

LSNReviews

From: pshukla@cnwra.swri.edu
Sent: Thursday, November 16, 2006 3:29 PM
To: Xihua He
Subject: Re: RE: RE: RE: Plan
Attachments: LCGoverningEquations.ppt

Xihua,

I have prepared a presentation on the localised corrosion in limited electrolyte environment. This presentation outlines the first principle based model for the system.

Sincerely

Pavan

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Process-Level Model for Localized Corrosion in Limited Electrolyte Environment

Pavan Shukla

Xihua He

Frank Song

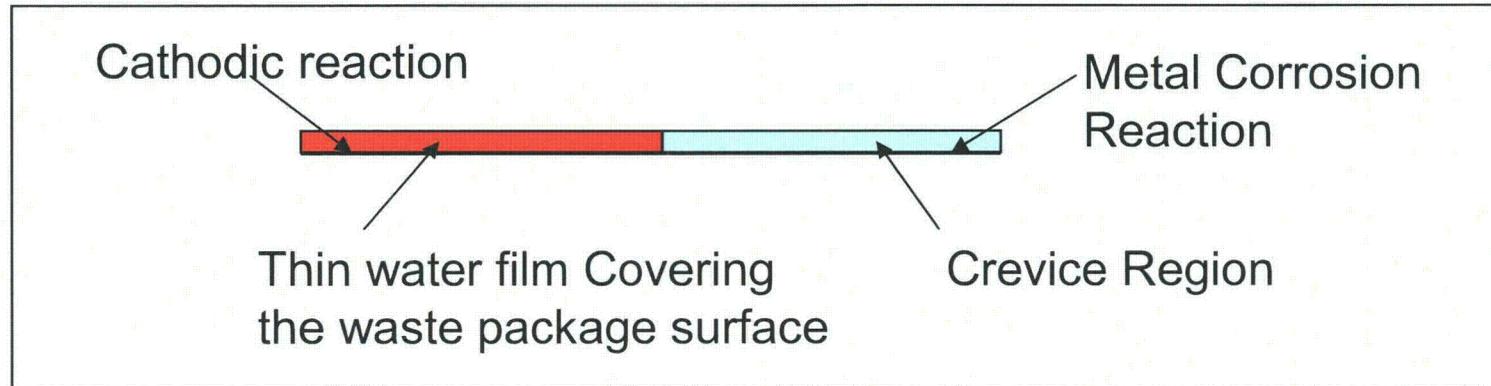
Background of Localized Corrosion in Limited Electrolyte Environment

- Waste Packages are expected to be covered by a thin film of in-drift water layer during the dust deliquescence and seepage. Waste packages will never be fully immersed in electrolyte solution, unless
- Hypotheses:
 - Even under suitable conditions that would initiate localized corrosion, the amount of electrolyte is not enough to sustain the localized corrosion of the Alloy 22
 - Presence of non-conducting dust particles in the in-drift water will further stifle the localized corrosion Alloy 22
- Objective of the modeling work: To test aforementioned hypotheses
- DOE's work:
 - Conducted modeling for SS316 in the limited electrolyte environment.
 - The model is two-dimensional and simplified
 - The model assumes a uniform current and potential distribution in the anodic region.
 - The model calculates the corrosion current produced for an assumed length of the cathodic region. The model neglects the three-dimensional effects of limited electrolyte present on the waste package surface.

Approach

- Develop a two-dimensional, and if necessary, a three-dimensional model to determine the minimum amount of electrolyte necessary to sustain localized corrosion under the presence of limited electrolyte. It is implicitly assumed that conditions to initiate the localized corrosion exist on the waste package surface.
- The model will be implemented for Alloy 22, and the available experimental data for Alloy 22 will be utilized to determine the necessary parameters for model development.
- The model will be further analyzed in the presence of non-conducting particles present in the electrolyte.
- As a first approach, a two-dimensional model will be implemented using MATLAB.
- The PDE toolbox of MATLAB will be used to solve the governing equations.
- Dr. Frank Song, Div. 20 Staff member, will help us construct and analyze the mathematical model.

