygen. For this reason, a protective oxide film (e.g. on Alloy 22) should eventually form after the sporadic occurrence of enhanced transient corrosion caused by anodic sulfur segregation. Based on these postulates, Passarelli et al. [47] and Ahn and Pan [1] conducted an assessment of the WP lifetime, assuming a cyclic behavior of sulfur accumulation, passive film breakdown (or enhanced passive corrosion rates), sulfur dissolution with molybdenum, and repassivation.

Their analyses present the corrosion penetration from the cyclic behavior of the transient fast (enhanced) corrosion caused by sulfur segregation at the metal–film interface and after slow (passive) corrosion from repassivation. The penetration depth (i.e. the amount corroded) will be the product of rate of slow corrosion ($\mathrm{CR_p}$) and period of time for slow corrosion ($\mathrm{Ct_p}$), added to the product of fast corrosion ($\mathrm{CR_f}$) and period of time for fast corrosion ($\mathrm{Ct_f}$):

$$\text{Penetration depth} = \sum[\mathrm{CR_p} * \mathrm{Ct_p} + \mathrm{CR_f} * \mathrm{Ct_f}] \tag{1}$$

The slow corrosion rate is primarily a passive current density, until sulfur significantly modifies the passive film structure and passive current density. The fast corrosion rate is a significantly enhanced corrosion rate if sulfur modifies significantly the passive film structure or leads to passivity breakdown.

The results showed the WP lifetimes at various fast corrosion times. The fast corrosion rate and its corresponding time were estimated from the current transient, with time before the repassivation for Alloy 22, at an applied potential in the passive regime [9]. The fast corrosion rate was varied from $\sim 1.04 \times 10^{-4}$ cm/year (4.1×10^{-5} inch/year) to 10^{-2} cm/year (3.9×10^{-3} inch/year), as an example of the active corrosion of Ni–2Mo alloys [37]. The transient time to reach the steady-state was 0.0119 years at the corrosion rate of 10^{-4} cm/year (3.9×10^{-5} inch/year).

In an attempt to make a more accurate calculation, two additional factors have been considered, i.e. (i) the potential effects of extended times for the segregated sulfur dissolution after passive film breakdown; and (ii) the extent of sulfur segregation affecting slow and fast corrosion rates.

Fig. 2 shows revised curves, using modified parameter values at the slow corrosion rate of 10^{-5} cm/year (3.9×10^{-6} inch/year), and 18 years before sulfur segregation and passivity breakdown take place (equivalent to 180 years at 10^{-6} cm/year [3.9×10^{-7} inch/year] with 100 atomic ppm sulfur). There were two postulates, 500 or 180 years [25,59]; and 180 years was chosen, conservatively, here. It is generally considered that long-term passive corrosion rate of Alloy 22 is in the range of 10^{-6} to 10^{-5} cm/year [$3.9 \times (10^{-7}$–$10^{-6})$ inch/year] at ambient temperatures from the long-term corrosion tests [15,9].

The questions in assessing the sulfur effects include: (i) can sulfur concentration less than one monolayer increase substantially the general corrosion rate in either a passive or active state; and (ii) is the dissolution time of segregated sulfur with molybdenum long enough, to be able to potentially decrease the WP lifetime of Alloy 22 by general corrosion? To answer these questions, two distinctive cases based on the available literature information are considered, regarding the perturbation of the involved parameters. The first case is when the segregated sulfur on the surface dissolves quickly, with molybdenum, at the fast corrosion rate. The second case is when the sulfur dissolution time is prolonged. Both cases evaluated the WP penetration depth in Eq. (1).

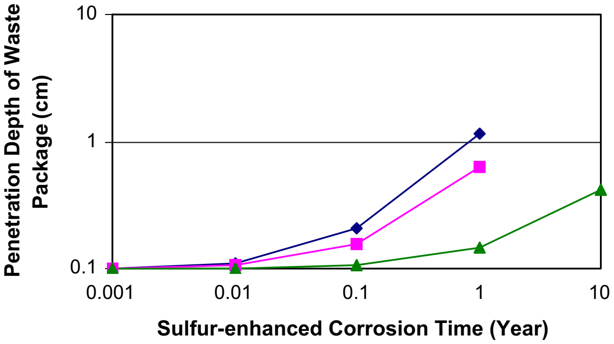

Fig. 2. Calculated penetration depth of waste package in 10,000 years, using Eq. (1). The slow corrosion rate was 10^{-5} cm/year (3.9×10^{-6} inch/year), and the fast corrosion rates were varied from 2×10^{-3} (top), 1×10^{-3} (middle) and 1×10^{-4} (bottom) cm/year. Expected repository conditions are likely to be Sulfur-enhanced Corrosion Time <<0.1 year (inch = 2.54 cm).

