

## HLWYM HEmails

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**From:** Gustavo Cragnolino [gcragnolino@satx.rr.com]  
**Sent:** Tuesday, February 13, 2007 5:36 PM  
**To:** Xihua He  
**Cc:** Yi-Ming Pan; Lietai Yang  
**Subject:** Re: NWTRB comments  
**Attachments:** Comments on NWTRB Letter\_XH\_LY.rev.doc

**Importance:** High

Xihua,

I read it and looks fine. I only remove the last sentence in the initial paragraph and correct a spelling mistake with deliquescence. Attached is the file with these corrections.

Gustavo

----- Original Message -----

**From:** [Xihua He](#)  
**To:** '[Lietai Yang](#)'  
**Cc:** '[Gustavo Cragnolino](#)'; '[Yiming Pan](#)'  
**Sent:** Tuesday, February 13, 2007 3:21 PM  
**Subject:** RE: NWTRB comments

All,

I combined the comments into one file, which is attached. The file is also at S:\YPan\NRC visit.

I appreciated Gustavo's prompt feedback on this.

Thanks,  
Xihua

-----Original Message-----

**From:** Lietai Yang [mailto:[ltyang@cnwra.swri.edu](mailto:ltyang@cnwra.swri.edu)]  
**Sent:** Tuesday, February 13, 2007 2:24 PM  
**To:** [xhe@cnwra.swri.edu](mailto:xhe@cnwra.swri.edu)  
**Cc:** 'Gustavo Cragnolino'; 'Yiming Pan'  
**Subject:** RE: NWTRB comments

[Xihua](#),

Enclosed is the modified file you may want to combine into your other file.

Thanks

-Lietai

-----Original Message-----

**From:** Gustavo Cragnolino [mailto:[geragnolino@satx.rr.com](mailto:geragnolino@satx.rr.com)]  
**Sent:** Tuesday, February 13, 2007 11:38 AM  
**To:** [xhe@cnwra.swri.edu](mailto:xhe@cnwra.swri.edu)  
**Cc:** Yiming Pan; Lietai Yang  
**Subject:** Re: NWTRB comments  
**Importance:** High

Xihua,

Attached are the two files with my comments. In your file I have followed your arguments and made corrections and changes in the text to clarify or amplify some points. In the Lietai's file all my comments are in italics.

Please take a look and decide how to incorporate my suggestions. If you combine everything in a single document I'm willing to take a look to the final text when it's ready. Let me know.

Gustavo

Gustavo Cragolino  
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(210) 493-8031  
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----- Original Message -----

**From:** [Xihua He](#)  
**To:** '[Gustavo Cragolino](#)'  
**Sent:** Monday, February 12, 2007 5:05 PM  
**Subject:** RE: NWTRB comments

Gustavo,

My comments are in the attachment.

Thanks,  
Xihua

-----Original Message-----

**From:** Gustavo Cragolino [mailto:[gcragnolino@satx.rr.com](mailto:gcragnolino@satx.rr.com)]  
**Sent:** Sunday, February 11, 2007 8:28 AM  
**To:** [xhe@cnwra.swri.edu](mailto:xhe@cnwra.swri.edu)  
**Subject:** Re: NWTRB comments

Xihua,

I will send you my comments on Tuesday morning.

Gustavo

----- Original Message -----

**From:** [Xihua He](#)  
**To:** [Gustavo Cragolino](#)  
**Sent:** Friday, February 09, 2007 3:49 PM  
**Subject:** NWTRB comments

Gustavo,

I attached my comments on the NWTRB letter. Also, I attached the Board letter in case you don't have it with you. Please provide your feedback to me by Tuesday morning if possible.

