HLWYM HEmails

From: Andy Jung
Sent: Thursday, March 08, 2007 5:57 PM
To: Gustavo Cragnolino
Cc: Yi-Ming Pan
Subject: RE: Teleconference with J Payer (lead, S & T) on Corrosion
Attachments: key issues_meeting_Joe Payer_rev00.doc

Hi Gustavo,

I prepared the key issue summary relating Long-term persistence passive film of Alloy 22. The summary will be utilized for teleconference meeting tomorrow. Most issues have been raised at 2001 NWTRB meeting. Please review this summary and give your feedback as soon as possible. Thanks,

Andy

-----Original Message-----
From: Yiming Pan [mailto:ypan@cnwra.swri.edu]
Sent: Tuesday, March 06, 2007 5:24 PM
To: Corrosion_Group
Cc: Sitakanta Mohanty
Subject: FW: Teleconference with J Payer (lead, S & T) on Corrosion

All,

The Center staff will meet in room A137 this Friday (3/9/07) at 1:00 pm central time.

Thanks,
Yiming

-----Original Message-----
From: Tae Ahn [mailto:TMA@nrc.gov]
Sent: Tuesday, March 06, 2007 9:59 AM
To: Yi-ming Pan; James Rubenstone; Sheena Whaley; Tae Ahn
Cc: Brittain Hill; Bret Leslie; Mahendra Shah; Timothy McCartin
Subject: Teleconference with J Payer (lead, S & T) on Corrosion

Item Type: Appointment
Start Date: Friday, 9 Mar 2007, 02:00:00pm (Eastern Standard Time)
Duration: 2 Hours
Place: O3B2

Prasad Nair of BSC called me again. We will focus on Long-Term Persistence of Passive Film. For deliquescence/localized corrosion, DOE is preparing a response letter to NWTRB. Others are basically the same as ongoing/summing up work. Actually, Jim has also suggested a prioritization. Prasad will set the meeting tentatively from 2:00 to 4:00 pm (NRC), 3/9 (Friday). Please let me know if you have any suggestion. Thank you, Tae

Hearing Identifier: HLW_YuccaMountain_Hold_EX
Email Number: 436

Mail Envelope Properties (hjung@cnwra.swri.edu20070308175600)

Subject: RE: Teleconference with J Payer (lead, S & T) on Corrosion
Sent Date: 3/8/2007 5:56:44 PM
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From: Andy Jung

Created By: hjung@cnwra.swri.edu

Recipients:
"Yi-Ming Pan" <ypan@cnwra.swri.edu>
Tracking Status: None
"Gustavo Cragnolino" <gcragnol@cnwra.swri.edu>
Tracking Status: None

Post Office:

Files	**Size**	**Date & Time**
MESSAGE	1609	3/8/2007 5:56:00 PM
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Options
Priority: Standard
Return Notification: No
Reply Requested: No
Sensitivity: Normal
Expiration Date:
Recipients Received:

Key Issue summary
(Long-term Persistence of Passive Film of Alloy 22)

1. Long-term stability and presence of a thin and conformal chromium oxide underlayer:
From the currently available short-term and 5+ year long-term experimental data, DOE assumed that long-term stability of the passive film on Alloy 22 could be maintained by the formation of a thin and conformal chromium oxide film with a sufficiently low general corrosion rate under the potential repository conditions to ensure the lifetime of the waste packages.(Bechtel SAIC Company, LLC, 2004, 2003). Primary finding from 5+ year long-term corrosion test facility is that the metal-oxide does not thicken appreciably with time in mimic SAW, SCW and SDW at 90 ^{o}C, however, the exact nature of the oxide could not be determined due to the interference from other carbon and iron deposits from the tank lining dissolution and silicate scale (Orme, 2005).

2. Cr depletion:
One of potential degradation mechanisms on the risk-significance is chromium depletion phenomena. DOE observed the lower Cr concentration (<20 at% from the AES results) at the interface between the metal and the oxide film of Alloy 22 after short-term potentiostatic polarization test (Orme, 2005). The lower Cr content at the interface can affect to the formation of protective Cr-rich oxide film. In the event of film breakdown by any reason, the newly formed oxide film may not have the same composition (i.e., lower Cr content) and/or structure (i.e., less compact) as the original oxide film, which could increase the corrosion rate of Alloy 22. Lloyd et al. (Lloyd, 2003) observed substantially higher passive current densities and lower overall Cr content of the oxide on Alloy C-276 (Ni-16Cr-16Mo-4W-5Fe) comparing those on Alloy 22 (Ni-22Cr-14Mo-3W-5Fe) in 1 M NaCl and 0.1M H_2SO_4 at 85°C.