Case 1: 10^{-5} cm/year [3.9×10^{-6} inch/year] of the slow corrosion rate is assumed. After the passive film breakdown because of a formation of a sulfur monolayer near the metal–film interface, the sulfur is assumed to be dissolved with molybdenum at the fast corrosion rate. The slow corrosion time is long, whereas the fast corrosion time for sulfur dissolution is relatively short with molybdenum. As the corrosion rate is higher, the sulfur concentration on the surface can be lower, assuming the sulfur dissolution time could be shorter, and assuming the sulfur can be removed by bonding with molybdenum during the dissolution process, similar to the Ni–2Mo system [37]. Therefore, the contribution to the penetration depth by the sulfur effect is not significant, considering the very short period of fast corrosion time compared with the relatively long slow corrosion time in Eq. (1).

The first subcase is made, based on data from Jones et al. [24] and Windisch et al. [63]. Their data for Alloy 22 indicate that the passive current density does not change with sulfur accumulated up to 2 at.%, without data beyond 2 at.%, of sulfur. Assuming the passivity breakdown at 2 at.%, sulfur is assumed to be dissolved with molybdenum at the fast corrosion rate. The net sulfur effect in the penetration depth is negligible because the time of slow corrosion rate is long and the time of fast corrosion rate is short. The second subcase is to consider the increased slow corrosion rate. This subcase may include increased temperatures or enhanced passive current density with sulfur segregation, as mentioned in the available literature on the subject, above. An increase by a factor of 10 is used from the temperature dependence of a passive corrosion rate [15] and from the variation of passive current density with sulfur noted in the literature quoted above. A factor of 10 did not show significant sulfur effects in Eq. (1).

Case 2: The sulfur may not dissolve quickly from a monolayer removal. The dissolution times were slower in acid solutions for Ni–2Mo [37] and Fe–17Cr–14.5Ni–2.3Mo [19], compared with the metal corrosion rates. Fig. 3 shows the sulfur dissolution behavior for these systems. From the initial 100% sulfur coverage, sulfur dissolves rapidly, to lower than about 30% coverage, at which point the surface appears to be in a passive state. According to Marcus [34], passive film may be broken down when the sulfur coverage is near 100%. The sulfur dissolution time is short – in the range of an hour. The passive current density did not change significantly at a sulfur coverage less than about 30%. The fast corrosion rate can increase, at most, by a factor of 100 with sulfur coverage [37,19,39,40,12,13]. The ratio of active and passive current densities for Alloy 22 is less than a factor of 10 [63], which is smaller