Thanks,  
Xihua

**Hearing Identifier:** HLW\_YuccaMountain\_Hold\_EX  
**Email Number:** 1646

**Mail Envelope Properties** (001601c74bf\$59bc29c0\$6400a8c0)

**Subject:** Re: NWTRB comments  
**Sent Date:** 2/13/2007 5:36:04 PM  
**Received Date:** 2/13/2007 5:41:42 PM  
**From:** Gustavo Cragolino

**Created By:** gcragnolino@satx.rr.com

**Recipients:**

"Yi-Ming Pan" <ypan@cnwra.swri.edu>  
Tracking Status: None  
"Lietai Yang" <lyyang@cnwra.swri.edu>  
Tracking Status: None  
"Xihua He" <xhe@cnwra.swri.edu>  
Tracking Status: None

**Post Office:** dimension

<b>Files</b>	<b>Size</b>	<b>Date &amp; Time</b>
MESSAGE	3050	2/13/2007 5:41:42 PM
Comments on NWTRB Letter_XH_LY.rev.doc		54336

**Options**

**Priority:** High  
**Return Notification:** No  
**Reply Requested:** No  
**Sensitivity:** Normal  
**Expiration Date:**  
**Recipients Received:**

## Part I. Comments on the NWTRB Letter Regarding Seepage-Induced Localized Corrosion

*We tend to agree with the comments of the Board in their Conclusion and the two paragraphs of additional observations. For us it is still not clear why DOE can screen out deliquescence induced corrosion (localized and general) with the data available. Our main problems with the Board letter are the points discussed below.*

- The Board stated that “The majority of the workshop dealt with the possibility of accumulated dust functioning as a crevice and causing localized corrosion.”

This statement seems to be incorrect. During the meeting, nobody raised the issue that dust functions as a crevice former. The majority of the presentations and discussions in the workshop dealt with the possibility of having salt deliquescence brines constituting an aggressive electrolyte that may cause localized corrosion if a crevice exists. In Joe Payer’s presentation, he discussed that the type of crevice former affected the crevice corrosion initiation probability. Ceramic washer wrapped with Teflon tape is the most severe crevice former and ceramic washer caused no crevice corrosion.

- Page 5, paragraph 3. The Board stated that “The only limiting factor to crevice-corrosion crack growth becomes the continuous supply of  $\text{Cl}^-$  to maintain the reducing acid inside the crevice. Under laboratory conditions where the crevices are purposefully tightly clamped and times are relatively short, diffusion of chloride into the crevice may be curtailed as the crevice propagates, precipitation of solid corrosion products may occur near the mouth of the crevice where the solution attempts to return to neutrality, and the crevice may effectively be “stifled.” In practice, however, the crevice-corrosion propagation rate may slow down until the interior of the crevice can be replenished in chloride, to form HCl and allow the reaction to continue.”

Based on the most accepted mechanisms of crevice corrosion, the  $\text{Cl}^-$  anions must diffuse (it could be an electromigration contribution too) into the crevice to balance the positive charge of the  $\text{H}^+$  ions produced by hydrolysis of the metal cations formed by the dissolution of the alloy in the crevice. The production of  $\text{H}^+$  ions in the crevice is the cause and the migration of  $\text{Cl}^-$  anions into the crevice is the consequence. The main corrosion product inside the crevice,  $\text{NiCl}_2$ , is mostly soluble, and even though precipitated corrosion products (e.g.,  $\text{Ni}(\text{OH})_2$ ) can be formed outside the crevice where the pH is close to neutral or even higher, it doesn’t seem that this process may impede the transport of  $\text{Cl}^-$  anions into the crevice, as demonstrated by some of our experiments in which crevice was not stifled as discussed below..

The most likely reason for the repassivation of crevice corrosion observed in our tests is that as crevice corrosion results in deeper penetration, the IR drop increases. The driving force for metal dissolution inside the crevice decreases, which leads to less alloy dissolution, less concentration of metal cations, and a lower concentration of  $\text{H}^+$  ions. This leads to a decrease of the  $\text{Cl}^-$  concentration inside the crevice. As a result, the critical solution composition in terms of pH and  $\text{Cl}^-$  concentration required for crevice corrosion propagation is not maintained and repassivation of the crevice occurs.

