

Considerations of the Role of the Cathodic Region in Localized Corrosion

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Abstract –The ability of wetted cathodes of limited area to support localized corrosion sites on passive materials exposed to atmospheric conditions was studied computationally. The analysis pertains to conditions where metal surfaces are covered by thin layers of moisture in contrast to conditions of full immersion. The moisture may be a continuous layer or in patches with and without particulate on the surface. These conditions are of interest for the surfaces of the waste packages at the proposed Yucca Mountain Repository where waste packages are supported in air. The cathode capacity was characterized by the total net cathodic current, I_{net} , which the surface surrounding a localized corrosion site (i.e., a pit or crevice) could supply. The cathode capacity increases with increasing cathode area, but it saturates at finite cathode sizes due to the resistance of the thin electrolyte layer. The magnitude of the capacity depends on the water layer thickness, the solution conductivity, and the electrochemical reaction kinetics. The presence of particulates is treated by considering both volume and surface coverage effects. The limited electrolyte volume under thin film conditions can lead to rapid pH changes which decrease the cathode capacity due to the slower electrochemical kinetics at elevated pH. These effects can make localized corrosion less likely to be sustained.

I. INTRODUCTION

The overall goal of this study is to quantify the extent to which the rates of localized corrosion can be supported by cathodic reactions within a surrounding thin electrolyte, as shown schematically in Fig. 1. Such quantitative understanding is important to understanding the robustness of the structural materials for use in the waste packages at the proposed Yucca Mountain Repository because the likelihood that localized corrosion, once initiated, will be able to propagate depends critically on the ability of the surrounding cathodic surface to support the dissolution rates of the sites undergoing localized attack. If the wetted area around the localized corrosion site cannot support cathodic reactions sufficiently, the localized corrosion site will stifle and can eventually fully repassivate. The primary goal of this work is to identify and quantify the effects of the physical and chemical parameters that control the cathode capacity of a wetted surface. The analysis pertains to conditions where metal surfaces are covered by thin layers of moisture in contrast to conditions of full immersion. These conditions are of interest for the surfaces of the waste packages at the

proposed Yucca Mountain Repository where waste packages are supported in air.

Metal surfaces that are not fully immersed in waters can be exposed to moisture from thin layers of water and moist particulates that contain ionic species. These ionic species can originate from the water source (e.g., rain or dripping), dissolution of atmospheric gases, soluble species in any solids present, or from the deliquescence of hygroscopic salts. For passive metals exposed to atmospheric conditions, the localized corrosion processes of pitting and crevice corrosion are of the most interest. Pitting corrosion may initiate on a free surface if the potential is sufficiently oxidizing and the concentration of an aggressive species, e.g., chloride, is sufficiently high. Precipitates, metal oxide scales as well as geometrical crevices may generate occluded local geometries that trap electrolytes and thus promote crevice corrosion due to the development of acidic solutions by hydrolysis of dissolution products.

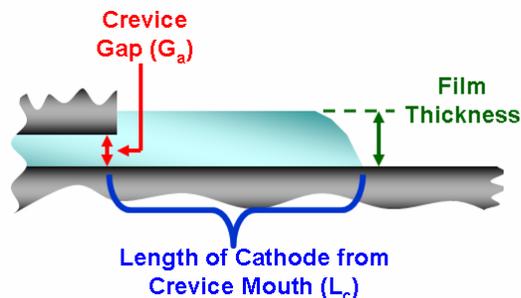


Fig. 1. Schematic diagram of the cathodic region on a metal surface outside of an anodic crevice corrosion region.

For pitting or crevice corrosion to proceed, both anodic and cathodic processes are necessary. The metal loss and damage occurs at the anodic sites where metal atoms go into solution as soluble metal ions, and these oxidation reactions at the anode generate electrons. For the corrosion to proceed, the electrons must be consumed by reduction reactions at cathodic sites on the metal surface at or away from the anodes. For metals exposed to aqueous solutions in contact with air, the reduction of dissolved oxygen is the most prevalent reduction reaction to consume electrons. Other reducible species in the aqueous solution can also contribute to the net cathodic current; however, no other species than oxygen is likely to be present in significant quantities with respect to total cathodic current capacity. For natural conditions with no externally applied currents, the electrons generated at the anode must be balanced by the electrons consumed at the cathode. Thus, the metal dissolution cannot proceed at a rate greater than the rate of the cathodic reactions.