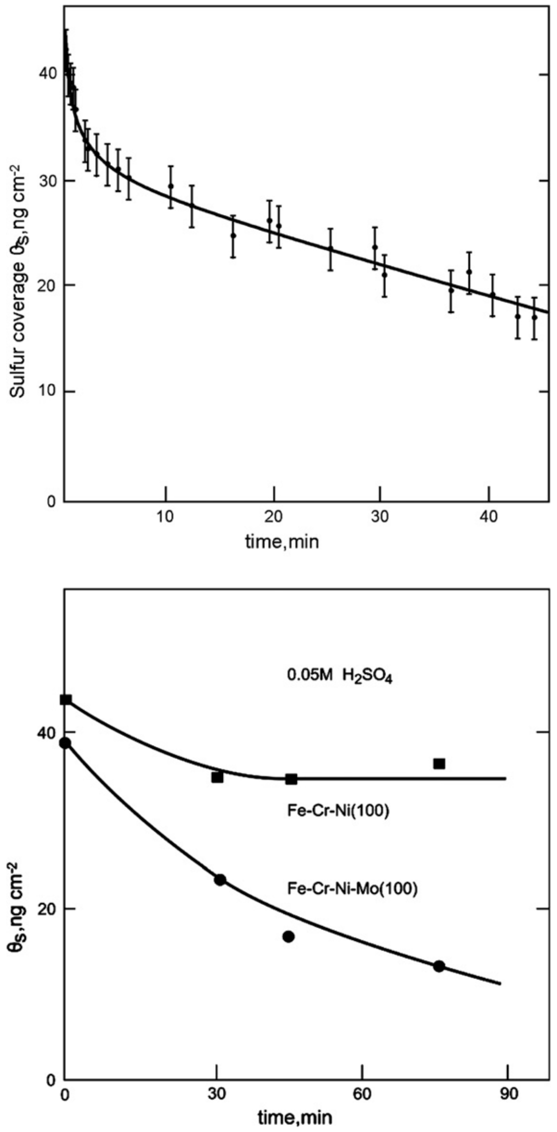

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Fig. 3. Surface coverage of sulfur with time showing sulfur dissolution. The first figure is for Ni–2a/o Mo (100) with pre-sorbed sulfur (initial coverage 43 ng/cm^2) and polarized in the active region at 320 mV/SHE in 0.05 M H_2SO_4 [37]; the second figure is for sulfur coverage on Fe–17Cr–12.6Ni (100) and Fe–17Cr–14.5Ni–2.3Mo (100) alloys in 0.05 M H_2SO_4 at the corrosion potential [19]. (1 ng/cm^2 = 1.42×10^{-11} lb/in^2) (First) Reprinted from 'The Electrochemical Society, Inc. [1989]. All rights reserved. Except as provided under US copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in 'The Role of Alloyed Molybdenum in the Dissolution and the Passivation of Nickel–Molybdenum Alloys in the Presence of Adsorbed Sulfur' by P. Marcus and M. Moscatelli in J. Electrochemical Soc., vol. 136, No. 6, 1989 (Second) Reprinted from Publication 'The Role of Molybdenum in the Dissolution and the Passivation of Stainless Steels with Adsorbed Sulfur' by A. Elbiache and P. Marcus, Corrosion Science, vol. 33, No. 2. pp. 262–269.

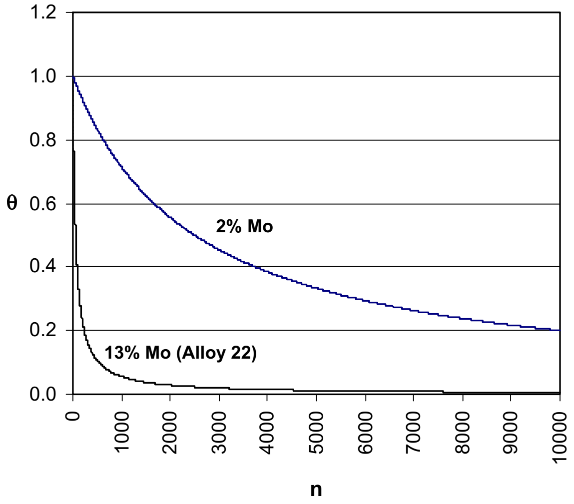

Fig. 4. Calculated sulfur dissolution kinetics for 13% Mo (Alloy 22 case) based on the model by Marcus and Moscatelli [37]. 'θ' is fractional sulfur coverage; and 'n' is atomic plane number under corrosion ~1-h corrosion for 10,000. The upper curve is the model fitted to experimental data of Ni–2Mo (a/o), from Marcus and Moscatelli [37].

than the alloys noted in the available literature. Using the sulfur dissolution time, up to 100 times of the tested time of an hour (i.e. 100 h), in Fig. 2 (assuming sulfur could be embedded deeper), the net sulfur effect in the penetration depth is not significant, along with these variations of corrosion rate. For Alloy 22, the bulk concentration of molybdenum is about 13% by weight, higher than molybdenum concentrations in nickel- and iron-based alloys (e.g. 0–2.3 wt.%) in the available literature, which may lead to faster sulfur dissolution, according to Marcus and Moscatelli [37]. For example, Fig. 4 shows a simulation of sulfur dissolution with varying molybdenum concentration, using the formula by Marcus and Moscatelli [37].

