From: Pavan Shukla
Sent: Tuesday, December 11, 2007 10:09 AM
To: Xihua He; Todd Mintz; Yi-Ming Pan
Cc: Tae Ahn; Greg Oberson
Subject: FW: Estimation of the Water Reduction Reaction on Ti Drip Shield
Attachments: Estimation_of_water_reduction.pdf

All,

I have written a three-page document which outlines a simple method for estimating the rate of hydrogen evolution on the titanium drip shield. This method can be easily adopted and contribution of the water reduction reaction at the corrosion potential can be determined. I hope you find this help and are able to implement it for determining a realistic performance of the titanium drip shield due to hydrogen absorption. Please feel free to call or write if you have questions.

Sincerely
Pavan

-----Original Message-----
From: Keith Axler [mailto:kaxler@swri.edu]
Sent: Monday, December 10, 2007 9:40 AM
To: 'Pavan Shukla'
Subject: RE: Estimation of the Water Reduction Reaction on Ti Drip Shield

I think that is a fine illustrative defense on why the corrosion potential measurements are essential. Please proceed to socialize this with Xihua and Todd.

Keith Axler, Ph.D.
Manager, Corrosion Science and Process Engineering
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Southwest Research Institute
6220 Culebra Rd
San Antonio, TX 78238-5166

From: Pavan Shukla [mailto:pshukla@swri.edu]
Sent: Monday, December 10, 2007 9:35 AM
To: 'Keith Axler'
Subject: Estimation of the Water Reduction Reaction on Ti Drip Shield

Keith,

Please see the following attached file with respect to the calculation of the hydrogen evolution rate at the Ti drip shield. After your comments, I will mail this to Xihua and Todd.

Sincerely
Pavan K. Shukla
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Subject: FW: Estimation of the Water Reduction Reaction on Ti Drip Shield
Sent Date: 12/11/2007 10:08:47 AM
Received Date: 12/11/2007 10:08:48 AM
From: Pavan Shukla

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Files	Size	Date & Time
MESSAGE	1727	12/11/2007 10:08:48 AM
Estimation_of_water_reduction.pdf	61633	

Options
Priority: Standard
Return Notification: No
Reply Requested: No
Sensitivity: Normal
Expiration Date:
Recipients Received:

I have prepared this document in response to the discussion we had last week with respect to the estimation of the hydrogen evolution on the titanium drip shield.

With respect to the cahodic reduction reactions, the following two reactions could occur in the alkaline solution

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

The second reaction will be dominant only if corrosion potential is sufficiently negative. Otherwise, the oxygen reduction reaction will be the dominant reaction. However, the water reduction reaction will proceed, albeit at a slower rate, even if corrosion potential is high.

If value of corrosion potential is known, and kinetic parameters of the oxygen reduction and water reduction reaction are also known, one can easily estimate the rate of water reduction reaction, and thus calculate the rate of hydrogen evolution reaction.

The method to calculate the kinetic rate constants for the oxygen reduction and water reduction reactions are provided below.

Oxygen Reduction Reaction

Near the corrosion potential, the rate of oxygen reduction reaction can be expressed by the following equation to account for mass-transfer-limited current in kinetic rate expression

$$i_{c,O_2} = -\left(\frac{1}{i_{lim,O_2}} - i_{O_2,ref} 10^{(V - E_{O_2,ref})/\beta_{O_2}} \right)^{-1} \qquad (1)$$

where

i_{lim,O_2}	—	the mass-transfer-limited current
V	—	potential drop across metal/solution interface (Volts)
$E_{O_2,ref}$	—	reference potential for the $i_{O2,ref}$
$i_{O2,ref}$	—	reference current density at $E_{O_2,ref}$
β_{O_2}	—	cathodic Tafel slope for the oxygen reduction reaction (Volts/decade)

The parameters in Eq. (1) can be estimated by conducting a polarization curve for the oxygen reduction reaction. It's better to conduct the polarization curve using a rotating disk electrode. This will give an opportunity to control the mass transfer and accurately delineate the kinetic and mass transfer regimes in the polarization curve. The oxygen reduction polarization curve will look like the plot presented in Figure 1.