The other important factor that controls the crevice corrosion propagation of Alloy 22 is the kinetics of the cathodic reaction. Our experiments show that crevice corrosion of

Alloy 22 coupled to an Alloy 22 plate can not be initiated under naturally corroding conditions (open circuit) in air saturated solutions without the addition of a strong oxidant such as the  $\text{Cu}^{2+}$  cations in the form of  $\text{CuCl}_2$ . After the addition of  $\text{CuCl}_2$ , crevice corrosion can be initiated but it tends to stifle and eventually, in most cases, repassivation occurs. However, when Alloy 22 is coupled to Platinum, a metal in which the kinetics of the cathodic reaction in air saturated 5 M NaCl solution (the oxygen reduction reaction) is strongly accelerated, crevice corrosion can be initiated under open circuit conditions without the addition of  $\text{CuCl}_2$  and steady propagation is maintained. Other experiments in which Alloy 22 was coupled to a Titanium Grade 7 demonstrated that steady propagation of crevice corrosion can be maintained but requires the addition of  $\text{CuCl}_2$  to the air saturated 5 M NaCl solution. In conclusion, it appears that stifling and repassivation are not the results of the depletion of  $\text{Cl}^-$  anions as the arguments of the Board letter suggest but is mostly controlled by the efficiency of the cathode and the IR drop in the crevice.

- Page 5, paragraph 3. The Board stated that “Crevice corrosion seldom is observed to be stifled under industrial conditions. If it were, crevice corrosion would not be a particular problem for practical applications.”

Stifling of crevice corrosion strongly depends on the material, temperature, and solution chemistry. In industrial applications crevice corrosion is a problem because in many cases the alloys used (e.g., stainless steels) are marginally resistant to crevice corrosion. When more corrosion resistant alloys are used such as Alloy 22 the probability of having crevice corrosion decreases significantly, but it is not known if under certain conditions, even though crevice corrosion could be initiated, it doesn't lead to failure or penetration because the crevice corrosion process was arrested.

- Page 5, Paragraph 4. The Board stated that “Under repository conditions, where the times will be exceptionally long, it is doubtful that any crevice corrosion that might occur because of chlorides would be stifled because of diffusion considerations. Laboratory studies such as those conducted by He and by Scully [Scully/Bocher 2007]<sup>1</sup> do not appropriately model a chloride-induced crevice condition since they are performed with concentrated chloride solutions, often with low pHs. Thus, no appreciable concentration gradients are established.”

It appears that the Board thinks that our experiments are not relevant to the repository conditions because we are using a concentrated chloride solution in the bulk environment and therefore when the crevice is active there is no significant concentration gradient between the environments outside and inside the crevice. The Board thinks that in the repository a strong concentration gradient would be expected because a dilute seepage solution may exist outside the crevice and a concentrated solution will be generated inside the crevice. While this may be true in terms of the  $\text{Cl}^-$  concentration, it is not valid with respect to pH because our tests are conducted with solutions of neutral pH.

We share the concern of the Board regarding the validity of laboratory tests to conduct a realistic evaluation of the probability of arresting crevice corrosion in the repository conditions once initiated. Nevertheless, the importance of understanding the influence of all factors in the propagation of crevice corrosion cannot be disputed and our experimental work is advancing in that direction. In the letter of the Board there are some general concepts that cannot be applied to the case of Alloy 22 and in some cases

erroneous statements. In the last paragraph of page 4 it is emphasized that nitrate (and molybdates and tungstates) are strong oxidant but this is not the case at pH above 3. Only nitric acid is a strong oxidant and its role is to increase the potential to the range in which passivity occurs rather than established or repair the film. The other anions are typical inhibitors derived from the fact that are oxyanions of weak acids.

Additional work should be conducted in the area of deliquescence induced general and localized corrosion to complement the work done at lower temperatures. At these temperatures corrosion under limited-thickness liquid films should be conducted. Also the variability in crevice gap associated to the advance of the corrosion front should be evaluated further.