There are some data that show enhanced corrosion rates or localized corrosion attack, under the sulfur influence. According to previous studies [39,46], the effect of sulfur on the corrosion resistance of the metals which exhibit passive films (e.g, Ni and Ni–Fe alloys) were almost identical whether sulfur is present in the alloy or sulfur species are adsorbed on the metal surface from the solution. Fang and Staehle [20] noted that passive current density of Alloy 600 varied in about 3 orders-of-magnitude, depending on sulfur valence states in 10^{-2} M solutions of sulfur oxyanion at pHs of 3.5 and 6, at 25 °C (77 °F) and 95 °C (203 °F), respectively. Smailos [51] showed that Hastelloy C4 (a family alloy of Alloy 22) showed pitting with 6×10^{-4} M Na_2S at 150 °C (302 °F) in a NaCl-rich brine. However, the long-term corrosion test facility (LTCTF), for 5 years, in simulated Yucca Mountain environments did not show effects of sulfur influence, as this sulfur was not in detrimental ionic forms (e.g. S^{6+}) [8,6,7]. The potential Yucca Mountain environments include both chlorides and oxidizers such as nitrates, carbonates/bicarbonates, and sulfates. Oxidizers seem to effectively compromise chloride-induced localized corrosion [15]. It is postulated that sulfur accumulation closer to a monolayer would take about 500 years, with 100 atomic ppm of sulfur at the general corrosion rate of 10^{-6} cm/year [3.9×10^{B7} inch/year] [24]. However, increasing temperature will decrease this time. If dripping groundwater occurs on the WP, it may remove the dissolved sulfur readily, as Lin et al. [29] estimated the volume of dripping groundwater on the WP with and without focused flow. In the reference [24,63], there was no clear indication of localized corrosion for Alloy 22 in the presence of 2 at.% of sulfur. However, further investigation into the presence of a monolayer of sulfur was suggested, to simulate the long-term effect of sulfur on localized corrosion susceptibility.

The purpose of these case studies is to obtain insights from literature data and models, most of which stem from Marcus and his coworkers. Additional uncertainties arise when available information considers specific environmental conditions (e.g. temperature, pH, and water chemistry) representative of the potential repository. Specific example uncertainties include: (i) the changes of corrosion rate with sulfur accumulation; (ii) the dissolution rate of sulfur from the metal surface after the passive film breakdown; (iii) the repassivation rate or continuous propagation rate of localized corrosion in the presence of chlorides as well as oxidizers such as nitrates, carbonates/bicarbonates and sulfates; and (iv) temperature effects. The detrimental effect of sulfur segregation can be reduced or eliminated by a reduction of the initial sulfur content in the alloy during the metal fabrication.

2.2. Conformance of chromium oxide

A thin chromium barrier oxide less than 5 nm thick [2.0×10^{-7} inch] appears to be responsible for the passivity in nickel-based alloys [35,30]. This postulate is widely accepted because of data obtained under short-term electrochemical test conditions. However, during long-term corrosion, there were uncertainties about the chemistry of the base metal near the passive film. Some laboratory tests indicate chromium depletion phenomena. Orme [44] observed the lower chromium concentration (<20 at.% from the Auger Electron Spectroscopy results) at the metal–oxide interface of Alloy 22, after short-term potentiostatic polarization tests. The lower chromium content at the interface could affect the formation of protective Cr-rich oxide film. If passive film breakdown/dissolution occurs, the newly formed oxide film may not have the same composition (i.e. lower chromium content) or structure (i.e. not as compact) as the original oxide film, which could increase the corrosion rate of Alloy 22. Nevertheless, the long-term immersion tests in the LTCTF, for 5 years, in simulated Yucca Mountain environments [8,6,7] showed a decrease in general corrosion rates with time.

Also, DOE's test results show exceptions, in conformance of chromium oxides, both in electrochemical tests of Alloy 22 in Na–K–Cl–NO_3, up to 220 °C (428 °F) and in LTCTF long-term immersion tests, for 5 years, in simulated Yucca Mountain environments [8,6,7,14,45,44]. In the long-term immersion tests for over 5 years, some samples were analyzed, measuring general corrosion rates, and analyzing passive film chemistry, using X-ray Photoelectron Spectroscopy. Some of the surface analysis results did not seem to fully support the presence of a chromium oxide layer or chromium in metal near the oxide. Instead, there were some indications that silica in the solution, or from test facilities, appeared to be deposited on the surface. Silica is a constituent, in the seepage or deliquescence solution, within the potential Yucca Mountain repository conditions [58,59]. Similar silica deposits were observed in long-term tests by Dunn et al. [15]. After 2 years immersion in 4 M NaCl simulated groundwater, at a pH of 7.5, at 95 °C (203 °F), the surface analysis showed silica deposits with nickel oxide as the main constituent, rather than chromium oxide [15]. In the analogue studies of Josephinite, it was considered that andradite, a ferric silicate with a composition given by $Ca_3Fe_2\ (SiO_4)_3$, appears to have helped preserve a nickel–iron alloy Josephinite in a pristine state, for at least thousands of years [52]. Additional uncertainties arise about the role of chromium oxide or other deposits in protecting the intact metal surface. Other oxides could have played a role in the protection.