Corrosion cells under natural conditions, *i.e.*, with no externally applied current, can vary significantly from the experimental arrangements in the most common laboratory experiments where electrochemical instruments (potentiostats) are used with external cathodes. The latter essentially ensures that sufficient cathodic current is provided to meet any anode demand, and cathodic limitations are not observed. Furthermore, most experiments are conducted under fully immersed conditions with highly conductive solutions. This arrangement also favors conditions that avoid a regime of cathodic limitations on the corrosion propagation. For applications in which the surface of interest is fully immersed in an electrolyte and there is a large and effective cathode, such laboratory arrangements are appropriate and have been useful in understanding and predicting actual corrosion behavior.

Under atmospheric conditions, cathodic limitations can control the rate of anodic dissolution. Conservation of charge requires that all electrons liberated during an

oxidation reaction such as dissolution at one location be consumed by a reduction reaction either locally or at another area. Localized corrosion sites generate far more electrons than can be consumed locally, so the ability of the pit or crevice to interact with the surrounding area is critical to propagation of corrosion.

The ability of two areas of a surface wetted by a thin layer of solution or by a layer of moist particulate to interact is controlled by the conductivity of the solution between them, the geometry of the water layer (*i.e.*, its thickness), as well as the electrochemical kinetics of the two areas (*i.e.*, the potential-current density relationships). Both the solution conductivity and electrochemical kinetics depend upon the solution pH which is affected by the electrochemical reactions. This coupled interaction is further affected on the wetted surfaces due to the substantial changes in pH that can occur in the limited volume of solution present.

Experimental measurements of electrochemical and corrosion processes occurring in thin electrolyte layers are challenging due to the small dimensions involved, and the difficulty in using measurement tools that were developed for corrosion under full immersion. Thus, computational studies can serve an important role in defining the experimental space in which experiments should be focused to most efficiently map out the important dependencies.

In this paper, we summarize some of the early findings of our continuing work in this area. The potential and current distributions on a wetted metal surface coupled to a localized corrosion site have been characterized computationally, and the effects of various parameters, such as electrolyte layer thickness and composition, temperature, and the amount and nature of any particulate present have been probed. The figure of merit for the ability of an external cathode to support a localized corrosion site is the cathodic current capacity (I_{net}). Its value depends on the kinetic and physiochemical parameters of the interface and the electrolyte layer. It should be noted that while this work describes the spatial distribution of the current on the cathode, it does not consider the spatial distribution of current at the anode. It is the distribution of current at the anode that determines the penetration rate. That is, if a localized corrosion site is larger, but generates the same amount of current, the penetration rate is lower.

Although the primary focus of this work is on the role of the cathodic region in the localized corrosion of passive metals that are covered with thin layers of moisture or with layers of moist particulate, the general considerations are also relevant to metals covered by

thicker layers of moist particulate and metals that are fully immersed.

The factors that determine and control the cathode capacity of the cathodic region to support anodic dissolution (maximum reduction current) are discussed. The information is drawn primarily from the results of computational analysis of the cathodic behavior associated with the crevice corrosion of a passive metal in thin layers of electrolyte [1, 2]. The computational analysis is continuing and experimental studies are also underway to validate the analytical results. Here, we discuss initial results concerning the controlling factors and identify some of the scenarios where the propagation of localized corrosion are limited by the cathodic processes.

II. EFFECTS OF SOLUTION CONDUCTIVITY AND GEOMETRY ON THE CATHODE CAPACITY

The important characteristics of the cathodic region associated with a localized corrosion cell include the water chemistry (i.e., ionic species and concentration), conductivity, geometry (thickness and wetted area), temperature, and the electrochemical reduction reaction kinetics. Properties of the electrochemical reactions of importance are reversible potential $E_{o,c}$, exchange current density $i_{o,c}$, Tafel slopes β_c , and limiting currents for mass transport control. Experimental kinetic data for relevant electrochemical reactions as well as physiochemical data such as conductivity and diffusion coefficient of oxygen are needed to ground computations in reality.