Governing Equations for cathodic region



- It is assumed that the oxygen reduction reaction in the cathodic region is dominant reaction
- The rate of oxygen reduction reaction at the cathode surface is given by:

$$i_C = i_o \exp \left\{ - \left(\frac{\alpha_C}{RT} \right) \left[V^{cathode} - E_o^{cathode} - \phi \right] \right\}$$

i_c : cathodic current due to oxygen reduction

$E_o^{cathode}$: the thermodynamic potential for oxygen reduction

$V_{cathode}$: metal potential on the cathode site (equal to zero for free corroding condition)

Governing Equations for Cathodic Region (continued)

- In the presence of mass-transfer limited current, the total current at the electrode surface is given by:

$$\frac{1}{i_{total}} = -\left(\frac{1}{i_{lim}} + \frac{1}{i_c}\right)$$

- The mass transfer limited current is given by:

$$i_{lim} = \frac{nFD_{eff}C_b}{\delta}$$

- Potential distribution in bulk solution is given by the Laplace's equation:

$$\nabla^2 \phi = 0$$

Governing Equations for Anodic Region (continued)

- It is assumed that dominant corrosion reaction in the anodic region of the electrode is dissolution of the nickel.



- There are other species present in the electrolyte solution. These species are: H^{+} , OH^{-} , Na^{+} , Cl^{-} , Ni^{2+}
- The hydrogen reduction reaction in the cathodic region is neglected.
- As a first approach, no homogeneous reaction in the electrolyte solution is considered in the model
- Potential distribution in bulk solution is given by the Laplace's equation:

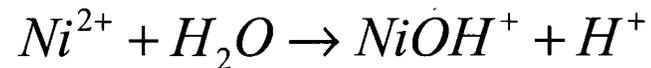
$$\nabla^2 \phi = 0$$

Governing Equations for Anodic Region (continued)

- It is assumed that electroneutrality holds in the electrolyte solution present in the anodic and cathodic sides:

$$\sum_{i=1}^n z_i C_i = 0$$

- Hydrolysis of Nickel ion is assumed to take place in the solution.



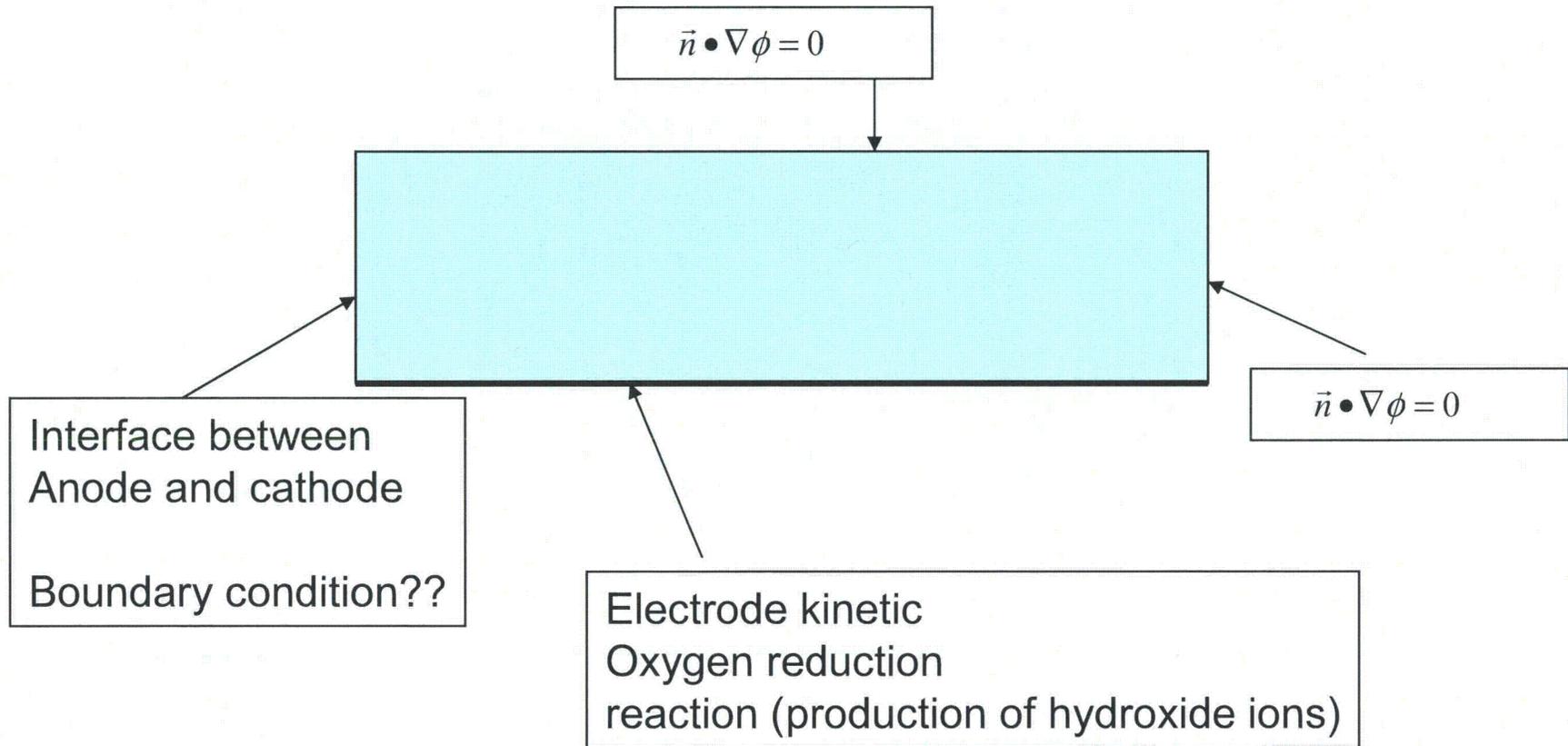
- The flux of species i in the solution is given by

