LSNReviews

From: Pavan Shukla [pshukla@cnwra.swri.edu]
Sent: Tuesday, January 23, 2007 10:22 AM
To: Todd Mintz; Xihua He; Yi-Ming Pan; Roberto Pabalan
Subject: Revised work plan
Attachments: LimitedElectrolyte_ThinFilmV3.ppt

All,

I have substantially revised the work plan based on your suggestions.
Please take a look at this and let me know if I missed anything.

Sincerely
Pavan

Properties Page

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Date: Tue, 23 Jan 2007 09:21:53 -0600
From: Pavan Shukla <pshukla@cnwra.swri.edu>
Subject: Revised work plan
To: Todd Mintz <tmintz@cnwra.swri.edu>, Xihua He <xhe@cnwra.swri.edu>,
Yi-Ming Pan <ypan@cnwra.swri.edu>, Roberto Pabalan <rpabalan@cnwra.swri.edu>
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Localized Corrosion of Alloy 22 in Limited Electrolyte Environment

Pavan Shukla

Xihua He

Roberto Pabalan

Tae Ahn

Outline

- Background
- Objective
- Preliminary Calculations
- Proposed Work
- Proposed Approach
- Summary

Programmatic Background

- Waste packages are expected to be covered by a thin film of electrolyte layer during dust deliquescence and seepage

- CNWRA Experimental observations in dust deliquescent brines
  - High general corrosion rates (1-10 μm/year) of Alloy 22 at 150 and 180 °C
  - Localized corrosion has not been observed but its possibility can not be ruled out

- DOE plans to screen out the localized corrosion due to dust deliquescence brines
  - Amount of dust-deliquescent brines is too low to cause waste packages corrosion
  - DOE experiments show localized corrosion in dust deliquescent brines[1]
  - Uncertainty of waste package damage due to dust deliquescence corrosion remains to be resolved[2]

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1. Newer Alloy 22 Data and Their Relevance to High-Temperature Localized Corrosion. Raul B. Rebak. Presentation at the NWTRB Workshop on Localized Corrosion of Alloy 22 in Yucca Mountain Environments. Las Vegas, Nevada. September 26, 2006.
2. United States Nuclear Waste Technical Review Board, Jan. 12, 2007, Arlington, Virginia

Programmatic Background (Cont'd)

- Under Office of Science and Technology International (OSTI) program of DOE, Dr. Joe Payer and others have conducted modeling work to determine the role of the amount of electrolyte and the presence of dust particles on localized corrosion of stainless steel at 25 °C.

- It is not clear if the modeling results will be used in the license application, but its purpose is to support the DOE plan for screening out of localized corrosion due to dust deliquescence.

- The primary goal of the proposed work is to evaluate the technical basis for screening out the localized corrosion due to dust deliquescent brines

- The proposed work will also be useful to develop an improved understanding of localized corrosion during seepage
  - CNWRA has developed an abstracted model for localized corrosion during seepage
  - Model parameters are determined using the experiments conducted under fully immersed condition

Technical Background

- To initiate and sustain localized corrosion, the number of electrons produced by the anodic reactions must be consumed by the oxygen reduction reaction
  - Localized corrosion would be stifled if reaction rate of oxygen reduction reaction is limiting
- Details of modeling work conducted by Dr. Joe Payer and others:
  - Based on available experimental data on corrosion of stainless steel in the sodium chloride salt solution at room temperature
  - Two-dimensional model to determine the effectiveness of cathodic capacity in supporting the anodic (metal dissolution) reactions
  - Three-dimensional model to evaluate the role of non-conducting dust particles on cathodic capacity of the Alloy 22 surface