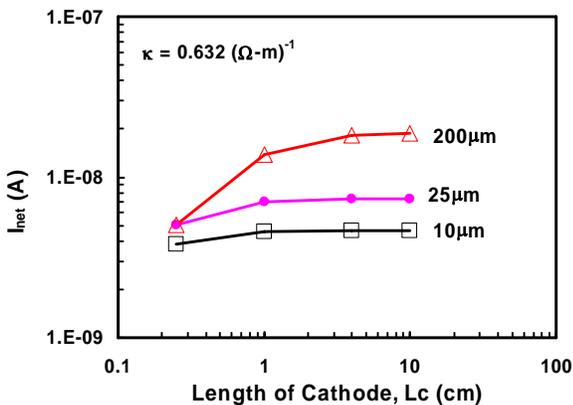


Fig. 2. Effects of cathode length and water layer thickness on the cathode capacity. The amount of cathodic current available saturates with increased cathode length. Assumed width, 1 cm. This conductivity is that of 1 M NaCl based on dilute solution theory.

Fig. 2 shows the results of a set of calculations determining the cathode capacity as a function of cathode length (assuming unit width) and electrolyte layer thickness [1]. For all electrolyte layer thicknesses, the cathode capacity saturates at long cathode length. This result implies that portions of cathode farther from the localized corrosion site than the length at which the I_{net} saturates (e.g., 10 cm for the 10 micron electrolyte layer) do not contribute significantly to maintaining an active localized corrosion site.

Fig. 3 shows the effects of both water layer thickness and temperature. It has been shown [1] that for the conditions considered¹ the cathode capacity increases with the square root of the water layer thickness. Increased water layer thickness increases the cathode capacity by decreasing the resistance between the localized corrosion site and any position on the surrounding wetted cathode, thereby allowing more current to be delivered at a constant potential. Increased temperature has two major effects. It increases the conductivity (by more than a factor of six for the case considered in Fig. 3) and it increases the electrochemical kinetics, leading to more cathodic current being produced at any given potential (in the absence of mass transport limitations – see below).

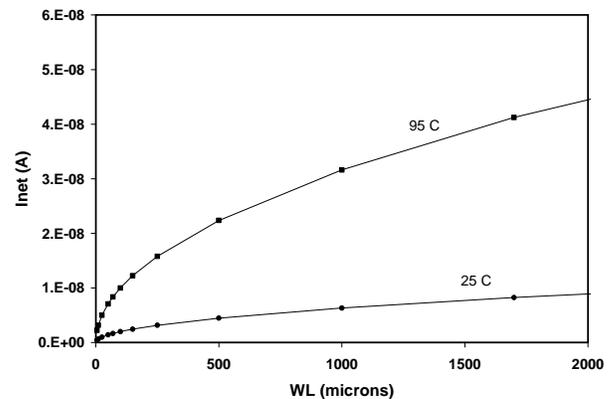


Fig. 3. Effect of water layer thickness and temperature on the cathode capacity. Assumed width, 1 cm.

Full parametric studies [1] of the effects of the physical and chemical variables listed above demonstrated that the largest effects are due to changes in the conductivity, with the effect of cathode length also being important over the range of parameter values appropriate for atmospheric corrosion of stainless steel.

This result is in marked contrast to what would be observed for a surface under full immersion conditions in

¹ Constant solution chemistry and electrochemical kinetics

a conductive electrolyte. For such immersed conditions, the less restricted geometry would make similar changes in conductivity have a smaller effect.

III. EFFECT OF PARTICULATES ON THE CATHODE CAPACITY

At the proposed Yucca Mountain Repository, the waste packages will never be fully immersed in water; however, the metal surfaces could be in contact with moisture and particulates or deposits. These particulates in the electrolyte layer affect the corrosion process principally in two ways: (i) increased ohmic resistance of the electrolyte due to a volumetric blockage effect (volume effect) and (ii) partial blocking of the electrode surface thereby increasing the reaction kinetic resistance (surface effect). To account for these phenomena, we introduce separate corrections for each of the two effects.

(i) Volume Effect: The bulk electrolyte blockage by the particles requires the current lines to by-pass the impermeable particles increasing the resistivity of the system. Bruggeman's equation [3] is applied to provide an equivalent effective conductivity:

$$k_{\text{eff}} = k(1 - \phi_{\text{particles}})^{\frac{3}{2}} \quad (1)$$

where;

$$\phi_{\text{particles}} = \frac{V_{\text{particles}}}{V_{\text{solution}} + V_{\text{particles}}} \quad (2)$$

Fig. 4 indicates that as the volume fraction of the particulates in solution ($\phi_{\text{particles}}$) increases to about 60% there is an almost linear decrease in conductivity. At high particle loading (in excess of $\sim 60\%$), rapid decline in the effective conductivity occurs.