The point defect model (PDM) describes the barrier layer of chromium oxide responsible for passivity in stainless steels and nickel-based alloys [31,10,28,57]. Generally, currently available models assume the passivity from the barrier layer of chromium oxide in Alloy 22, and modeling results support this assumption. Having accepted that the thin chromium oxide layer is responsible for the passivity, there are uncertainties about the long-term behavior of chromium oxide in protecting the intact metal surface under potential Yucca Mountain repository conditions. The questions could include whether the barrier layer would grow continuously, if the structure and chemistry would be altered during the continuous growth, or whether the altered layer would become unprotective with growth.

The PDM and subsequent analyses in Alloy 22 suggest that the barrier layer is likely to have a finite thickness [56]. The outer surface of the barrier layer may become porous and continuously dissolve chemically, whereas the inner surface of the barrier layer may move continuously inward. The net effect could be to keep a steady-state thin-barrier layer of a constant thickness over an extended period of time. Laboratory tests support a steady-state thin-barrier layer [56]. Models show a finite thickness for passive film under oxidizing conditions [56]. However, the LTCTF shows continuous decrease of general corrosion rates after 5 years [6,7]. As mentioned previously, the uncertainties in LTCTF test results may need to consider effects of, for example, silica deposits which could have played a role. NRC's resolution of key technical issues commented that longer-term tests would be very useful [61]. The natural analogue studies of nickel-iron meteorites indicate that the dissolution must have proceeded congruently [52], implying a steady-state for long-term stability. The PDM for passive dissolution suggests that congruent dissolution can lead to a long-term reduction in corrosion rates and thus a prolonged WP life time [52]. It is considered that a stoichiometric congruent dissolution is sustained in a steady-state.

Based on the PDM model [49], extended the modeling to evaluate various transport mechanisms of passive oxide layers of nickel–chromium–molybdenum alloys under low temperatures. Cation interstitials were identified as charge carriers. The dissolution of the alloy in the form of interstitials causes the creation of vacancies in the alloy, which may lead to void formation, in Alloy 22, under potential Yucca Mountain repository conditions. Therefore, long-term effects could lead to the spallation of passive film by void formation. Although transient passivity may be lost, repassivation is expected in a relatively short time period. This spallation and repassivation could occur randomly over the entire metal surface. [49] postulate that this statistical process could result in the roughening of the metal surface. However, their estimate of the surface roughening did not significantly increase the corrosion rates.

Lastly, most literature data and models related to the behavior of a barrier were obtained at ambient temperatures. In the potential Yucca Mountain repository environment, the temperature could go up to at least 200 °C (392 °F) [32]. Even at this high temperature, aqueous conditions could persist in the presence of mixed deliquescent salt deposits [64]. Under these high-temperature deliquescent conditions, test results suggest that the general corrosion rate decreases with time [64].

2.3. Other potential degradation processes

The outer container of the WP may form crevices as a result of contacts with other engineering components, rock falls, or mineral deposits. For thousands of years, corrosion products from passive general corrosion in the crevice would be accumulated, although no crevice corrosion is initiated [26]. In a crevice of limited aqueous volume, chemistry may become altered as chemical species could be sorbed on the surface of the accumulated corrosion products [50]. The anion species of interest, such as chloride, nitrate, sulfate, carbonate/bicarbonate, fluoride, and silicate in solutions may lead to either localized corrosion promotion, or more benign conditions, by sorption process to the surface of the WP outer container. On hydrous ferric oxide, 10^{-5} M sulfates showed sorption greater than 20% at pH lower than 6 at ambient temperature [18]. Suleiman et al. [54] observed anion-selective sorption with the iron rust membrane, to stabilize pitting in 304L stainless steel. In the LTCTF results, in various simulated solutions, for about 5 years, any indications of long-term localized attacks from anion sorption in the crevice were not observed, at up to 90 °C (194 °F) [8].

