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U.S. Nuclear Regulatory Commission
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Subject: Submittal of Revised Intermediate Milestone—Natural Analogs of High-Level Waste Container Materials—Experimental Evaluation of Josephinite, Intermediate Milestone 06002.01.081.340

Reference: E-mail from Tamara Bloomer to B. Sagar dated September 10, 2003—Acceptance of Intermediate Milestone 06002.01.081.340, "Natural Analogs of High-Level Waste Container Materials—Experimental Evaluation of Josephinite"

Dear Ms. Bloomer:

Enclosed is the revised version of the subject intermediate milestone on the experimental investigation of josephinite as a natural analog of high-level waste container materials. As noted before, the josephinite sample used in this study was characterized as a predominant awaruite phase, with a composition close to the stoichiometry of Ni_3Fe , and covered by a serpentine alteration layer in its outer surface. Electrochemical studies showed that josephinite exhibited passivity at a higher pH than did a synthetic cast nickel-iron alloy of similar composition and was found to be slightly more susceptible to pitting corrosion. The passive film formed on the josephinite has a duplex structure consisting of an iron-rich hydroxide outer layer and a nickel-rich oxide inner layer. Results obtained from this investigation provide an appropriate characterization of the environmental conditions leading to passivity and localized corrosion. Passivity alone, however, does not provide a satisfactory explanation for the survivability of josephinite in nature. The relationship between the passive behavior of the metal surface and the formation of the alteration layers needs to be established in understanding the survivability of josephinite. Enclosed with the report is the CNWRA staff response to the NRC comments.

If you have any questions regarding this report, please feel free to contact Gustavo Cragolino at (210) 522-5539 or myself at (210) 522-5439.

Sincerely yours,



Vijay Jain
Element Manager
Corrosion Science & Process Engineering

VJ:jg

Attachments

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**RESPONSE TO NRC STAFF COMMENTS ON THE CNWRA REPORT
"NATURAL ANALOGS OF HIGH LEVEL WASTE CONTAINERS
MATERIALS-EXPERIMENTAL EVALUATION OF JOSEPHINITE"**

Comment: DOE's immersion test results showed the deposit of mineral compounds as discussed in Chapter 5. Nonetheless, currently the slow corrosion rate from these tests is understood due to the passive layer underneath this mineral deposit. This report does not provide information on the (10 - 20) Å layer beneath Serpentine mineral deposits (alteration layers) on Josephinite. Considering that the difference of minerals deposits is understandable between the DOE tests and Josephinite from the different environmental conditions, the identification of the passivity underneath the mineral deposit may be one way to address the future work which the report suggests to understand the relationship between the passive behavior and the formation of the alteration phase.

Response: No change in the report. Even though this is a difficult task, the examination of the metallic layer beneath the alteration layers can be conducted as suggested in the report. It is included as an activity in the FY 2004 OPS plan if additional resources become available.

Comment: Regarding looking for the evidence of the point defect model of long-term passive behavior of a Ni-Cr-Mo alloy, the void formation may occur only if the solid state transport mechanism across the passive layer is the same as that in the system where the void is predicted.

Response: The text was clarified to indicate that in both cases, josephinite (or Ni₃Fe) and Alloy 22, the solid state transport mechanism across the passive layer is cation conduction according to the point defect model (PDM) The transport is presumably dominated by Cr interstitials in the case of Alloy 22 whereas cation vacancy conduction predominates in the case of josephinite. Although the rate of transport of cation interstitials is presumably far more slower than that of cation vacancies, voids by coalescence of vacancies in the metal substrate should be the result of transport by both types of charge carriers in the long term. According to the PDM, voids cannot be formed by coalescence of vacancies if anion vacancy conduction predominates. It was noted that even though voids were not observed in the josephinite sample, the corrected statement does not constitute an invalidation of the PDM.

Comment: Lack of chlorides in the void is contrary to the observation in meteorite, which was reported in the previous report (CNWRA 2002-02). Does this indicate no localized corrosion in Josephinite? In addition, it doesn't seem to be appropriate to look for chloride in the crack or voids, unless the cracks or voids are from localized corrosion and growing SCC cracks.

Response: For clarity, the text was modified to indicate that the crack or voids filled with serpentine do not contain chloride and therefore, they were not the result of corrosion processes.

Comment: Although criticism/evaluation is an important aspect of the scientific investigation, important findings should not be overshadowed because of this nature. This report may extend to highlight benefits from this study. For examples many observations indicate the validity of modern electrochemical corrosion theory which is currently adopted in assessing the long-term waste package performance. It is important to increase our confidence in the currently available theory until better theories come later. Such evidence includes: similar electrochemical behavior (especially passivity) between Josephinite and the synthetic nickel-iron alloy used; Josephinite is more corrosion resistant compared with buried iron-base objects as a result of the presence of nickel.

Response: The text was modified in a couple of places following the recommendation of this valuable comment.

Comment: In p. 5-3, the corrosion rate of Josephinite is reported to be very high compared with the long survival time of Josephinite. However, we also need to consider the different geological environmental conditions and various mineral size. The opposite inference may be the passive current density continued to be lowered with the protection of growing outer passive layer or mineral deposits.

Response: This comment is being addressed in several parts in the report, and in particular at the end of Chapter 5 by introducing an additional sentence.