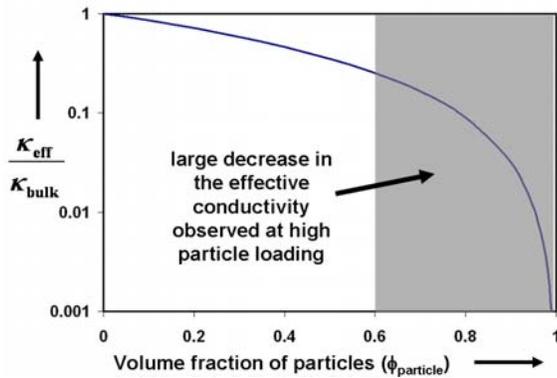


Fig. 4. Effect of particle loading (ϕ_{particle}) on the effective solution conductivity (κ_{eff}).

This significant increase in the solution resistance at high particle loading was found to considerably decrease the cathode current capacity.

(ii) Surface Effect: The area correction accounts for the fact that the reaction kinetics model is based on the entire electrode area (A_{total}), yet in reality, the particles block a portion thereof. The covered portions of the cathode force the current to “concentrate” in the exposed active regions (Fig. 5) corresponding to a current density i_c at the electrode. Further away from the electrode, the average current flux (i_s) is no longer influenced by the surface coverage. The relationship between i_s and i_c follows from a total current balance:

$$i_c = \frac{A_{\text{exposed}}}{A_{\text{total}}} i_s \quad (3)$$

Accordingly, we correct the electrode kinetics expression by modifying the rate constant (the exchange current density, i_0) by an equivalent term, i_0' , which accounts for the partial surface blockage [2];

$$i_0' = i_0 \frac{A_{\text{exposed}}}{A_{\text{total}}} \quad (4)$$

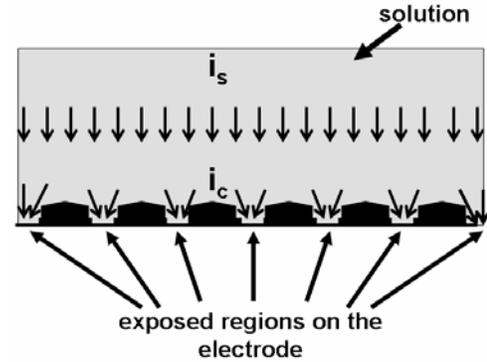


Fig. 5. Schematic of the “squeezing” effect on the current density at the electrode due to its partial coverage by the particles.

The cathode capacity obtained from computational simulations carried out in the simpler, homogeneous, electrolyte systems applying the above corrections for the equivalent conductivity and electrode kinetics are compared to the cathode capacities obtained by 3-D modeling of the actual heterogeneous particulate/electrolyte configurations based on the shape, size and distribution of the inert embedded particles. This system is represented in terms of a uniform distribution of a monolayer of particles of predetermined size, shape and arrangement in a thin electrolyte film covering the

cathode surface. The particles are inert and of the same height as the electrolyte film. Although such a system does not necessarily match a real system, it provides a foundation for comparisons with experiments and likely represents a reasonable estimate for a surface with particulate. The cathode capacity of the particulate system is simulated as a function of the length of the cathode (L_c) in Fig. 6 using the process parameters listed in Table I.

TABLE I. Kinetic parameters used in the simulation of electrolyte films with 25 μm cubic particles ($A_{\text{active}}/A_{\text{geometric}} = 0.306$, $V_{\text{solution}}/V_{\text{geometric}} = 0.306$). The thickness of the electrolyte layer (WL) is 25 μm .

E_0 V_{NHE}	i_0 A/cm^2	α_c	E_{tp} V_{NHE}	E_{cor} V_{NHE}	i_L A/cm^2	κ S/cm
0.19	10^{-9}	0.59	-0.31	0.09	2.2×10^{-4}	1.21×10^{-2}

It is evident that simulations of the homogeneous electrolyte system incorporating both the volume and surface coverage corrections reproduce accurately the cathode capacity obtained by the 3-D simulation of the actual particulate system. However, either the area or volume corrections by itself is insufficient in predicting the cathode capacities in the range explored. For the scenario presented here, as the length of the cathode increases beyond 0.1 cm, the potential drop due to solution resistance becomes appreciable, and the area correction alone cannot predict the cathode capacity. On the other hand, just employing the correction for the bulk conductivity, significantly overestimates the cathode capacity. In general, particulates presence on the cathode surface has a similar effect to cathode passivation, since both reduce the cathode capacity similarly.