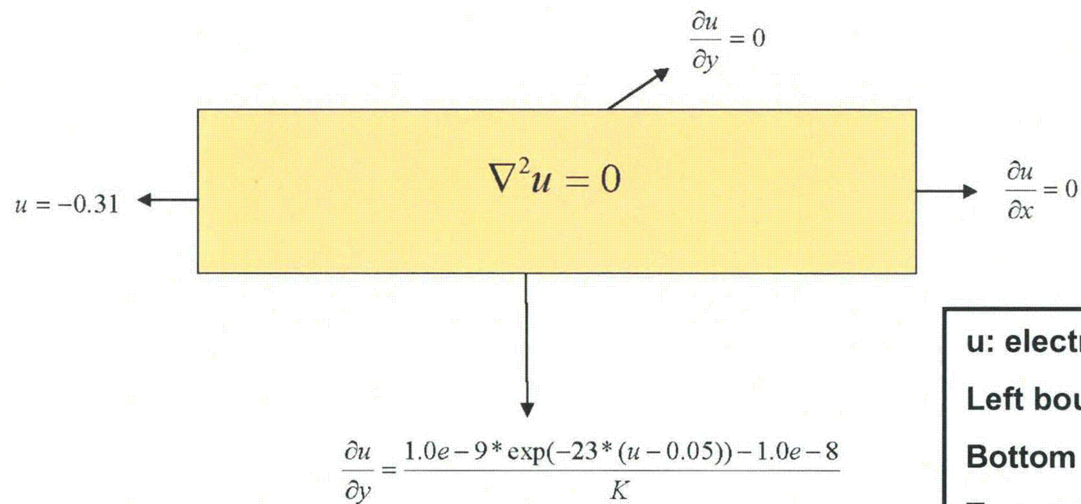
Objective

- Review assumptions used in the model developed by the OSTI program
  - Amount of electrolyte present on the waste package surface during dust deliquescence (1.8 $\mu L/cm^2$) (ENG3)
  - Thickness of electrolyte film (18 μm as stated by DOE) (ENG3)
  - Dust particles characterization and their effect on ionic properties of the electrolytes, and cathodic reaction (No reactions under the dust particles) (ENG1)

- Develop physico-chemical models using the experimental data available for Alloy 22 in the repository environment
  - To estimate the cathodic capacity of the Alloy 22 surface during seepage and dust deliquescence condition,
  - To determine the effect of dust particles on cathodic capacity,
  - To determine the role of anodic and cathodic chemistry, and temperature on localized corrosion, and high-rate general corrosion.

Preliminary Cathodic Capcity Calculation: Under Thin-Film Condition

- A preliminary two-dimensional model is developed based on the approach presented at NWTRB workshop[2, 3]
- The model parameters are selected from published work of Cui et al.[3] and Kelly et al.[4]
- Model evaluates the cathodic capacity of stainless steel surface covered with thin film of salt water at 25 °C



