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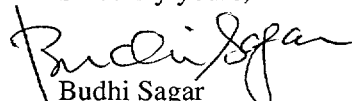
U.S. Nuclear Regulatory Commission
ATTN: Mrs. Deborah A. DeMarco
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Subject: Programmatic review of Long-Term Passive Dissolution and Localized Corrosion of Alloy 22

Dear Mrs. DeMarco:

Attached is a paper that complements the presentation made by Gustavo Cragnolino at the U.S. Nuclear Waste Technical Review (NWRTRB) International Workshop on Long-Term Extrapolation of Passive Behavior held on July 19-20, 2001 in Arlington, VA. The paper was requested by the NWRTRB to be placed in its web site, together with the contributions of the other 13 participants in the workshop, and eventually will be published in a public document. Please contact Gustavo Cragnolino at (210) 522-5539 if you have any questions regarding this paper.

Sincerely yours,


Budhi Sagar
Technical Director

BS:GC:jg

Enclosure

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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 $95^\circ C$), and pHs (0.7 to 8.0), and found that the current density is slightly dependent on potential and such environmental variables (Cragnolino 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 $1.25 \times 10^{-10} A/cm^2$, 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 $95^\circ C$ under an applied potential of $0.1 V_{SCE}$, a current density close to $1.0 \times 10^{-8} A/cm^2$ 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 $0.1 \mu m/yr$. 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, Cragnolino 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 will be 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_{rcrev}
T decrease	(+)	(+)
pH increase	(-)	(0)
$[\text{Cl}^-]$ increase	(-)	(-)
$[\text{NO}_3^-]$ or other inhibitors increase	(0)	(+)
$[\text{HCO}_3^-]$ increase	(-)	(0)
$[\text{F}^-]$ or other activators increase	(-)?	(-)?
$[\text{S}_2\text{O}_3^{2-}]$ 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_{rcrev} 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_{rcrev} . 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_{rcrev} for Alloy 22 even in relatively dilute chloride solutions at 95 °C. This decrease in E_{rcrev} 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_{rcrev} 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_{rcrev} 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.

Acknowledgment

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References

Brossia, C.S., L. Browning, D.S. Dunn, O.C. Moghissi, O. Pensado, and L. Yang. *Effect of Environment on the Corrosion of Waste Package and Drip Shield Materials*. CNWRA 2001-003. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses. September 2001.

Cragolino, G.A. D.S. Dunn, Y.-M. Pan, and O. Pensado. Corrosion Processes Affecting the Performance of Alloy 22 as a High-Level Radioactive Waste Container Material. *Scientific Basis for Nuclear Waste Management XXIV*. K.Hart, Ed. Materials Research Society. Warrendale, PA. Symposium Proceedings (In press).

Dunn, D.S., G.A. Cragolino, and N. Sridhar. An Electrochemical Approach to Predicting Long-Term Localized Corrosion of Corrosion-Resistant High-Level Waste Container Materials. *Corrosion*. Vol. 56, pp. 90-104. 2000.

Dunn, D.S., C.S. Brossia, and O. Pensado, Long-Term Dissolution Behavior of Alloy 22: Experiments and Modeling. *NACE Corrosion 2001*, Paper No. 01125. Houston, TX: NACE International. 2001.

Macdonald, D.D. The Point Defect Model for the Passive State. *Journal of the Electrochemical Society*. Vol.139, pp. 3,434–3,449. 1992.

Pensado, O., D.S. Dunn, and G.A. Cragolino. Modeling of the Passive Film on Nickel-Chromium-Molybdenum Alloys. *Symposium on Corrosion of Metals and Alloys. Materials Research Society (MRS) 2000 Spring Meeting*. San Francisco, CA. April 2000.