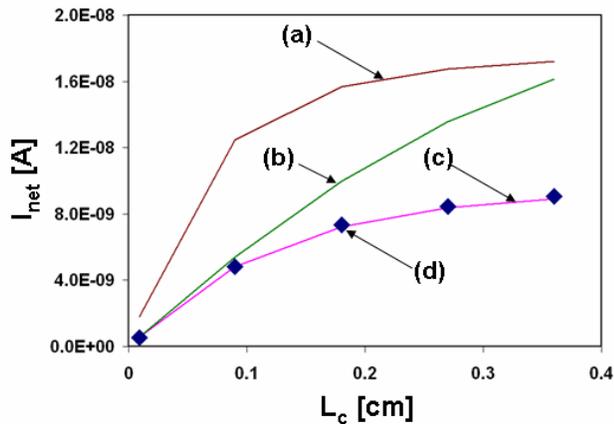


Fig. 6. Effect of the cathode length on simulated cathode capacities in the presence of particulates (a) homogenous electrolyte corrected only for the volume effect (Eq. 1), (b) homogenous electrolyte corrected only for the area coverage effect (Eq. 4), (c) homogenous electrolyte

corrected for both volume and area coverage effects, (d) complete simulation of the 3-D current distribution (\blacklozenge) in the presence of particulates. Simulation parameters are given in Table I.

IV. EFFECT OF THE CATHODIC REACTION CHEMISTRY

The predominant cathodic reaction is oxygen reduction which causes the electrolyte near the cathode to become increasingly alkaline:



The hydroxyl accumulation in the thin layer will cause the reduction potential to shift in the cathodic direction:

$$E_0' = E_0 - 0.059 \cdot \text{pH} \quad (6)$$

This in turn will decrease the driving force for the cathodic reaction and hence reduce the cathode capacity. A segmented electrode, with different reduction parameters for each segment, was modeled. The low hydroxyl ion diffusivity localizes the pH variation at the electrode segment position since the lateral dispersion of hydroxyl ions is negligible during the time scales considered.

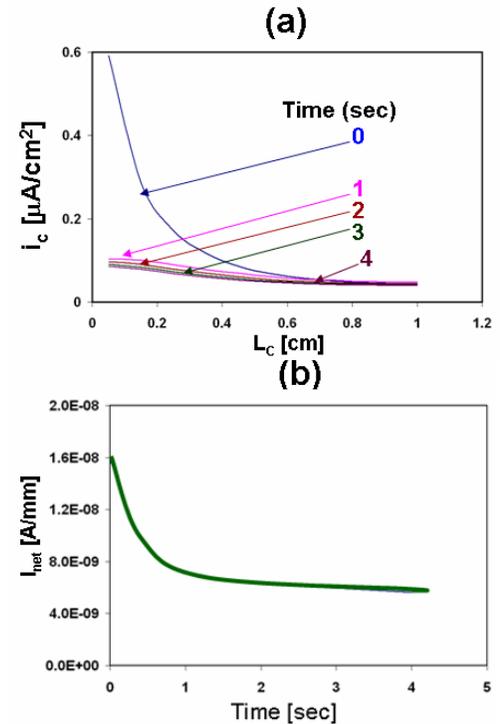


Fig. 7. Effect of pH variations on the cathodic current (a) time dependent current distribution due to local pH variation (b) total cathode capacity as a function of time.

As the pH increases with time, the current density close to the crevice opening, where the pH changes are largest (due to the high local current density), shows a steep decline (Fig. 7 (a)). The total current supported by the cathode also decreases with time, as shown in Fig. 7 (b). This indicates that the cathode capacity to sustain localized corrosion will decrease with time due to the increase in the local pH.

It should be noted that the aim of this work is to identify important parameters affecting cathode capacity. In a full localized corrosion simulation, the linking of the chemistry at the mouth of the crevice must be taken into account. For example, the increased pH on the cathode side can interact with low pH solution emanating from the crevice. The resulting pH will depend on the details of the chemistry and transport for a given scenario. One likely scenario involves the precipitation of metal oxides/hydroxides near the mouth as these are sparingly soluble at neutral pH; a region of pH that must exist somewhere between the high pH of the cathode and the low pH of the anode.