$$N_i = z_i u_i F c_i \nabla \phi - D_i \nabla c_i$$

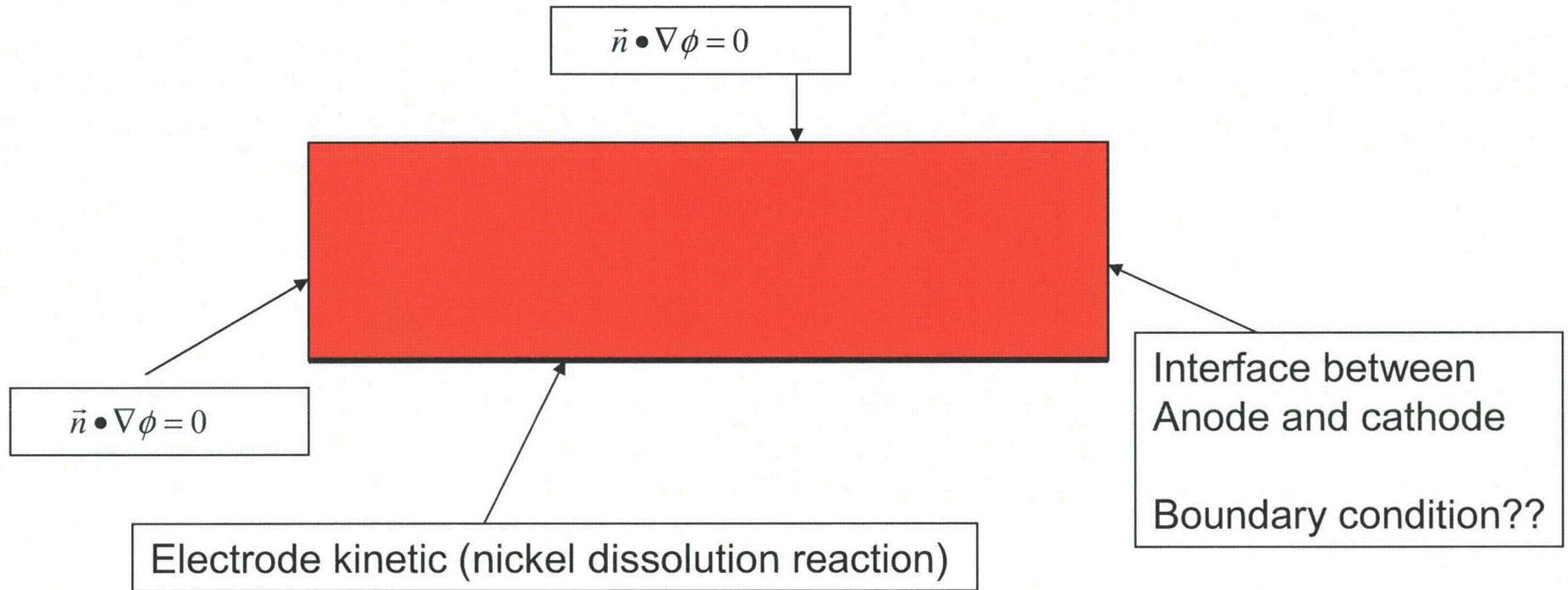
- The concentration of each species is governed by the material balance equation:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + R_i$$

Boundary Conditions for Cathodic region



Boundary Conditions for Anodic region



Unknowns

- Boundary conditions at the anode and cathode interface
- Reaction kinetics parameters
- Other possible anodic reactions
- Effect of passive layer on anodic and cathodic reaction rate