u: electrolyte potential

Left boundary: interface between anode and cathode

Bottom boundary: Oxygen reduction reaction

Top and right boundary: electrolyte/air interface

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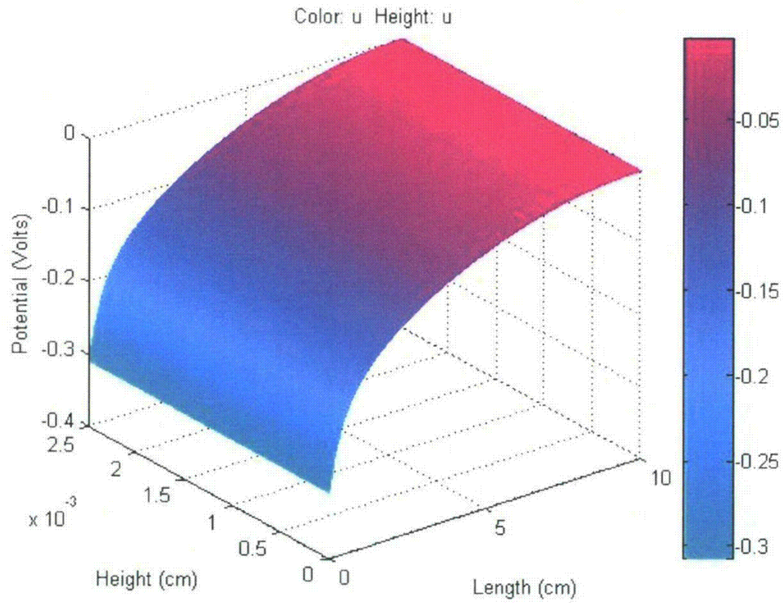
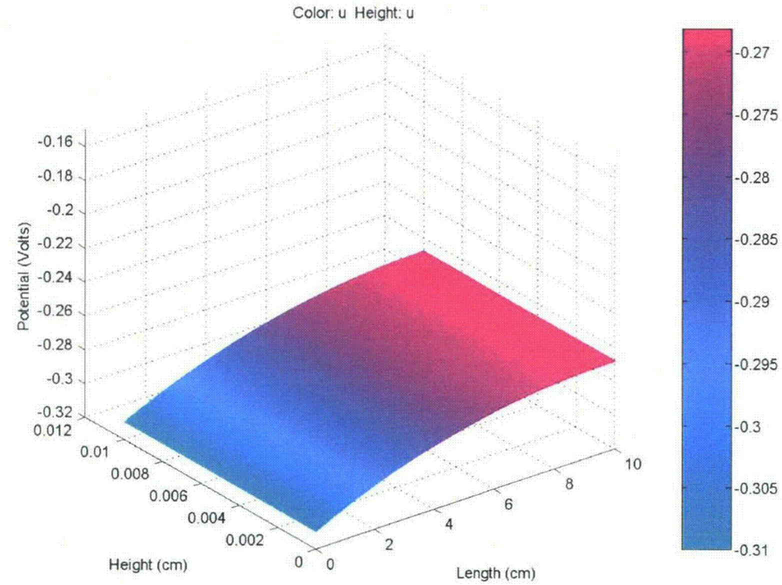
3. F. Cui, F. Presuel-Moreno, R. Kelly, "Computational modeling of cathodic limitation on localized corrosion of wetted SS 316 at room temperature", Corrosion Science, 47, 2005, 2987-3005.
4. R. G. Kelly, A. Agarwal, F. Cui, X. Shan, U. Landau, J. Payer, "Considerations of the Role of the Cathodic Regions in Localized Corrosion", IHLRWM, Las Vegas, April 30-May 4, 2006.

Preliminary Cathodic Capacity Calculation: Under Thin-Film Condition (Cont'd)