Non-passive corrosion from anodic sulfur segregation and void formation could be further accelerated if a large cathodic surface area of semiconducting corrosion products is available [26,27]. There could be more porous film under episodic dry/wet processes [26,44,16]. Transient non-passive corrosion would be increased by a factor of the ratio of the increased surface area of accumulated cathodic corrosion products to the geometric flat cathodic surface area. However, many long-term corrosion data often show the evolution of a rough morphology, with an increase of the metal surface area, by a factor of less than 10%, for the case of void formation [49]. Although this postulate could be valid in some systems such as carbon steel, there has been little evidence reported regarding the development of large surface area of cathodic corrosion products in corrosion–resistant alloys. For example, Ni–Cr–Mo alloys show duplex corrosion products with inner compact oxides and outer porous hydroxides. Although the inner compact oxide layer is semiconducting, and its thickness is kept constant, the accumulating outer porous hydroxides are insulators [2]. Recently, it was also recognized that the large cathodic surface may not serve as an effective cathode, especially in a limited water volume. The throwing power for cathodic reactions to balance with corresponding anodic reactions could be very limited [27].

3. Susceptibility and propagation of crevice corrosion

This section addresses how crevice corrosion could be assessed over periods of thousands of years, based on short-term laboratory data. The behavior of induction times for crevice corrosion is discussed to attain insights for long-term extrapolation. This section also addresses to what extent the WP surface area could be open for radionuclide release, if crevice corrosion occurs. The opening of the WP surface area may be very restricted, if there is a low likelihood of aggressive groundwater chemistry, limited crevice area, and limited pit area inside the crevice. Finally, the sensitivity of the WP opening area to the actual radionuclide release is discussed, using a system performance assessment code. It is noted that many insights gained here are from analogue data and models.

3.1. Quantity and chemistry of groundwater

Under the potential Yucca Mountain repository conditions, only small amounts of water could drip onto the WP [29]. Furthermore, the water will be blocked in the presence of intact drip shields [58]. Radionuclides in the WP will emit heat in the potential Yucca Mountain repository. The heat will gradually decay over thousands of years. Accordingly, the temperatures of the WP and the potential Yucca Mountain repository will decrease gradually, too. Depending on the temperature, the groundwater chemistry may vary by the processes of evaporation and concentration. There is a low likelihood of potential water compositions that could cause localized corrosion [48].

3.2. Induction time

Typically crevice corrosion propagates in the crevice in the form of isolated pits or connected pits. Therefore, existing relevant models and data are discussed here, for the initiation times for pitting corrosion and crevice corrosion. [28] and Urquidi–Macdonald and Macdonald [57] developed the PDM, for the critical potential, and the induction times, for the pitting corrosion of passive metals. The induction time was formulated with: the applied potential minus the pitting potential (ΔV); the charge on a cation; transient aqueous diffusion time; a constant relating the potential drop at the film/solution interface and applied potential; and a function of chloride activity, critical potential, diffusivity of cation vacancy, and a critical amount of metal holes.

An example calculation of induction times, based on the void nucleation theory, for the system of passive iron, in borate buffer solutions, at 25 °C (77 °F) [28] shows that induction time is very sensitive to ΔV as the applied potential becomes close to the pitting potential. Borated solutions are considered to be ideal for the mechanistic understanding of pitting. The induction times increase sharply from laboratory time scales of 10^2–10^5 s (i.e. 0.03–28 h) within 50 mV of ΔV, eventually infinite as $\Delta V \sim$ zero. This suggests that the long-term pitting potential is very close to that measured in laboratories (in this case within 50 mV). This result indicates that long-term pitting potential is captured by short-term laboratory experiments, as long as the external environment or the passive state remains unchanged. The sensitive dependence of the induction time on the potential is very typical in most aqueous or solid-state nucleation phenomena [3,4]. Similarly, the distribution of the range of the induction time modeled for the system of Fe-17Cr in 3.5% NaCl solution, at 30 °C (86 °F) [57] is further evaluated for a longer period of time. Increasing the distributed induction time from the averaged induction time of less than 100 s to ~1 year, the frequency of pitting occurrence decreased drastically by more than 10 orders-of-magnitude. This in turn suggests that the measured induction times in laboratory time scale may be sufficient for assessing the induction times for thousands of years.