V. EFFECT OF MASS TRANSFER LIMITATION

For metal exposed in air, the cathodic reaction predominantly involves O_2 reduction. Other reducible species if present in the aqueous solution would contribute, but these are typically at low concentrations and make no significant addition to the net cathodic current. The oxygen diffuses towards the cathode through the thin electrolyte film of thickness WL . The oxygen flux reaches a limit when its concentration at the electrode drops to zero, giving rise to the maximal, transport limited current density:

$$i_L = \frac{nFD_{O_2}C_{O_2}^{sat.}}{\delta} \quad (7)$$

δ is the effective boundary layer thickness for oxygen diffusion. δ is equal to the film thickness, WL , when the film thickness is either identical to the height of the particles or is much thicker. In intermediate cases, an effective “ δ ” needs to be calculated.

As shown in Fig. 8 (a), the limiting current may impose a limit on the cathode capacity. Clearly, an increase in the electrolyte film thickness or a decrease in the concentration of dissolved oxygen will decrease the limiting current. Fig. 8 (b) depicts the effect of increasing the electrolyte film thickness on the cathode capacity. A marked reduction in capacity is noted particularly for thicker films. When the electrolyte film is very thin, the transport limitations are insignificant and the process is kinetically controlled.

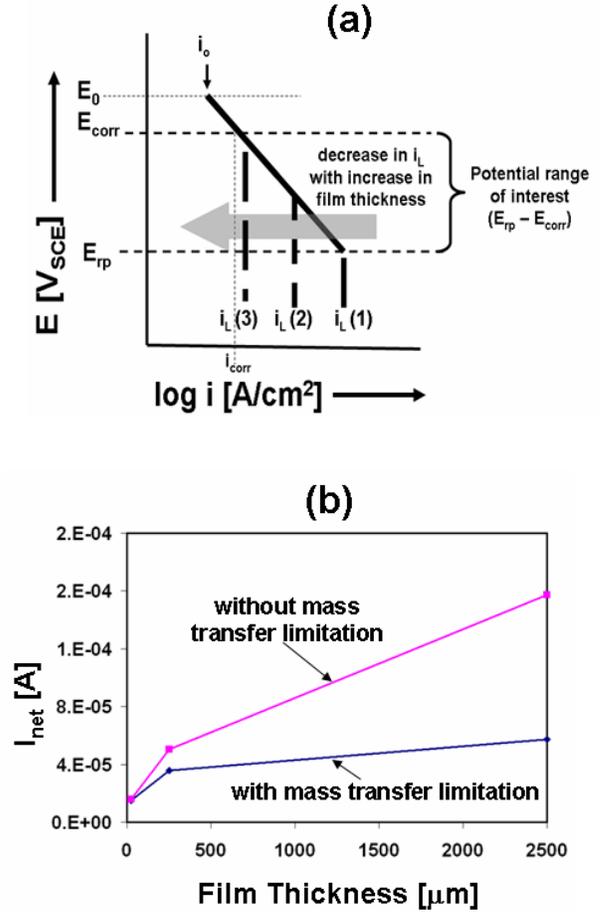


Fig. 8. Effect of mass transfer limitations on the cathode capacity (a) schematic of the transport limited cathodic polarization curve (b) the cathode capacity with and without mass transfer limitation as a function of the electrolyte film thickness.

VI. CONCLUSIONS

1. At the proposed Yucca Mountain Repository, the waste packages will never be fully immersed in water; however, the metal surfaces will more likely have thin electrolyte layers including particulates or deposits.
2. Localized corrosion on passive metals exposed to thin electrolyte layers can be limited by the ability of the surrounding cathode to supply current to the active site.
3. The cathode capacity increases with increasing cathode area, but saturates at finite cathode sizes due to the resistance of the thin electrolyte layer. The magnitude of the cathode capacity depends on the water layer thickness, the solution conductivity, and the electrochemical kinetics.

4. The presence of particulates can be accurately taken into account by considering both volume and surface coverage corrections.
5. The limited electrolyte volume under thin film conditions can lead to pH changes which increase the alkalinity (pH) on the cathodic surface and decrease the cathode capacity due to the slower electrochemical reaction kinetics at elevated pH.
6. Any net decrease in cathode capacity would make localized corrosion less likely to be sustained.

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The views, opinions, findings, and conclusions or recommendations of authors expressed herein do not necessarily state or reflect those of the DOE/OCRWM/OST&I.

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