3. Anodic sulfur segregation:
Many literature data for Ni-based alloys showed an enhanced corrosion rate due to detrimental effect of sulfur impurity in the alloys which segregates to the metal surface and inhibits the oxide film formation (*Marcus, 1995*). Increased sulfur content from 2 at% to 5 at% on the metal surface of Alloy 22 after 29 days immersion in NaCl solution has been also observed by DOE (*Jones, 2006*). Even if alloy additions such as chromium and molybdenum are known to counteract the detrimental effect of sulfur in nickel by formation of molybdenum sulfides and chromium oxide, respectively, the reported mean general corrosion rate of Alloy C-4 (Ni-18Cr-17Mo-3Fe) in NaCl-rich brines containing $6X10^{-4}$ M Na_2S at 150°C was 510 nm/yr for 12-month test period, which was about seven times higher than the corrosion rate in the absence of Na_2S (Smailos, 1993). Assuming that the sulfur content in Alloy 22 is 100 appm at a corrosion rate of 0.01 μm/yr could accumulate a monolayer of sulfur on the metal surface in 500 years if 100 percent of the sulfur atoms is retained at the surface (Waste package Materials Peer Review Panel, 2002).

4. Instability at high temperature or under wet dry conditions:

In dry conditions a thicker oxide is likely to be formed at higher temperature. A problem could be the presence of a water layer with high concentration of salts at a relatively high temperatures. In addition, the behavior of this thicker oxide is not known when further exposed to cool and humid conditions. The lack of data makes it difficult to make a rational comparative analysis of the two situations.

5. Ion sorption through corrosion products and development of large cathodic surface area:

Detrimental synergisms from the simultaneous enrichment of anions such as Cl- and F- from the electrolyte on the waste package surface by sorption process of anion into the passive layer itself has been identified as a possible detrimental effect on the long term passivity. The gradual development of a deposited outer hydroxide layer on top of the passive film will promote localized corrosion at potentials below crevice repassivation potential. Suleiman et al [1994] observed anion selective sorption with iron rust membrane to stabilize pitting in 304L stainless steel.

Surface area increases by roughening would also increase overall cathodic efficiency. In the presence of large surface area of semiconducting corrosion products, passive dissolution of metal can be accelerated to be balanced with the increased cathodic reaction.

6. Increased cathodic kinetics:

The production of H2O2 and other products by radiolysis from gamma radiation and other reducible species (i.e., O2, Fe3+) can results in an increased passive dissolution by increasing cathodic kinetics and possible degradation of passivity. There is no evidence that radiation damage of the passive film of Alloy 22 will alter its protective properties.

7. Film spallation by vacancy accumulation at metal-oxide interface:

Another issue is a film breakdown due to void formation at metal/film interface by accumulation of cation vacancies during long-term exposure at elevated temperature, as assumed the point defect model as a principal mechanistic model. This void formation leads to mechanical spalling of the passive film and could affect the long-term stability of the passive film by increasing the effective general corrosion rate of Alloy 22 by surface roughening.

List of references

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Lloyd, A. C., D. W. Shoesmith, N. S. McIntyre and J. J. Noel. “Effect of temperature and potential on the passive corrosion properties of Alloy 22 and C276", J. Electrochem. Soc. Vol.150 (4) B120-B130, 2003.

Marcus, P., “Long Term Extrapolation of Passive Behavior”, Proceedings from the International Workshop on Long term Extrapolation of Passive Behavior, Arlington, Virginia, July 19-20, 2001. A. A. Sagues and C. A. Di Bella, eds. Arlington, Virginia: U. S. Nuclear Waste Technical Review Board. pp.55, 2001.

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Suleiman, M.I., I. Ragault and R.C. Newman. Pitting of stainless steel under a rust membrane at very low potentials. Corrosion Science. Vil.36. pp.479-486. 1994