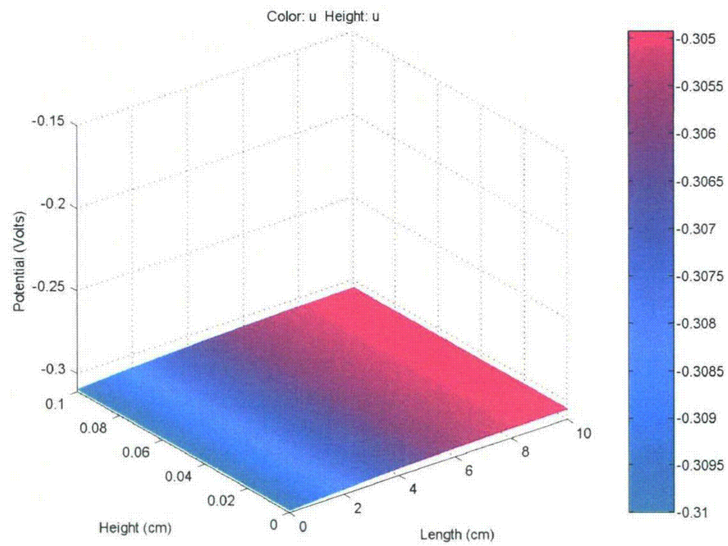
Height: 25 μm, Length: 10 cm



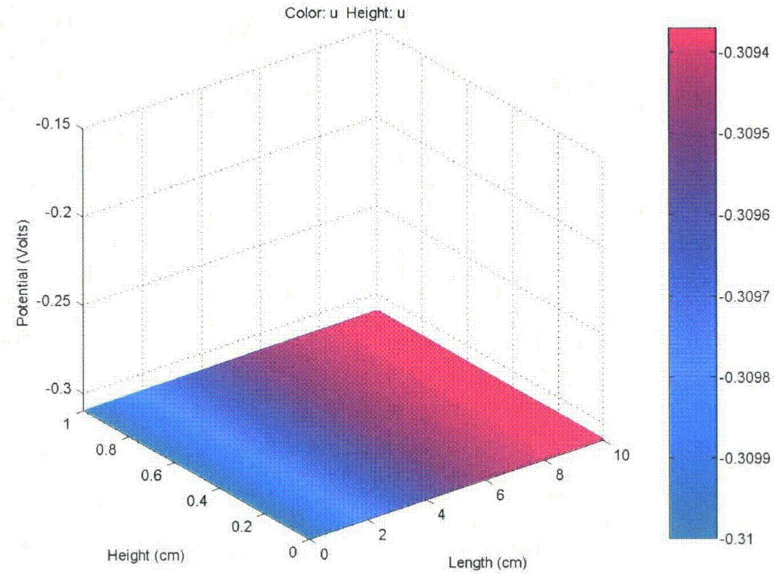
Height: 100 μm, Length: 10 cm

- Four simulations for varying thickness of the cathodic film for 1.0 M KCl solution
- Figure on the left (for 25 μm thick film on the cathode):
  - larger potential drop along the length of the cathode
  - less current is produced by the cathode
- Figure on the right (for 100 μm thick film on the right):
  - Potential drop is less steep compare to 25 μm thick film
  - As a result, more current is produced by cathode

Preliminary Cathodic Capacity Calculation: Under Thin-Film Condition (Cont'd)



Height: 1000 μm (0.1 cm), Length: 10 cm



Height: 1 cm, Length: 10 cm

- Two additional potential distribution calculations for 0.1 cm and 10 cm thick films
- Potential drop is negligible along the length of the cathode for both film thickness
- Cathode on the electrode surface is effective in producing the oxygen reduction current
- Influence of electrolyte thickness on cathodic current reduces for thicker films

Proposed Work

- Evaluate DOE's two-dimensional model for cathodic capacity
  - Preliminary calculation are performed for film length of 10 cm long in 1.0 M KCl electrolyte
  - Estimate cathodic capacity for varying electrolyte conductivities, film lengths and thicknesses
  - Estimate the quantity of electrolyte present on waste package surface during the dust deliquescence and seepage

- Develop physico-chemical model to evaluate the cathodic capacity of Alloy 22 in the repository environment
  - Develop an oxygen reduction reaction rate expression for Alloy 22 during dust deliquescence and seepage
  - Calculate the cathodic capacity of the Alloy 22 using the oxygen reduction rate expression for Alloy 22
  - Estimate the amount of electrolyte that would sustain the localized corrosion during dust deliquescence and seepage
  - Estimate the influence of dust particles on cathodic capacity

- Develop a two-dimensional composite model that accounts for cathodic and anodic chemistry, effect of migration, and temperature

Proposed Approach

- Estimate the amount of electrolyte during dust deliquesce and seepage conditions
  - Speciation calculation
  - Mass balance and flux splitting during seepage
  - Use of surface tension and contact angle measurement for estimating the thickness of the film

- Develop oxygen reduction rate expression for Alloy 22
  - Published data on oxygen reduction reaction on Alloy 22 by D. Macdonald[5] and others[6]
  - CNWRA and DOE reports to collect information on experimental data dealing with oxygen reduction rate expression

- Effect of dust particles on cathodic capacity
  - Particles size and shape distribution using the DOE data
  - Effective electrolyte conductivity using the Bruggeman's model
  - Explicit representation of dust particles in the electrolyte: two- and three- dimensional models

- Computational tools for model development
  - MATLAB for two-dimensional model
  - FLOW-3D for three-dimensional model
  - CNWRA Staff has expertise in using the two computer codes

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5. A. Davydov, K. Rybalka, L. Beketaeva, G. Engelhardt, P. Jayaweera, D. Macdonald, "The kinetics of hydrogen evolution and oxygen reduction on Alloy 22", Corrosion Science, 47, 2005, 195-215.
6. A. Lloyd, "The Effects of Temperature and Potential on the Passive Properties of Ni-Cr-Mo Alloys", Ph.D Thesis, University of Western Ontario, 2004.

Summary

- DOE plans to screen out localized corrosion of Alloy 22 during dust deliquescence, however, sufficient technical basis does not exist under Yucca mountain program

- Waste packages are expected to be covered by thin electrolyte film during dust deliquescence and seepage

- Thickness of electrolyte film has influence on cathodic capacity of the corroding surface

- It is expected that under fully immersed condition, the localized corrosion will not be limited by cathodic reactions

- CNWRA Staff needs to further investigate the role of electrolyte film and dust particles on the cathodic capacity