A similar behavior was observed in the crevice corrosion of Alloy 825 in chloride solutions at 95 °C (203 °F) [17]. When the applied potentials are lowered from the breakdown potential to the repassivation potential, crevice corrosion was observed in a longer-term exposure, as the potential was lowered. However, the potential range showing crevice corrosion at various times was wider than ΔV in the pitting corrosion discussed above. Based on this observation, the repassivation potential was taken as the critical potential for long-term crevice corrosion [55,53]. The physical models for the repassivation potential also include the nucleation process. For example, Okada [43] formulated the repassivation potential, based on the oxide reformation in the occluded area, as the criterion for the repassivation. Therefore, the induction times for repassivation (i.e. repassivation times for existing pits from varying environmental conditions) should behave similarly to the induction times for pitting corrosion, in a long-term extrapolation. The measured repassivation potential in the laboratory time scale may serve as the critical potential for crevice corrosion in long time periods. However, the choice of the repassivation potential is conservative. Without (i) forced current or potential or (ii) addition of oxidizers, it has not been reported that crevice corrosion of Alloy 22 is initiated, except in very severe solutions of 4 M $MgCl_2$ at 95 °C [22]. In this severe solution, the repassivation potential is likely to be close to the pitting potential.

The induction times for crevice corrosion, discussed above, were assessed further, assuming that the occluded crevice has a critical chemistry. Therefore, the times to reach the critical chemistry also need to be evaluated. Many models and experimental data on the time- dependent chemistry and pH in the occluded crevice area were presented [11,62] for active and passive metals in reviews and models. Data and models predict that the crevice area will be under critical potentials, and pH, for initiation of crevice corrosion within the laboratory test time of days. If such critical environments could not form swiftly, models suggest that crevice corrosion would not occur in longer periods of time. Therefore, the laboratory data could be used for the long-term prediction of localized chemistry.

3.3. Crevice area

In the current design of the potential Yucca Mountain repository US Department of Energy [58], crevice corrosion could be initiated if accumulations of rock rubble cause drip shield buckling and contacting the WP [21]. The potential crevice is from the contact of drip shield and the WP, and could be quite tight, because the rock rubble applies only localized stress onto a buckled drip shield. Current structural analyses of the contact area suggest that the contact area could be restricted but extensive on the order of fraction, $10^{-2} - 10^{-1}$ of total WP surface area. Although contacts between the pallet and the bottom of the WP also may create the potential for crevices, the crevice formed by buckled drip shields and the top of the WP may lead to the highest potential for groundwater intrusion and subsequent radionuclide release.

Given a tight crevice area, the areas of welds on the WP appear more susceptible to crevice corrosion for Alloy 22, in simulated Yucca Mountain environments [48]. In the actual metal fabrication, the weld area is still small, on the order of fraction, ~0.01 of total WP surface area (based on ASM Handbook vol. 6, [5], and estimated heat input), compared with the total WP surface area. Relatively small crevice and weld areas further restrict the potential for release of radionuclides from the opening area of the WP.

3.4. Pit area, inside crevice, from crevice corrosion

In simulated groundwater of the potential Yucca Mountain repository, He and Dunn [23] conducted experimental studies, of crevice corrosion propagation, of Alloy 22, in 5 M NaCl solutions, at 95 °C (203 °F). Initially, crevice corrosion preferentially started around the edge and spread immediately after initiation, toward the center of the crevice former and partially away from the crevice former toward the non-creviced specimen surface. Gradually, some corrosion sites repassivated and the crevice corrosion propagation was limited to some deep sites. The penetration evolution, with time, indicated a strong stifling tendency of Alloy 22 crevice corrosion propagation (stifling refers to a decrease of penetration rate compared to that predicted by theoretical calculation). The details of the Alloy 22 penetration rate and crevice corrosion stifling and repassivation in 5 M NaCl solutions at 95 °C (203 °F) are described by He and Dunn [23]. The crevice corrosion process could continue in the potential repository environments for a longer period of time than testing times, however, the opening area caused by crevice corrosion could be very restricted. Fig. 5 shows the current transient, indicating that active corrosion occurs in a large area in the first 2 days, and gradually it is restricted to a very small area within 2 more days. Microstructural examinations after tests were made to confirm this indication. Microscopic examination further shows that the dimension of the active pits is on the order of 10 B 100 μm [$3.9 \times (10^{-4}–10^{-3})$ inch] and the area fractions of the deep penetration sites are on the order of 0.01–0.1. The initial rate of active corrosion could be higher than the recorded values because of a limited recording sensitivity and only a fraction of the crevice area was attacked even initially. Therefore, the small area opening by pits inside the crevice may further restrict either water intrusion into, or radionuclide release from, a potentially breached WP.