Comments: a) Use the second sentence in the Introduction (1st para. It is recognize...). In the abstract to explain why we are considering analogs; b) Last sentence first paragraph of Introduction. Part 63.114 only gives analogs as an example of the types of information needed for PA. Please make that clearer in this sentence; c) 3rd Para. 1st sent. ... Types of Alloys or type of alloy?; d) 1.1 1st para. Second sentence add that after ..."cited as evidence (that) the corrosion..."; e) Section 3.1 1st para . Why was the solution simplified with respect to that used in the LTCTF?; f) Section 4.1 Page 4-2 please verify that the X-PS has the capabilities to evaluate thickness and accurately see less than 30 A;;g) Section 5 page 5-5 The paragraph about LLNL is out of place I suggest you remove it from there, and h) Section 6 3rd para. 1st sent. Clarify in-depth sputtering or depth profile by sputtering.

Response: All these comments which are mostly editorial were considered and appropriate changes were made. Responding to f) it should be clarified that XPS has such capability as clearly noted in Figure 4-2. Responding to h) even though in-depth sputtering is a well accepted terminology it was added in-depth ion sputtering to clarify better the processes of removing thin metal layers sequentially by ion etching as described at the beginning of Section 4.1.

Comment: Very good analysis between the passive behavior of Josephinite vs. an as cast Ni₃Fe sample. However, we need more info on how the Josephinite passivity differs from C-22 passivity because this is what is important to take away from this type of report. This should be an easy paragraph or section. Basically, the passive region associated with C-22 covers a much greater potential and chemistry range. They explain bits here and there without a concise place to

discuss this point. This is a major point that needs to be addressed. A great place to put this info would be in the summary and page 5-4.

Response: A couple of paragraphs were added to clarify the difference between Alloy 22 and Josephinite, including two figures with anodic polarization curves of Alloy 22 in solutions identical to those used for Josephinite. From these figures comparison can be drawn regarding passive range, pitting initiation and repassivation potentials, and other features that reveal substantial differences between the two materials.

Comment: Similar to comment above, it would be nice to try to compare the anodic polarization curves for similar conditions between C-22 and Josephinite. Of particular interest is a comparison between the passive current densities between these two materials at similar pHs. Furthermore, the critical and repassivation potentials are significantly different between Josephinite and C-22. In fact from my recollection, the region of localized corrosion susceptibility is VERY/EXTREMELY different between these two materials.

Response: See response above.

Comment: Understandability, they do not compare the complex C-22 passive film to the Josephinite passive films because they are currently getting that data for C-22. However, I would think it may be useful to describe the differences (as we know them) between the C-22 passive film and the Josephinite passive film.

Response: The comparison was made using data recently published by Lloyd, et al. (2003) to describe the differences in composition of the passive film formed in both materials.

Comment: More information on the intermetallic nature, crystal structure, and bonding characteristics should be presented for both Josephinite and cast Ni_3Fe . A small section on characteristics and physical properties may be in order so that we get a feel for how different this mineral is compared to an engineered alloy. After looking up the data yesterday and today, I believe these Josephinite and Ni_3Fe intermetallics are metallicity bonded unlike covalently bonded intermetallics such as NiAl . This in itself is important to distinguish. Furthermore, the crystal structure is important to understand if there are any crystallographic differences that may be different between the Josephinite and Ni_3Fe , i.e. they say its ordered, but, is it body-centered cubic or FCC ordered. This info should already be out in the literature and be placed in section 2.3.1 and 3.2, respectively.

Response: Most of the information requested has been included in this revision.

Comment: An inference was made on page 5-5 that the crack in the sample could have been caused by an SCC crack that filled with sediment and caused further crack propagation. Furthermore, they suggest that H^+ embrittlement due to the long range ordering may be a possible cause for the crack. They should also note here that ordered alloys and I guess minerals for that matter have very little ductility and high tensile strengths. These ordered type materials typically fail by

brittle fracture (I can give numerous examples from Ti, Ni, Al, and other alloy systems) and are only exacerbated by enhanced H+ embrittlement especially in these Ni-based alloys. They may need to add this type of information into this section.

Response: A sentence was added with an appropriate reference to indicate the loss of ductility of nickel base alloys as a result of long-range ordering reactions after thermal exposures.

Comment: Localized corrosion pits were detailed in many sections and I would like to see some data on the relative size of these pits and the pit propagation rates. This would also make for a good comparison to C-22.

Response: Micrographs were added to show typical pits found on both the josephinite and cast Ni₃Fe alloy samples after anodic polarization to potentials above the pitting initiation potential.

Response to Comments of James Rubenstone:

Leaving aside the comments on the Executive Summary and that on the DOE investigation which seems to be a matter of clarification, the followings points are a response to this set of comments which are paraphrased and summarized.

Comment: This comment refers to the estimated age of the josephinite sample.

Response: Text was added to clarify this point in more detail, even though it is clearly recognized that the available data is insufficient to establish a close estimate.

Comment: This comment refers to the origin of josephinite and the discussion regarding this issue in the geological literature. It is noted, however, that the ultimate origin of the josephinite has no bearing on its applicability as a natural analog for waste package materials.

Response: No change was introduced in the text because no quotable reference was provided to disprove the arguments of Bird and coworkers. In the text we were avoiding this discussion by quoting the different viewpoints without subscribing to any of them. We agree with the last sentence of the comment above.

Comment: This comment refer to the arcuate marks on the cut face of the sample.

Response: It is clarified in the text that the arcuate marks are a result of the cutting process.

Comment: This comments refers to units listed as in mm in the report.

Response: The original text had the correct units in μm . The geek letter was not recognized by the printer in the production of the report. It will be checked to avoid the same mistake in the revised version.

The final comment from Rubenstone regarding the role of the alteration layers is accepted as a valuable recommendation. However, it should be noted that it is based on the results presented in the report. If needed, further work will explore, as indicated in the report and in a response above, the relationship between the altered layers on the rock surface and the preservation of passivity by the metallic core.