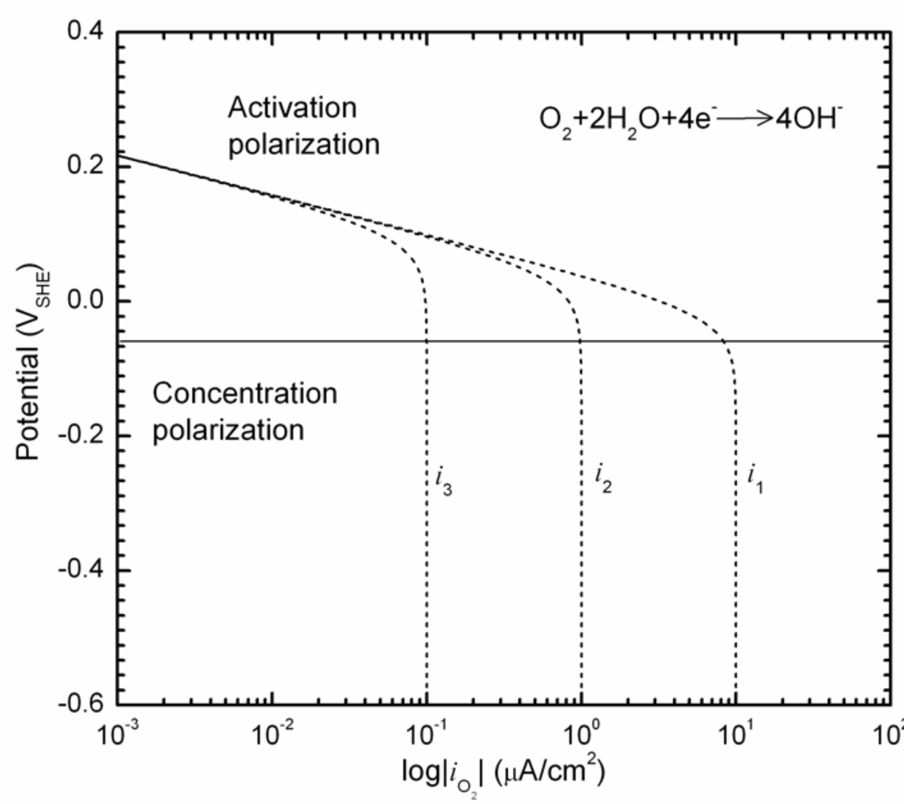

Figure 1. The hypothetical polarization curve for the oxygen reduction reaction. i_1, i_2, and i_3 are different values of the mass transfer limited currents. The mass transfer limited current will change with the changing value of the rotation speed if experiments are conducted using a rotating disk electrode.

While conducting the polarization curve, please ensure that the solution is sufficiently aerated. This will ensure that the water reduction reaction is suppressed or occurs at a minimum rate. The limiting current can be calculated directly from the polarization curve. Any potential value in the activation region can be assigned to $E_{O_2,ref}$ and the corresponding current will become $i_{O_2,ref.}$ The tafel slope can be easily calculated using the data in the activation region of the polarization curve.

Water Reduction Reaction

The following kinetic rate can be adopted for the water reduction reaction

$$i_{c,H_2O} = -i_{H_2O,ref}\, exp^{\left(V - E_{H_2O,ref}\right)/\beta_{H_2O}} \qquad (2)$$

where

i_{c,H_2}	—	current density due to water reduction reaction (Ampere/cm^2)
V	—	potential drop across metal/solution interface (Volts)
$E_{H_2O,ref}$	—	reference potential for the reference current density $i_{H_2O,ref}$

$i_{H_2O,ref}$ — Reference current density at reference potential $E_{H_2O,ref}$
β_{H_2O} — cathodic Tafel slope (Volts/decade)

A cathodic polarization curve can be conducted in a deaerated solution to determine the kinetic rate constants for the water reduction reaction. It is extremely important to deaerate the test solution sufficiently so that the oxyge reduction reaction does not interfere with the water reduction reaction. However, tafel slope of the water reduction reaction is very difficult to estimate using the polarization curve because, irrespective of amount of purging from the solution, there will be some oxygen left in the solution which will interfere with the water reduction reaction at high potentials. $E_{H_2O,ref}$ and $i_{H_2O,ref}$ can be easily calculated using the polarization curve but β_{H_2O} needs to be calculated in the following step. It is important to adopt the values of $E_{H_2O,ref}$ and $i_{H_2O,ref}$ at sufficiently cathodic values. This will ensure that oxygen reduction reaction does not interfere.

Corrosion Potential, Corrosion Current and Estimation of β_{H_2O}

Regular polarization experiments can be conducted to measure corrosion potential and corresponding corrosion current for titanium alloy in different solutions. At the corrosion potential, the net current density i_{net} is given by

$$i_{\text{net}} = i_{\text{corr}} + i_{\text{c},H_2O} + i_{\text{c},O_2} \tag{3}$$

where

$i_{\text{c},O2}$ — current density due to oxygen reduction reaction (Ampere/cm^2)
$i_{\text{c},H2O}$ — current density due to water reduction reaction (Ampere/cm^2)
i_{corr} — corrosion current density (Ampere/cm^2)

Once corrosion potential and corrosion current densities are known, β_{H_2O} can be estimated by solving Eq. (3) by setting i_{net} equal to zero. If β_{H_2O} is known, the current generated due to water reduction reaction can be calculated using Eq. (2). This current can be compared to the oxygen reduction current at different values of the corrosion potential and corrosion current densities.