3.5. Radionuclide release

Radionuclide release may start after WP failure, due to groundwater entering the WP by seepage. The amount of the groundwater seepage could be very restricted through the small WP opening area described above. This seepage groundwater can mobilize the radionuclides by waste form dissolution. Mobilized radionuclides can be released out of the WP through a potential opening of the WP surface. The released radionuclides may be transported through groundwater flow and into the environment, which might result in a dose to the public. Relative to other processes in the performance assessment, opening area has a large effect on radionuclide release rates, based on the exercise results using NRC's total-system performance assessment code [42]. For example, over a 10,000 year period, a 4-order-of-magnitude increase in surface area results in an approximately 2-order-of-magnitude increase in radionuclide release rates [1]. The disproportionality between the surface area and the radionuclide release rate occurs because several mechanisms for radionuclide transport (e.g. diffusion or advection) are involved. Microstructural analyses did not indicate that individual pits get bigger for more radionucluide releases.

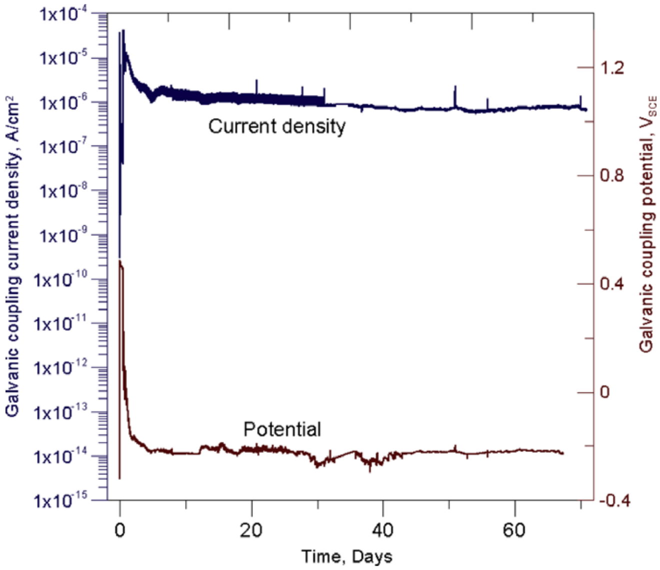

Fig. 5. Current transient during crevice corrosion propagation of Alloy 22 in 5 M NaCl solutions at 95 °C (203 °F) [23] (cm^2 = inch^2/6.45).

4. Summary

Laboratory analyses and data from industrial and natural analogs suggest that long-term passivity may be persistent, for Alloy 22, under potential Yucca Mountain repository conditions. Detrimental sulfur segregation, however, may occur in a time period longer than hundreds of years. The alloy's molybdenum content, however, allows the possibility of the segregated sulfur to quickly dissolve, and Alloy 22 can become repassivated quickly, as well. A PDM offers insights for long-term conformance of chromium oxide passive film. Such a model suggests that a steady-state passive film may be maintained, as the outer layer dissolves and the inner layer is regenerated continuously. However, effects from other constituents such as silica deposition, may have helped protect the pristine metal surface. There are additional degradation processes, such as mechanical spallation of passive film by void formation, porous film development by episodic dry–wet process, anion selective sorption, and large cathodic surface area development, that show less evidence for creating accelerated corrosion. An evaluation of induction times for crevice corrosion and relevant pitting corrosion suggests that the induction times are short, typically measurable in a laboratory. The short induction times measured indicate that laboratory test data may represent long-term corrosion rates. The potential Yucca Mountain repository may have low volumes of groundwater and a small probability for unfavorable water chemistry, producing limited opportunities to induce crevice corrosion. If crevice corrosion were to occur, the opening area could be restricted by the effects of metal fabrication, limited crevice area, and pit formation in the crevice. A performance assessment of the total-system suggests that radionuclide releases appear sensitive to the opening surface area of the WP.

Acknowledgement

The authors wish to thank C. Ryder and R. Sun, of NRC, for, respectively, a numerical iteration, and a careful review.

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