## **Part II. Comments on the NWTRB Letter Regarding Deliquescence-Induced Corrosion**

### **Points on Page 2**

DOE's and EPRI's positions are that the answers to the final two questions are NO. Their positions appear to rely on the role of nitrates in both the deliquescence process and in mitigating corrosion, based on the following observations/assumptions:

- **Salts are in small amounts in airborne dusts in the Yucca Mountain vicinity.**

There is no strong experimental evidence to show that corrosion rate is low if the amount is small. Need to be verified. Small amount of salt may form thin film of liquid and if there is no mechanism to consume the salt, thin film corrosion may give high corrosion rate.

*DOE relies on the amount of salts to make their case, and the Board did not question this.*

- **Any stable chloride-containing brine formed by deliquescence at high temperatures must have significant fractions of nitrate.**

The nitrate inhibition concept are challenged by the recent DOE report (Dixit, et al, 2006) in which localized corrosion was observed under deaerated and pressurized solutions (in autoclaves) with NO<sub>3</sub>-to-Cl ratio of 7.4 and 0.5 at 160 °C and 220 °C, respectively (see below).

- **Brines formed by deliquescence at high temperatures may change with time, e.g., by degassing HCl or HNO<sub>3</sub> (Bryan 2006; King 2006).**

The board discussed several possibilities regarding degassing. If HCl degas first, the remaining solution will be benign for localized corrosion; if HNO<sub>3</sub> degas first, the remaining solution will be more detrimental. DOE also argued during the question and answer period that the degassing of HNO<sub>3</sub> will lead to the disappearance of liquid salts because the chloride-rich solution will not be soluble. Therefore, the ultimate effect fo degassing in any case will be beneficial. However, degassing phenomena has not been experimentally demonstrated. It should be verified.

- **Only limited amount of salt and brine are available to initiate corrosion. The average volume was only 1.8 uL/cm<sup>2</sup> which corresponds to 18 um liquid film. Doe claim that such dust would be held in the insoluble dust.**

This value (18 um thick) need to be verified. Also, as mentioned in Item 1, thin film of liquid may cause higher corrosion rate. There is no evidence to show that the liquid will be sucked into the dust under the Yucca Mountain conditions. The 18 um value was probably derived based on the assumption that the dust will be evenly distributed on the entire waste package. This assumption does not account for the facts that some places will collect more dust and some places will collect less dust.

### Points on Pages 6 and 7

- **Concentrated chloride/nitrate brines have been postulated to degas, and at least one laboratory test confirmed volatility of some acid species [Yang, 2006].** This statement is not completely true. The presentation did not show any degassing data. During the Q/A, when asked by the audience about the pH measured in the condenser, the presenter answered that the pH was low, but the low pH was not reproduced in later experiment. There is uncertainty regarding degassing. We are not sure about the degassing phenomena at this time.
- **It has been postulated that nitrates are effective inhibitors at ratios as low as 0.5 at temperatures as high as 200 o C [ King, 2006].**

This is contradictory to a recent DOE report (Dixit, et al, 2006) in which localized corrosion was observed under deaerated and pressurized solutions (in autoclaves) with NO<sub>3</sub>-to-Cl ratio of 7.4 and 0.5 at 160 °C and 220 °C, respectively.

The autoclave test condition may simulate the conditions, in terms of oxygen fugacity, in some parts of the repository where sufficient ground water continuously move towards the heated zone of the drift and is evaporated into large amount of water vapor. This large amount of water vapor will lower the partial pressure of oxygen in the heated zone because the total pressure in the drift will be ambient.

*We think DOE should do more test on the volatility of HCl and HNO<sub>3</sub>, otherwise, the whole repassivation concept is in jeopardy because the corrosion potential reported for the subject system was lower than the repassivation potential. The whole DOE localized corrosion model is based on the repassivation potential model.*

- **For the environments postulated for the repository, with acid degassing, the evolution of the relative humidity in the repository is such that the package will not be wet until temperatures have declined to the vicinity of 100-120 oC.**

Here the degassing mechanism is not supported by experimental results.

